OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

19627

Advances in Materials Technology: MONITOR

Issue 24/25 February 1992

SURFACE ENGINEERING - A CONSULTANCY REPORT

Dear Reader,

This is number 24/25 of UNIDO's state-of-the-art series in the field of materials entitled **ADVANCES IN MATERIALS TECHNOLOGY: MONITOR.** This issue is devoted to the subject of **SURFACE ENGINEERING - A CONSULTANCY REPORT.**

This Monitor intends to present a survey of the present status of scientific understanding and practical application. It thus provides an international forum for the exchange of information on new technologies on surface treatment. The main article for this Monitor has been written for us by Dr. Venkateswaran Sankaran, India.

We invite readers to share with us their experience related to any aspect of production and utilization of materials. Due to paucity of space and other reasons, we reserve the right to abridge the presentation or not publish them at all. We also would be happy to publish your forthcoming meetings, which have to reach us at least six months prior to the meeting.

Due to financial constraints we cannot accept new subscribers for the time being and also ask for your understanding that we cannot send all the requested copies of back issues as many of the past Monitors are currently out of print.

For the interest of those readers who may not know, UNIDO has inaugurated the **MARINE INDUSTRIAL TECHNOLOGY MONITOR.** The Microelectronics Monitor and the Genetic Engineering and Biotechnology Monitor are also being published. For more information please write to the Editor of the respective Monitor.

Industrial Technology Development Division

CONTENTS

1. SURFACE ENGINEERING

A Consultancy Report
by Dr. Venkateswaran Sankaran

Surface engineering is a rapidly developing discipline which makes possible the design and manufacture of composites (not only metallic but also ceramic and polymeric based), with a combination of bulk and surface properties unobtainable in either the base or the surface material.

The principal reason for the growing importance of this technology is that the destructive forces in most technological applications concentrate on the exterior of a component, thereby requiring surface properties that are intentionally different from the core. This applies to a wide range of engineering applications ... be it the tip of a cutting tool, the combustion chamber of a jet engine, the valve in a chemical plant, an internal engine component and so on.

In this article, an attempt is made to review (a) the state-of-the-art in this field, (b) recent developments and industrial applications and (c) the future trends in this area.

A. State-of-the-art

Surface engineering has been practised, although in crude forms, for thousands of years. Indeed one can find evidence of quench hardening of weapons as early as 880 BC in Homer's Odyssey, wherein he compares the hissing of the snake in the eyes of Cyclops to the hissing of an armourer's sword during tempering.

The writings of the German monk Theophilus refer to carburizing case hardening in the eleventh century and the Chinese archaeologists have unearthed evidences to show that early Chinese used decomposing soya bean to enrich red hot swords with nitrogen and carbon, to improve their strength and toughness.

Nevertheless, it was not until the end of the nineteenth century - beginning of the twentieth century, that new surface engineering techniques could be envisaged due to dramatic improvements in electrical technologies.

Surface engineering techniques gained further impetus due to the growing commercial maturity of a wide range of electrically based surface technologies like laser and electron beam processing, plasma thermochemical techniques and plasma enhanced coating techniques.

Today, just like gasoline is essential to exploit the potentials of a motor car, surface engineering is essential in the application and exploitation of high performance engineering materials. This is especially true due to both the escalating costs of high performance structural materials and the increasingly high life-cycle requirements of high performance systems.

Surface engineering techniques generally consist of surface treatments, where the composition or the mechanical property of the existing surface is altered, or a different material is deposited, as thin films or coatings, to create a new surface.

Surface treatments thus include, on the one hand, mechanicals processes, such as shot-peening, which work-harden the surface; thermal treatments, like laser or electron beam heating, which harden the surface by quenching constituents in solid solution; diffusion treatments, like carburizing and nitriding, which modify the surface composition; chemical treatments, such as etching and oxidation, which either remove material or change the composition by chemical reactions; and ion implantation, where the surface composition is modified by accelerating ions to high energies and implanting them into the near-surface layers.

Deposition techniques, on the other hand, include traditional electrodeposition and chemical conversion coating methods, as well as newer techniques such as thermal spraying, where a plasma or electric arc is used to melt a powder or wire source, and droplets of molten material are sprayed onto the surface to produce a coating; physical vapour deposition, in which a vapour flux is created by a physical process such as evaporation, sputtering, or laser ablation; and chemical vapour deposition, where a reaction of the vapour phase species with the sample surface produces a coating.

The new surface engineering treatment techniques together with the traditional surface treatments have a profound influence on a number of engineering properties, as can be seen in figure 1 (see page 18).

The thickness of the engineered surface can vary from several millimetres for weld overlays to a few micrometres for physical vapour deposited and chemical vapour deposited coatings, while the depth of surface modification induced by ion implantation is less than or equal to 0.1 micrometres. In all, the surface treatment techniques cover five orders of magnitude in thickness, as shown in figure 2 (see page 18). Similarly, the coating hardnesses span a wide range ... 250-300 HV for some spray coatings, 1,000 HV for nitrided steels, 1,300-1,600 HV for detonation gun (D-gun) carbide in metal cermet coatings, 3,500 HV for titanium nitride PVD coatings and up to even 10,000 HV for diamond coatings.

Each surface engineering technique has advantages and limitations, which must be evaluated for a specific application. The choice of material and treatment is dictated by the three zones of the component or tool: the substrate, the interface and the surface, as indicated in figure 3 (see page 19). For instance, the substrate may need to combine strength and lightness, while the coating may need to be hard and chemically inert, and at the interface a strong bond will be essential.

When a single engineering property is required, the designer and the materials engineer have a relatively easy task. However, situations often arise that require a combination of two or more properties. It is in such situations that duplex or multiple surface treatments are becoming increasingly popular. In figure 4 (see page 19) is shown some of the typical duplex surface treatments that are currently being employed in the design of components that operate under complex conditions. There can be no doubt that the scope for duplex or multiple surface treatments to provide an array of surface engineered products is virtually unlimited.

Let us now take a look at some of the latest developments and applications in this field.

B. Recent developments and industrial applications

1. Shot peening

Shot peening is a well established method of surface treatment which, when carried out in a controlled manner and to a selected specification, can markedly increase a component's life by changing the undesirable stress patterns that may have been introduced during machining or forming operations. Recent developments in duplex peening and often triple peening is now used to form complex NC-machined parts to shape.

Finishing operations like grinding often leave the component in tension or compression, which results in considerable variations in fatigue strength. In such cases, shot peening of components after finishing introduces compressive stresses which greatly improves fatigue properties. The increase in fatigue strength of steel after shot peening is illustrated in figure 5 (see page 19). It can be seen that in a steel of 50 HRC, peening increases the fatigue strength to almost twice that of smooth unpeened material, and almost four times that of notched unpeened material. In components such as gears or aerospace parts made from higher hardness materials, notch sensitivity is even more significant. Similarly, if a part in the hardened state is knocked or scratched during subsequent manufacture or on assembly, a notch could be created that might significantly affect the fatigue strength. In such cases, shot peening is beneficial, as it has a high degree of damage tolerance.

The achievement of optimum results using shot peening requires an understanding of the substrate stress profile and how it is affected by the different shot peening parameters. The effects of varying the shot hardness are shown in figure 6 (see page 20). Shot peening with shot harder than the component material gives a high level of surface compressive stress, usually 60 per cent of the UTS or more. If the shot is softer than the workpiece, compressive stresses are still induced, but can be as low as one third of the UTS. In applications such as high grade gears, where surface finish is important for reduction of noise and prevention of pitting or spalling, the use of shot softer than the part gives the required increase in fatigue strength without the excessive disturbance obtained with the hard shot.

Reduction of shot size has the effect of moving the maximum subsurface compressive stress closer to the surface (see figure 7 on page 20), which increases the surface stress, but results in a shallower compressive surface layer. In order to obtain maximum surface compressive stress, duplex shot peening is used, in which the first peening is carried out with large shot, to obtain the depth of the residual compressive stress, followed by similar coverage using small shot, to produce high residual surface stress and a consequent increase in fatigue properties. Many times, duplex shot peening is the only way to impart fatigue strength in a critical component, without involving expensive redesign.

Another area where shot peening is being increasingly applied is in the production of aircraft wings, fuselage and door panels using shot peen forming.

2. Laser surface treatments

Light amplification by stimulated emission of radiation (LASER), owes its origin to the early work of Albert Einstein, on stimulated emission (which was essential to the development of laser technology), who postulated it in 1917, as a novel type of radiation. However, it was not until 1960 that the first working laser was produced by Maiman. Since then, devices for laser have become a huge technical and commercial success story.

The laser is an optical oscillator/amplifier which produces an optical beam which is nearly parallel. The power of the beam required for material processing is commonly between 100-10,000 W. Currently, only carbon dioxide laser, yttrium aluminium garnet (YAG) or neodymium glass solid state laser are usually used for industrial purposes, though powerful argon, ruby and Excimer lasers have also been developed.

The impact of laser in surface treatment can be judged from the current list of surface treatments for which laser is used:

- Transformation hardening
- Surface melting
- Surface alloying
- Surface cladding
- Particle injection
- Laser chemical vapour deposition
- Laser physical vapour deposition
- Enhanced plating
- Shock hardening
- Pulsed laser deposition.

These processes differ only with respect to the power density, interaction time and whether material is added to the interaction zone, as illustrated in figure 8 (see page 21). Some of the features of laser surface treatments, listed above, will now be discussed.

(a) Laser transformation hardening

The first use of laser in transformation hardening was in 1966, and today there are several hundred lasers in practical use. Transformation hardening is achieved by passing a laser beam over the surface of a hardenable material, usually a ferritic steel. A thin layer is thereby rapidly heated to above the austenizing temperature in the short time that the beam is incident. Once the beam has passed, this surface layer is quenched by the conduction of heat into the still cold bulk material of the component. The quench rate is usually fast enough to give hardening by the formation of martensite, without the need for an outside coolant. The surface is usually treated to reduce the reflectivity (using matt paint/graphite/MoS_2 or graphite-sodium silicate or shot blasting, shrouding with a reflective dome etc.).

This process is confined to those materials which exhibit solid phase transformations and whose transformed structures quench to harder structures.

The advantages of laser heat treatments are:

- The treatment can be localized to a required area or pattern.
- The heat input is low and confined to a thin surface layer, giving minimal distortion and a reduction in the maximum forces in the component.
- There is no surface disruption, except for a slight volume increase due to phase change.
- No quenchant is required, expect on very small parts.
- The treatment can be carried out on the finished part, as distortion is nil and coolant contamination is not there.
- Accurate control of the treated depth is possible.
- The hardness depth profile can be shaped by controlling the power density distribution.
- The process can be easily automated.
- Process speeds are relatively high, leading to high productivity.
- Rapid quench leads to fine-grained structure.

The current uses of laser transformation hardening include:

- Increasing strength and hardness.
- Improving lubrication.
- Reducing wear.
- Rehardening martensitic stainless steel.
- Increasing fatigue life.
- Tempering metals.
- Creating carbide surfaces.
- Creating unique geometric patterns.

In table 1 (see page 35) are listed some of the current applications of laser transformation hardening.

(b) Laser surface melting (LSM)

The experimental setup for laser surface melting is similar to that for transformation hardening, except that in this case a near focused laser beam is used. The surface to be melted is shrouded in an inert atmosphere. The main characteristics of this technique are as follows:

- Moderate to rapid solidification rates, producing fine near homogenous structures.
- Little thermal penetration. This results in little distortion and the possibility of operating near thermally sensitive materials.
- Surface finish of about 25μm is rather fairly easily obtained.
- Process flexibilities possible.

Process variations centre around controlling the reflectivity, shaping the beam and shrouding the melt pool. The reflectivity is difficult to control due to melting process. However, the initial reflectivity is controlled in the same manner as for transformation hardening. The optical arrangements vary according to the method used to produce the required spot size or beam shape, which may be required to control the flow in the melt pool, as well as for the method used to protect the optics from spatter and fume. Molybdenum reflective optics are consequently being used, as they are relatively easier to clean.

Three areas of current interest, wherein LSM is being used, are in cast irons, tool steels and certain eutectics which can form metallic glasses at high quench rates. They are all essentially non-homogenous materials which can be homogenized by LSM. Cementite/ledeburite structures are formed in cast irons. The hardening effects come from austenite-to-martensite and graphite-to-cementite changes. Similarly, martensite/austenite fine structures are formed in stainless steels, forming residual compression in martensitic steels and residual tension in austenitic steels. The tension affects the corrosion properties. In titanium, highly dislocated fine structures are formed. Further, very hard, fine carbide dispersions with high hot hardness are produced in tool and special steels, using this technique. In case the hardness is very high, there is a tendency to cracking, which is usually offset by pre-heating.

The fact that laser surface alloying is almost the same process, and offers the possibility of vastly improved hardness, wear, or corrosion properties, and the fact that LSM treated cast irons and tool steels require machining or finishing, may explain the reason why LSM is not being currently used in production.

(c) <u>Laser surface alloying</u>

This is similar to laser surface melting, except that in this case another material is added to the melt pool.

The main characteristics of this process are the following:

- Most materials can be alloyed into different substrates. The high quench rate ensures that segregation is minimal.
- The thickness of the treated layer can be from 1-200 microns. Using Q-switched lasers, very thin, very fast quenched alloy regions can be obtained.
- Loss of some very volatile components can be expected.
- Other characteristics are similar to laser melting.

The process variations are similar to that encountered in surface melting except that an alloy ingredient has to be added. The alloy can be placed in the melt zone by:

- Electroplating.
- Vacuum evaporation.
- Pre-placed powder coating.
- Thin foil application.
- Ion implantation.
- Diffusion, e.g., boronizing.
- Powder blowing.
- Wire feed.
- Reactive gas shroud, e.g., C_2H_2 in Ar or just N_2.

Using this method, a wide variety of surface alloys can be prepared. The high solidification rate even allows some metastable alloys to be formed in the surface. All this can be done by non-contact method and hence is easy to automate. Some of the systems that have been examined so far, using this technique, are shown in table 2 (see page 35).

(d) Laser surface cladding

The objective in laser cladding is to fuse an alloy onto the surface of a substrate with the minimum of dilution by the substrate. Entire areas are clad by overlapping single clad tracks, as shown in figure 9 (see page 21).

The process can be carried out by either preplacing a powder on the substrate, or by blowing the powder into the melt pool generated by the laser, (see figure 10 on page 21). It can also be effected by applying the clad material as a wire, sheet, plasma spray coat or electroplate coat.

The advantages of the blown powder laser clad process are:

- Controlled levels of dilution.
- Localized heating which reduces thermal distortion.
- Controlled shape of clad within certain limits.
- Thickness between 0.3-3 mm in one pass.
- Smooth surface finish (25 microns).
- Good fusion bonding.
- Fine-quench microstructures.
- Omni-directional.
- Non-contact method of application.
- Easily automated.

The process variations are:

- Mixed powder feed - by which alloys can be formed in-situ or as non-homogenous deposits.
- Optical feed-back systems - which increase efficiency of utilization of the beam power by almost 40 per cent.
- Vibro laser cladding - in which the substrate is vibrated ultrasonically while the cladding proceeds. This method results in considerably less cracking and porosity.

Some of the claser cladding application efforts at production stage are listed in table 3 (see page 35).

(e) Particle injection

This process is similar to laser cladding by the blown powder route, except that the particles blown or propelled into the laser pool do not melt. The main advantages of this process are improved hardness and wear with reduced friction coefficients in some systems. Process variations centre around the particle delivery system, delivery pressure (vacuum or atmospheric), and gas shrouding systems.

In order to achieve a good surface layer, the hard embedded particles must be wetted by the metal matrix and they must be strongly bonded to it. It is also desirable that the particles do not suffer too much dissolution while lying in the melt pool. These requirements mean that the particles and the surface must be clean and the level of super heat must be kept as low as possible, compatible with the wetting condition.

This process shows considerable promise in the hardening of aluminium and its alloys by the injection of TiC, WC, SiC, or Al_2O_3 particles. It has also been applied to stainless steel.

(f) Laser chemical vapour deposition (LCVD)

This area of surface treatment covers two distinct processes: Thermally sensitive chemicals may be blown into a laser generated hot spot where they undergo pyrolysis, or, alternatively, the chemical vapour is decomposed by photolysis with laser radiation of a particular frequency.

This method has attracted considerable interest in those working in the areas of electronic circuits and thin wear-resistant films, like TiC. The early limitation of this process was the thermal spread in the substrate. However, the use of short pulsed lasers or higher powers has greatly offset this problem. As chemical rate control conditions dictate the formation of deposits, the deposition rates are low. If the temperature or the concentration in the vapour rises too far, then mass transfer rate control takes over and either a powdery or a rough deposit is formed. Thus, deposition rates are of the order of a few microns/minute. Adhesion of these deposits has usually been found to be very good. This is probably due to the fact that the laser continues to heat, and therefore allows diffusion, even after the deposit has first formed.

(g) Laser physical vapour deposition (LPVD)

The laser can be used as the heater in a sputtering apparatus or as a surface heater to control the location of physical vapour condensation.

(h) Laser enhanced electroplating

The irradiation by a laser beam of a substrate used as a cathode during electrolysis causes a drastic modification of the deposition process in the irradiated region. The interesting aspects of this process are:

- The possibility of rapid maskless patterning.
- Possibility of enhancing the plating rate in selected areas, and
- Possibility of modifying the structure of electrodeposited coatings.

The radiation must be able to penetrate the electrolyte and has therefore to have a shorter wavelength than the 10.6 micron radiation of a CO_2 laser. The lasers used usually are argon ion or Nd YAG lasers. The process can also be operated on electroless deposition processes.

(i) Laser shock hardening

When a short pulse of high power strikes a surface, it sends a shock wave through the surface. The wave is reflected within the substrate, generating a very high pressure similar to shot peening. However, with laser shock hardening there is very little discernible surface disruption. This process requires rather exotic ultra-short pulse high powered lasers.

(j) Pulsed laser deposition

In addition to the above techniques, mention must be made of the use of pulsed laser to "flash evaporate" complex materials and deposit a thin film, for example, new high temperature ceramic superconductors. An excimer laser pulse quickly vaporizes material constituents having widely varying vapour pressures and complex crystal structures, so the bulk composition is retained in the deposited film. This process has produced some of the highest quality films currently available today. The power and flexibility of pulsed laser techniques are expected to play a wide role in surface treatment applications in the coming decades.

Although pulsed laser evaporation technique has been known for almost two decades, it has only recently gained prominence in the deposition of high-critical temperature superconductors. In this technique, a pulsed laser beam is directed onto a bulk target having a composition similar to that of the desired thin film, and the material thus evaporated is deposited onto a substrate placed about 3-7 cm from the target. This technique provides a nearly perfect evaporation and deposition stoichiometry over a large area, and produces activated and ionized species which strongly facilitate the synthesis of films at low temperatures.

Using lasers to deposit $YBa_2Cu_3O_{7-\delta}$ films by evaporation/ablation from sintered bulk superconducting targets has become very popular and successful for producing high-quality superconducting thin films. The simplest hardware employed by different groups involves a laser system, an ultra-high-vacuum deposition chamber equipped with a rotatable target heater, and a substrate heating system, as shown schematically in figure 11 (see page 22). The laser is directed onto a bulk target and the evaporated/ablated material is deposited on a substrate placed parallel to the target. Due to the interaction of the incident laser beam with the evaporated material, a high-temperature plasma is formed which may extend from the target to the substrate. This laser-induced plasma is responsible for a number of unique characteristics observed in such PLE films. The thickness of the film is controlled by the irradiated spot size, pulse energy density and the number of laser pulses. The optimization of the laser parameters (e.g., pulse energy density, wavelength and pulse duration) and other processing variables (substrate-target distance, oxygen partial pressure, substrate temperature, etc.) is required to deposit good quality superconducting thin films.

Several types of lasers have been employed in the deposition of thin films, including excimer (pulse duration = 15-50 ns, wavelength = 193-308 nm), Nd-YAG (pulse duration = 5-15 ns, wavelength = 1,064 nm) and CO_2 (pulse duration = 25 ns, to continuous wave, wavelength = 10.6 μm) lasers. The films fabricated with long pulse duration and long wavelength lasers are plagued by several problems, like non-stoichiometric composition and a high density of particles, resulting, therefore in poor superconducting properties. Short wavelength excimer laser pulses, in contrast, have been particularly successful in fabricating films with excellent superconducting properties. The excimer laser beam is not only absorbed in the near surface layers, but also produces a greater degree of ionization in the laser-induced plasma as a result of photoionization and other related processes. This unique laser-solid-plasma interaction gives rise to stoichiometric evaporation and deposition of multi-component superconducting films. Under optimized conditions, the stoichiometric evaporation results from rapid localized surface heating and evaporation of the near surface layers, while the stoichiometric transport of vapour results from the very high forward directed velocities of different plasma species.

The deposition characteristics of this PLE technique are different from conventional thermal evaporation processes. The PLE films are characterized by the forward directed nature of the deposit with spatial thickness variations in the order of (cos ϕ), where ϕ is the angle between the radial vector and the target normal, whereas conventional thermal evaporation processes are of a cos ϕ spatial film thickness. Further, the ablated species in the laser generated plasma are characterized with kinetic energies in the range of 20-40 eV, which are two to three orders of magnitude greater than the thermal energies. These unique features of the PLE technique have been attributed to the complex nature of interaction of the incident laser beam with the target and evaporated/ablated material.

In figure 12 (see page 22) is shown a schematic diagram of the laser-target-plasma interaction occurring during PLE. Based on the nature of the laser-solid plasma interactions, three different regimes have been postulated. They are the evaporation regime, in which the laser beam interacts with the target material, resulting in evaporation of the target; the isothermal regime, in which the laser energy is absorbed by the evaporating material, leading to the formation and initial isothermal expansion of the partially ionized plasma; and the adiabatic regime, in which isoentropic expansion of the plasma takes place, resulting in film deposition. The first two regimes begin and continue during the duration of the laser pulse, while the adiabatic regime begins after termination of the laser pulse.

Figure 13 (see page 22) shows a schematic diagram of the interaction of a laser beam with a solid target. A part of the beam is reflected, while the remainder is absorbed over a characteristic absorption depth, given by α^{-1}, where α is the absorption coefficient. This value strongly depends on the wavelength of the incident laser beam and the band structure of the target material. The bulk $YBa_2Cu_3O_{7-\delta}$ have a carrier density of approximately 4 x 10^{21} per cm^3, which means that the laser radiation will be strongly absorbed in the near-surface layers. The photon energy from the laser is transfered into the lattice in a very short time ($<10^{-12}$ seconds). In nanosecond time scales, the heat diffusion distance in that target is in the submicron range (50-500 nm). Thus, only the near-surface layers of the target are rapidly heated and evaporated, which leads to stoichiometric evaporation of the material from the target.

The most significant advance in superconductor thin-film processing, especially using the PLE technique, is the development of in situ growth process i.e., a method which produces the superconducting phase during deposition, thereby eliminating the need for post-deposition annealing at high temperatures. There are several advantages of low-temperature in-situ films are more homogeneous and have a smoother surface, as well as a higher degree of crystallinity and much better superconducting properties. These films also show very reproducible superconducting characteristics and are less sensitive to phase segregation of impurities.

The inherent simplicity and the versatility of the PLE technique also allows easy fabrication of superlattice structures. By sequential irradiation of two separate targets, even single unit cell layers of $YBa_2Cu_2O_7$- and $PrBa_2Cu_3O_7$ have been grown by the PLE technique.

Excellent quality superconducting thin films can be grown on semiconductor substrates by depositing a buffer layer prior to the superconducting thin-film deposition. Using such methods, epitaxial superconducting films have been fabricated on yttria-stabilized zirconia (YSZ) buffer layers epitaxially grown on silicon subtrates. The PLE technique has also been successfully used to deposit expitaxial buffer layers of MgO, CeO_2 and PrO_2.

3. <u>Electron-beam surface treatment</u>

Electron beams can be used as the high energy source for surface treatment of materials, as an alternative to lasers. The first recorded demonstration that electron beam could melt metals goes back to 1877, when Sir William Crookes fused a platinum anode in a cathode ray tube. However, it was Thompson who, twenty years later, showed that these cathode rays were in fact beams of electrons. It was only in 1907 that Von Pirani made the first serious attempt to use this technique as a tool for melting. The application of this technique for surface treatments is of recent origin.

An electron beam requires a vacuum system and cannot be used for gas alloying with nitrogen. Alloying elements have to be pre-placed on the surface by spraying, plating or painting prior to melting. Electron beam, on the other hand, penetrates deeper into the metallic surface, is more energy efficient, and is not greatly reflected from inclined surfaces. This means that it can be used to treat complex components that could not be laser surface alloyed as the laser beam would be reflected rather than absorbed at the surface.

One such electron beam alloying process is the EBX method and the results of Amsler wear tests on such a coating are compared with laser nitriding in figure 14 (see page 23). Even at stresses up to 750 $MNmm^{-2}$, the wear rate is seen to be very low, compared to that of steel tested against the same counterface.

4. <u>Carburizing process</u>

The modification of surface properties of steel by adding carbon and hardening is a process that dates back to blacksmithing. While the basic principles remain the same, there has been continual research to streamline traditional processes and to develop new processes to achieve better quality control, better prediction of results, and more consistent results. The development of new equipment designs and processes for case carburization also is driven by the need to increase productivity, treat a wider variety of parts at variable cycles, lower stockpiles and inventories to reduce costs, establish just-in-time manufacturing concepts, and to produce higher quality parts. Developments in this area of surface treatment include high-temperature carburizing, plasma (ion) carburizing, vacuum carburizing and making continuous furnaces more flexible.

Regardless of the technique used, the principles of the carburizing process are the same. Carburizing is a diffusion limiting process, i.e., the time required to reach the desired carbon profile in the workpiece is governed by the rate of carbon diffusion into the part. Diffusivity increases exponentially as a function of absolute temperature; therefore, higher productivity is obtained by increasing the carburizing temperature. For example, increasing the carburizing temperature from 900°C to 955°C cuts the carburizing time by half, and going from 955°C to 1010°C, cuts the time by nearly half again, as illustrated in figure 15 (see page 23). Unfortunately, there are negative effects that accompany high-temperature carburizing: shorter furnace-hardware life and the possibility of a reduction in the mechanical properties of treated parts due to grain growth.

To overcome some of these problems, Surface Combustion Inc., together with Gas Research Institute, developed a new integral-quench furnace, known as the Ultra-case furnace. For example, in a conventional furnace, hearth-supports normally fail due to creep at higher temperatures. The new furnace (see figure 16 on page 24), incorporates a special arrangement that lifts the work off the hearth during the carburizing cycle, which reduces the stress on the hearth, thus keeping high-temperature creep within acceptable limits for satisfactory furnace operation. Improved heat-resistant alloys are used for the radiant tubes, which along with the high-efficiency regenerative burners, permit the use of higher operating temperatures at increased heating rates without experiencing unsatisfactory tube life. This combination results in equivalent furnace load ratings at 930° and 1065°C. By comparison, the conventional furnace has to be derated by about one third when going to the higher temperatures, making it more expensive to carburize at higher temperatures. The use of increased radiant-tube surface area also contributes to a faster heating rate, resulting in significant savings when processing larger workloads at higher temperatures.

Plasma (ion) carburizing offers several advantages over conventional gas carburizing including:

- Reduced cycle times.
- Ability to use higher temperature cycles without affecting furnace life.
- Consistent production of uniform case depth.
- Elimination of final machining by producing oxidation-free surface layers.
- Reduced part distortion.
- Uniform heat distribution in the hot zone.
- Ability to carburize steels with high chromimum content that are difficult to treat using an atmospheric process.

Plasma carburization is done in a special furnace using natural gas at sub-atmospheric pressure as the carbon source, which eliminates the need for generated gas. The carbon source is ionized and accelerated to the workpiece by means of an electric potential between the workpiece and the surroundings, producing a uniform glow discharge around the workpiece. This creates a very uniform carbon profile over the entire surface of the part being treated. Unlike gas carburizing, which uses an endothermic gas containing carbon dioxide and water vapour, there is no oxidant present in plasma carburizing, which almost completely eliminates intergranular oxidation at the surface of the workpiece.

Higher temperatures are used in plasma carburizing than in atmosphere carburizing. In addition, the glow discharge is very effective in supplying carbon, so the surface of the workpiece is saturated with carbon for a longer portion of the total carburizing time. The combination of effective carbon supply at a higher carburizing temperature permits a shorter cycle time without impairing product quality, resulting in a cleaner workpiece having less distortion compared with a conventionally carburized part.

The efficiency of carburizing depends on the amount of carbon at the part surface and the temperature and time. In atmosphere carburizing, the flowing gas supplies carbon to the surface, a mechanism having limited efficiency when carburizing parts containing holes or deep recesses, such as on gears. By comparison, the plasma carburizing is capable of penetrating such surface irregularities much better, resulting in a more uniform case.

Potential applications for plasma carburizing include very high-quality, precisely controlled parts such as gears, steering components, fuel injecting components, and other small parts that require a relatively shallow case (<1.25 mm).

The plasma carburizing furnace is usually similar to a two-chamber vacuum furnace, consisting of a loading chamber with an integral quench chamber separated from the high-temperature processing chamber by a vacuum tight sealing door.

Vaccum carburizing is another process which is capable of producing parts having improved mechanical properties at reduced heat-treatment cycle times. This is a non equilibrium, boost/diffuse-type carburizing process in which the steel being processed is austenitized in a rough vacuum, carburized under a partial pressure of hydrocarbon gas, diffused in a rough vacuum, and oil or gas quenched.

Furnaces used for vacuum carburizing can be made of either graphite or ceramic. Vacuum carburizing typically is either a four- or five-step process consisting of:

- Heating to the carburizing temperature (840-1040°C) and soaking only long enough to ensure part-temperature uniformity. During this step, any oxides on the part surface must be reduced either in a rough vacuum (graphite f rnace) or under a partial pressure of hydrogen (ceramic furnace).
- A boost step in which the vacuum chamber is back-filled with either pure hydrocarbon gas or a mixture of hydrocarbon gases, which dissociates on the part surface, providing saturated carbon to its solubility in austenite at the process operating temperature.
- A diffuse step under a rough vacuum to achieve the required carbon profile.
- Cooling to the hardening temperature and quenching in oil.
- An alternative step (for grain refinement) of gas quenching to an intermediate temperature, reheating to an austenitizing temperature, and oil quenching.

One of the early problems encountered in vacuum carburizing was the need to use high carburizing-gas partial pressures and gas-circulating fans to achieve case depth uniformity in large, dense loads. This led to furnace maintenance requirements which added to unit-processing costs, making the process uncompetitive in many carburizing applications. Recently, Hayes has enhanced the process by using a pulsed/pump technique for gas circulation. Controlled amounts of carburizing gas are pulsed under pressure into the heating chamber at variable rates to create a high kinetic energy flow. Pulsing is followed by either total or partial evacuation of the spent gas. This method allows processing moderate to heavy workloads, providing a uniform case depth, and also reduces gas consumption and furnace maintenance.

5. Plasma nitriding

The potential of nitriding in ionised gas was recognized as early as the 1920s by Bason, but it is the work of Berghaus that was, perhaps, instrumental in establishing this technique.

Plasma nitriding (also referred to as glow discharge nitriding or ionitriding) was used only to a limited scale up to the mid-1960s, when improvements in control systems allowed the discharge stability to be enhanced.

A typical schematic sketch of a plasma processing unit is shown in figure 17 (see page 24). Most of the control functions are now microprocessor based. In common with other nitriding techniques, nitrogen is introduced into low alloy or tool steels which contain nitride forming elements such as chromium, aluminium and molybdenum. Nitrogen combines with these elements producing a fine dispersion of alloy nitrides within the case. The strength of the surface region can be significantly increased by this process. Typical hardness profiles are presented in figure 18 (see page 25) on a range of materials. Plasma nitrided titanium alloys have been reported to show excellent performance in adhesive wear situations under low-to-medium load conditions.

The advantages cited for plasma nitriding over conventional gas nitriding are:

- Reduced treatment times (generally for materials with passive oxide films, e.g., austenitic stainless steel).

- Reduced gas and energy consumption (usually only when the loading densities are light).

- Metallurgically superior structures (provided there is a close control over the discharge parameters, atmosphere composition and temperature).

- Ease of jigging and masking under normal conditions.

- Non-hazardous processing.

The combined application of PVD and plasma nitriding is a typical example of a systems approach to surface engineering, where the surface and substrate properties are optimized for maximum performance. A typical example is the improvement in the wear resistance, produced by coating TiN by PVD onto pre-plasma nitrided low alloy steels.

6. Nitrocarburizing

Gaseous nitriding is usually carried out at about 570°C for about 2-3 hours to produce an adherent surface compound layer with good antiscuffing properties. Beneath the surface layer there is a diffusion zone up to 1 mm thick. On quenching, most of the nitrogen in the diffusion zone is retained thereby increasing the hardness and fatigue strength of the material. Post-nitriding oxidation treatments are usually carried out to increase the aesthetic properties of gaseous nitrocarburized components for the hydraulic industry. Black nitrocarburizing treatments, including the Nitrotec process, have been used to enhance the fatigue, wear, and corrosion resistance of mild steel type of materials. The Nitrotec process is fundamentally a derivative of the earlier gaseous nitrocarburizing techniques, with the important addition of a pre-quench oxidation sequence.

A typical schematic diagram of the modified sealed quench Nitrotec furnace is shown in figure 19 (see page 25). The time, temperature, and nitrogen potential in the Nitrotec process are manupulated to produce a compound with substantial porosity in the outermost layer. This porosity improves the response to the subsequent controlled oxidation and also provides a carrier for an organic sealant which further improves the corrosion resistance. Typical applications of this process include automobile windscreen wiper linkages, bumper armatures (in Austin Rover 80), seat sliders (Renault 25), and in the cost-effective viscous slip differential units (Ford Sierra/BMW).

In plasma nitrocarburizing, unlike in plasma nitriding, the treatments are performed in nitrocarburizing atmospheres consisting of nitrogen/hydrogen/methane or nitrogen/hydrogen/carbon dioxide. The aim is to enhance the corrosion and wear resistance of plain or low alloy steels through the production of an e-carbonitride layer on the surface of the component.

7. Induction hardening

The use of induction heating in metals processing is well known. Induction heating is equally applicable to surface and through-hardening. When the frequency of the alternating current to the inductor is high, the induced currents will flow close to the workpiece surface, and the heating effect will be concentrated there, as is appropriate for surface hardening. At lower frequencies the penetration depth will be high, and the whole workpiece will be rapidly heated.

Solid state invertors based on thyristors has had a significant effect on the way frequencies above mains (50 Hz) are generated for induction equipment. When first available, they operated at low frequencies, and hence were readily adopted for billet heating and other through heating applications. Today, the frequency range extends to 25 kHz and even more, enabling their role to be extended to surface hardening and similar duties. In addition, solid state frequency generators based on transistors have been recently developed, rated from 0.5 kW to 12 kW in the range 80-200 kHz. Built-in microprocessors, providing control of the generator and heating process, can be integrated with associated computer controlled process equipment, making the entire induction heating system more efficient, reliable and flexible.

Recent developments include dual-pulse induction hardening (DPIH), which is expected to be commercialized within two years. In this single-shot method, parts such as gears, pistons, camshafts etc., can be contour hardened in less than a minute using a single workstation and power supply.

Surface hardening of components produced from medium carbon steels remains the most popular application of induction hardening. There are two notably different ways by which induction hardening is used. Long runs of similar components are favoured in automotive engineering, as it is rapid and economical, and permits a high degree of automatic handling. Even for larger workpieces, the trend is for the whole area to be heated simultaneously (single-shot hardening) rather than traversing in inductor progressively along or around the workpiece.

In contrast, much shorter runs of components are favoured by contractors specialized in this kind of work. In figure 20 (see page 26) is shown one such typical example. While the setting-up time and hence labour content is high, induction heating proves cost-effective due to its inherent benefits i.e., selective hardening, low distortion and ability to develop deep cases in a short time.

8. Ion implantation

The modification of the near-surface region of materials by use of energetic ion beams has been investigated extensively in recent years. The original application of such techniques was to control the composition of semiconducting materials. The nature of the process allows any element to be introduced into the near-surface region of a solid in a controlled and reproducible manner that is independent of most equilibrium constraints. Due to the non-equilibrium nature of this process, composition and structures unattainable through conventional methods may be produced.

In ion implantation, the dopant or alloying element is the ion beam, which after an acceleration of tens to hundreds of kilo-electronvolts impinges upon the surface of the target. The energetic ion comes to rest by displacing atoms from their normal lattice sites by ionizing target atoms, thus producing a large number of point defects. Most defects are annihilated by recombinations shortly after the passage of the bombarding ion, but some survive. The resultant structure consists of the host (target) material with an impurity (alloying) addition and a defect structure characteristic of radiation damage.

Ion implantation has the following features:

- Allows precise control of the total number of injected ions;

- Permits independent control of the depth of penetration;

- Allows the use of all combinations of ions and target materials;

- Can achieve concentrations above the equilibrium solid solubility limit;

- Can be carried out at low or elevated temperatures.

Ion implantation received much publicity as a technique for improving wear resistance and for decreasing friction, and initially there was a flurry of experiments on ion implantation into a variety of materials that gave mixed results when tested. Subsequently, it was realized that a knowledge of the metallurgical system (substrate and implant species) being studied must be used in designing both the implantation procedure and the test procedure.

Wear is a complex interplay between mechanical and chemical processes at solid interfaces. An additional complication arises whenever a third component (e.g., a lubricant) is present between the two opposed surfaces.

Wear processes can be divided into four main types: adhesive wear, abrasive wear, corrosion or oxidative wear and surface fracture. In many real systems two or more of these mechanisms may occur simultaneously.

Implantation can affect the deformation mode of wear by modifying the composition and micro-structure of the near-surface layer. The flow strength (hardness) of the surface can be increased by solid solution strengthening or precipitate formation. The work hardening behaviour can be altered, as can be the defect structure produced. Implantation can reduce the deformation wear rate indirectly by reducing the coefficient of friction. Lowering the coefficient of friction reduces the intensity of the stresses transmitted to the surface. It can relocate the maximum shear stress from the uppermost layer to a depth well below the surface (10-20 per cent of the contact diameter).

Implantation of nitrogen into pure iron or steels (low to medium carbon, low alloy) causes a decrease in the wear rate, as measured by simple abrasive and sliding tests. The amount of decrease in the wear rate varies from "slight" to factors of 10-15, depending upon the test conditions. In most cases, no significant change in the coefficient of friction is observed.

Next in importance to nitrogen, is the implantation of titanium or titanium plus carbon, on ferrous materials. The general indication is that the coefficient of friction is reduced by 35-90 per cent and wear is reduced by up to 90 per cent in both abrasive and sliding wear tests on austenitic and martensitic steels. Implantations of C, P, Cr, Mo, or Ta have been reported to have no significant wear of 3135 steels, while tantalum implantation has been reported to cause an improvement in 9130 steel.

Nitrogen implantation in titanium and its alloys (which have very poor resistance to sliding wear) has shown to increase the hardness by a factor of 2, especially in the case of commercially pure α-titanium and in α/β alloy Ti-6Al-4V. Several other metals and alloys have also been studied; among them are ion implantation of boron, nitrogen or tin in aluminium and boron implanted in beryllium, just to mention a few. The large number of parameters involved in the implantation process and the mechanical testing for wear makes the task of noting general trends and principles very difficult. In general, improvements by factors of 2-3 in adhesive wear, and by a factor of 10 in abrasive wear due to increases in implantation-induced hardness have been observed. The greatest opportunity for reducing wear occurs for the oxidative mechanism; reductions by factors of 100-1,000 may be possible.

Ion implantation is also being used to improve fatigue strengths. It is generally believed that cracks initiate at or near the specimen surface, and that crack propagation is governed by the properties of the bulk material; hence ion implantation might be expected to influence the crack nucleation stage, but not the propagation stage.

Studies on the potential of using ion implantation to protect metals from oxidation at elevated temperatures have moved from the "scatter gun" implantation of as many different elements as possible to experiments based on an understanding of the oxidation mechanisms. Some success has been reported in metals that oxidize by anion migration to the oxide/metal interface, by altering the solubility of oxygen, and by blocking the short-circuit diffusion paths in cation controlled systems. It is difficult to say exactly how useful this process may be in improving the oxidation resistance, due to the complex mechanisms involved.

In the field of corrosion science, ion implantation has been used for several reasons. By doping metallic surfaces, the rate of anodic and/or cathodic reactions may be altered, often in such a manner as to lower corrosion rates considerably. Alloying for corrosion protection often requires expensive or scarce elements; hence, a surface treatment which places the alloying element where it is effective is very desirable. The metastable compositions and structures often produced by ion implantation offer new opportunities for applications.

The usual approach to the design of corrosion-resistant alloys is to promote passivity by adding elements which lower the passivation potential and critical current density. This is the reason for addition of Cr, Mo and Ni to iron. In some cases an inert species is added to a reactive metal to provide passivity by stimulating cathodic kinetics, e.g., addition of Pt to Ti. The passivated alloy results from the formation of a galvanic couple that has a corrosion potential more negative than the passivation potential of titanium.

Implantation of ions in ceramics is much more complex and less studied. There are at least two sublattices whose atoms have different masses and displacement energies. This situation affects the number and types of defects produced in the displacement cascade. The types of defects that can be produced are also strongly influenced by the requirements for local charge neutrality, local stoichiometry, and the nature of the chemical bonding of the particular lattice. Ionizing effects in ceramics may contribute significantly to the production of lattice defects, in contrast with metals where ionization effects are generally unimportant.

Metal-ion implantation has not evolved into a commercial industrial process for general application mainly because it was developed primarily for applications in the semiconductor industry, and the sophisticated equipment is too complex and costly for most basic-manufacturing companies. Recently, a joint venture by ISM Technologies Inc., and Nippon Steel Corp., Japan, that was aimed at overcoming this dilemma, resulted in the development of a low-cost, simple, and reliable metal-ion implantation based on the Mevva ion source, developed at Lawrence Berkeley Laboratory. The Mevva IV is considered to be a major breakthrough in providing cost-effective metal-ion implantation. The Mevva IV multi-cathode metal-ion implantation system, illustrated in figure 21 (see page 26), is fully computer controlled with cathode changing (ion implant species), instrumented beam stop, and infrared pyrometer to monitor workpiece temperature. It operates at voltages up to 100 kV, and has generated time-average currents up to 50 milliamperes. The ion source is shown mounted on top of a 107 cm diameter, 114 cm long stainless steel cryogenically pumped vacuum chamber. Mevva is very efficient in producing ion beams of refractory, noble and rare earth metals.

9. Electrodeposited composite coating techniques

Composite coating based on electroplating processes provides an alternative to flame sprayed coatings for engineering a range of properties like lubricity, wear and corrosion resistance into a surface.

Electrodeposited coatings are derived from two different plating processes, electrolytic and electroless plating, which can be applied to any conductive material. Coatings consisting of a co-deposit of inert material uniformly dispersed in a plated metal began to gain widespread acceptance, outside aerospace applications, since the early 1980s.

Conventional electrolytic plating, in which the component is used as the cathode, has the advantage that coatings of any thickness can be deposited, and they can be applied to selected areas of the component by using masking techniques. The coatings have excellent adhesion, forming a strong bond at the interface between the deposited and base metals. As the process is carried out at low temperatures, the added advantage is that there is no risk of deformation of the component. The drawbacks of the electroplating process are that some base materials require low temperature (150–400°C) de-embrittlement, and that deep holes, recesses and similar shapes are more difficult to plate and may require specially shaped anodes.

Electrodeposited composite coatings (ECC) maintain all the features described above, although a minimum coating thickness is required to trap the particles of the co-deposited materials. Successful ECCs formed by electrolytic methods require clean particles, typically 2–8 μm in size, to be dispersed uniformly throughout the electrolyte during the plating cycle. The particles must be processed so that they wet out and remain suspended in the solution, and it is also important to maintain the purity of the electrolyte.

Particles that have been successfully used in commercial ECCs to date include chromium carbide, silicon carbide and PTFE. The matrices used are restricted to those efficient in plating terms, i.e., nickel and cobalt.

Elnisil, a nickel/SiC ECC system, developed by Poeton, is currently being applied to air cooled aluminium cylinders in high performance motorcycle engines, chain saws and stationary engines. Porsche, Mercedes and BMW use Ni/SiC ECC. Other applications include extrusion screws for plastic injection machinery, high pressure valves, paper conversion equipment, water pumps, sand casting moulds, textile drawing machinery and die jaws used in the blowing of plastic films.

The incorporation of PTFE in an electroplated nickel results in exceptional wear resistance. Typical applications include pneumatic valves and cylinders, water pump shafts and bearings, hinges, machine tool slideways, and electroforming tools.

Electroless plating involves deposition of coatings from non-electrolytic solution of metallic salts and reducing agents by the action of heat. The process overcomes the disadvantages of electrolytic plating in that a coating of uniform thickness can be deposited on all surfaces, even narrow blind bores. Coating thickness is, however, limited to 60 μm, using normal techniques. One of the disadvantages in using electroless processes to create composite coatings is the tendency to plate any foreign body introduced into the plating tank, i.e., instead of the particles being introduced into the coating, they themselves become coated. This problem has been overcome in the Niflor process, in which submicron PTFE particles are introduced directly into an electroless nickel matrix.

Multi-stage processes are also being used to overcome the problems in creating composite coatings in electroless processes. The Nedox (Poeton) process, for example, involves the co-deposition of a coating of nickel onto the component's surface. The coating contains numerous linked micropores, which are enlarged by means of special treatments. These coatings are particularly useful for applications in the food industry, printing rolls, plastic or rubber moulds, and for seawater corrosion resistance and in other marine and aerospace applications.

10. Thermal spraying

Thermal spray processes have been used by manufacturers and repairshops for the past 70 years to deposit protective metals coatings on various substrates. Flame spraying, using an oxyfuel flame to melt a wire or powder feed material, was the first thermal spray process to gain wide acceptance. Specialized oxyfuel systems that deliver a high-velocity (up to hypersonic levels) spray stream are becoming popular.

Electric arc spraying and plasma spraying, which use electrical energy to melt the coating material, are commonly used today in an increasing number of applications.

All thermal spray processes require coating materials to be fed into a spray gun, where the material is either totally or partially melted and propelled as droplets towards the workpiece being coated. The droplets strike the workpiece, solidify, and build up a coating layer by layer, similar to spray painting.

Major developments in the combustion and arc-spray techniques have been the introduction of high velocity oxyfuel (HVOF) and inert gas wire spray systems, respectively.

The high velocity oxyfuel (HVOF) thermal spraying process uses an internal combustion (rocket) jet to generate hypersonic gas velocities of 1,830 m/sec. Combustion fuels used include propylene, acetylene, propane, hydrogen, etc., for spraying carbide and noncarbide coating materials. When burned with pure oxygen, these fuels produce gas temperatures greater than 2,760°C.

Combustion ignition, gas control, and powder feed are basically simple in HVOF systems. A pilot flame, typically operating on hydrogen and oxygen, is ignited manually, and flow rates of two main-jet gases are controlled by a flow meter. Electrically operated solenoids activate the main combustion jet. Power flow is also electrically controlled and feed rates are monitored automatically.

Powder is fed into the high-velocity gas jet in the coating-gun nozzle. Powders deposited include pure metals, carbides, alloys, and certain ceramics and plastics. Two typical HVOF thermal spray guns are shown in figure 22 (see page 27).

Advantages of HVOF over plasma spraying are higher coating bond strength, lower oxide content and improved wear resistance (higher hardness). Further, it has a higher deposit efficiency (75 per cent) compared to plasma spraying (45 per cent). An added advantage is that HVOF systems have about 50 per cent less spraying parameters to control compared with plasma spraying.

In table 4 (see page 36), some typical advantages of the coating properties of HVOF over plasma are listed. A comparative study between HVOF and other spray systems, with regard to WC-Co coatings, is shown in table 5 (see page 36). Similar comparisons between plasma and HVOF with regard to Cu-Ni-In coatings (typically applied to the root of gas-turbine blades) is shown in table 6 (see page 36). HVOF-sprayed aluminium-polyster (AL-PE) coatings, have been reported to show higher bond strength, hardness, coating density and improved resistance to hot gas erosion, compared to plasma sprayed coatings. The disadvantages of HVOF thermal spray process is that it requires more expensive wear-resistant tooling and special cooling techniques.

In the electric arc spraying process, two consumable wire electrodes (one positive and the other negative) advance simultaneously through insulated conduits into the arc-spray gun, where the wire tips approach each other at an acute angle. The wire paths intersect at a position in the centre of the atomizing gas stream, and an electric potential is applied across the wires to form an arc at the point of intersection.

The arc partially ionizes the gas and melts the wire, forming droplets that are atomized into smaller droplets and propelled towards the workpiece.

The coating consists of the sprayed metal plus nonmetallic inclusions formed by gas-metal reactions occuring both in the arc and in flight.

Gas-metal reactions and metal vaporization also can cause partial loss of alloying elements present in the feed wire. In addition, the hot, coated surface can be partially oxidized by the ambient air between spraying passes and immediately after spraying.

A typical electric-arc spray system is shown in figure 23 (see page 27). The arc spray process is much more energy efficient than flame-spray or plasma-spray processes. Further, the absence of flame eliminates damage that a flame can cause to plastics or other heat-sensitive substrate materials. Any metal wire can be sprayed over a wide range of spray rates, and at much higher spray rates compared to plasma or flame-spraying processes.

Despite these advantages, arc-spray process has not reached its full commercial potential as it is often not able to produce a dense, adherent coating having the required chemical composition. When air is used as the atomizing gas, a considerable amount of the sprayed metal is oxidized. Further, oxides deposited on the substrate as loose particles reduce the coating/substrate bond strength and the layer-to-layer adhesion. Oxide forming inclusions within the coating are often porous as are the metal/oxide interface. All these contribute to premature coating failure in corrosive service. In addition, the hard oxide inclusions can also cause reduced coating machinability.

The use of inert gas atomization (e.g., argon/nitrogen) in the arc-sprayed process, on the other hand, reduces the detrimental effects of metal oxidation. This is because a large proportion of the oxidation in air spraying occurs in and near the arc zone, where atomizing air exits from the gun, while inert atomization largely removes oxygen from this critical area.

Aluminium and aluminized (hot dipped) steels are used extensively for corrosion resistance in outdoor and industrial environments. In many instances, thermally sprayed aluminium coatings are more practical and cost efficient. Unfortunately, as much as 45 per cent of the aluminium wire atomized in air arc-sprayed guns is lost due to oxidation and/or vaporization in the arc or in flight, and blows away as fume and dust. Inert-gas atomization significantly improves deposit efficiency of aluminium on low-carbon steels. While the exact reasons are not known, it is presumed to be due to a reduction in the oxygen partial pressure in the arc and spray stream, which limits oxidation; a reduction in the arc temperature and due to the creation of a thinner oxide shell on large droplets increases the potential for their deposition and adherence to the workpiece.

Plasma spraying can be used to process virtually any material or materials combination. However the process has limitations, and many of the developments that have occured recently, as well as those that will emerge in the future, are a result of overcoming these limitations. The plasma spraying technique is complex and hundreds of factors influence the process. There are at least 12 independent parameters that have the strongest influence on coating properties and survivability. Many of the developments that have occurred in the industry in the past few years address the parameters via control, empirical or real-feedback looping, redesign of fundamental components, rethinking power supply design, and, to some degree, redesign of feed stock powders (e.g., chemistry, size distribution, and shape).

Mass flow control and metering have replaced traditional analogue gauges for handling gas used in plasma spray process, which enables digital outputs with feedback potentials. Similar control is being used for powder feed, which is capable of providing the operator with instantaneous powder-feed rate. The development of fluidized-bed powder feeders permits smooth flow with less pulsing of a wider range of powder types.

In the area of power systems, controlled-DC equipment with heat exchangers, designed specifically for plasma guns, have now become the rule.

On the manufacturing side, Sulzers plasma-technique has developed a plasma-control system in which all relevant parameters are displayed on a CRT. The system incorporates operator-friendly controls which is an indication of the future in this industry.

Development of the plasma gun has also progressed. For example, Perkin Elmer Metco introduced the APG (advanced plasma gun), which is capable of continuous automatic control of cathode-anode spacing, thus enabling a curette voltage control without using a secondary gas. Similarly, Browning Engineering and Flame Spray Industries have independently developed plasma wire guns which promise to provide relief from the problems associated with traditional powder feeding.

The growth of this technology has led to branching in new directions. For example, the plasma transferred arc (PTA) process, largely viewed as a welding tool has attracted renewed attention. Also of further interest is the use of radio frequency (RF) plasma of a relatively large size using reactive gases; very large particles (>100μm) can be sprayed using RF plasma leading to cost benefits. A limitation is that the deposit-substrate system must be heated to affect coating densification through sintering.

Plasma spraying in a reduced pressure chamber (with no oxygen present) allows the coating/substrate system to be maintained at a high temperature during processing. High temperature metal alloys can be added to refractory oxides to produce a composite coating having unique high temperature wear properties. Further extension of chamber spraying makes it possible to plasma-spray coat the interior of a large chemical handling pipe or tank, using the pipe or tank itself as a chamber from which air is excluded during spraying. Another aspect of chamber spraying is reverse-arc sputtering in which a highly efficient sputter cleaning process is obtained leading to a very good coating/substrate bond.

The melting and spraying of ceramics still remain largely in the realm of plasma spraying technology. Applications of ceramic coating include: insulation of electronic components, wear resistance of prosthetics, formation of high temperature superconductors, formation of hard diamond films, and formation of bulk ceramic composites.

Powders used in thermal spraying have a significant influence on the coating properties. Powders from different suppliers vary due to the different powder-manufacturing methods used. Thus, even though different starting powders appear equivalent with respect to chemical composition and particle size distribution, they may exhibit significant differences in the coating properties. Characteristics of "good" powders include: constituent purity, small particle sizes, commersurate particle-size distribution of the constituents, uniform constituent blending, and reliable feeding (good flowability). The end user must, therefore, have a good understanding of all powder characteristics to be capable of matching powder type, coating rate, deposition efficiency and price to achieve optimum coating peformance.

11. PVD-processes

The physical vapour deposition (PVD) process has been known as early as 1938, but it has become widely available only in the last 15 years.

The PVD technique can be classified either as evaporation deposition using resistance induction, arc, plasma, electron beam or thermionic electron beam evaporation sources, or as sputter deposition using diode, triode or magnetron (planar, cylindrical or post cathode) sputter sources, or as a combination of these two processes.

The PVD process has received the greatest interest among coating processes due to its flexibility in terms of depositing any material (whether single element or alloy), adhesion, throwing power (i.e., ability to coat complex parts), cost and environmental considerations.

Commercial electron beam-PVD (EB-PVD) coatings are produced in a vacuum environment, 10^{-2}-10^{-4} Nm^{-2}, with deposition rated often exceeding 25μm/min. Components are generally pre-heated in vacuum to between 800-1,100°C, and are rotated within the evapcrant cloud during the evaporation process, to ensure uniform coverage, as the process is usually "line of sight" at these pressures. Problems such as columnar grains with unbonded interfaces, known as "leaders" due to shadowing effects, can occur as the coating grows. High deposition temperatures result in increased surface diffusivity which reduces the density of these leaders. It also permits some minimal interdiffusion between the coating and substrate during the coating process cycle, ensuring good adhesion. Hence, coating spallation, a problem with many processing routes, is not a problem, provided the substrates are properly cleaned prior to coating.

The high rate of deposition makes it possible to coat as many as 500 standard sized parts in an eight-hour shift. Post coating processing includes glass bead peening and heat treatment, which results in complete closure of any remaining leaders.

In the sputtering process, positive gas ions (usually argon) produced in a glow discharge or plasma, bombard a target of coating material, discharging groups of atoms. These then enter the vapour phase and are deposited onto substrates to be coated. Deposition rates are much slower than the EB evaporation route, generally 10-20 μm/hour for a diode system or up to 50 μm/hour for a planar magnetron system. Magnetron systems which have magnetic plasma confinement adjacent to the target usually result in more uniform deposition and can virtually eliminate substrate heating during the deposition process.

Working pressures are of the order of $1\text{-}10^{-2}$ Nm^{-2}, depending on whether a DC glow discharge or RF plasma is used to generate ion bombardment. This offers excellent throwing power and good overall coverage of the components to be coated. Because of the low process temperature, the coatings are usually heat treated to produce the desired properties.

Both EB evaporation and sputtering can be combined with ion plating. Ion plating is essentially a PVD process in a soft vacuum in the order of $1\text{-}10^{-1}$ NM^{-2}, with evaporant depositing onto substrates held at a high negative potential. During ion plating, the components to be coated are initially bombarded with positive ions which are formed in the discharge. This removes oxides and other contaminants from the surface.

When the surfaces are sufficiently clean, the vapour source is energized and metal evaporant enters the discharge and is deposited onto the sample. With EB evaporation and ion plating deposition rates are typically 10-20 m/min.

It is estimated that over 300 PVD plants exist the world over, and the use of the process for coating of tooling is already extensive, especially for gear manufacture.

The use of PVD for depositing TiN and related compounds is of great commercial importance, and some of the attributes of PVD-TiN coating is listed in table 7 (see page 37). TiN coating by plasma assisted PVD (PAPVD) is the most dominant of these commercial processes. PVD is also being increasingly used for cemented tungsten carbide because it preserves sharp edges, whereas the traditionally used CVD treatment, operating at much higher temperatures, tends to round corners off.

Dual ion beam assisted deposition technique (IBAD), a temperature-controlled, high-vacuum process, that combines PVD via electron-beam evaporation, with simultaneous ion-beam bombardment, has gained commercial maturity in recent years. The combined features of IBAD are listed in table 8 (see page 37).

The concurrent ion stitching densifies the synthesized film and improves the adherence between almost any film and substrate, through the development of a graded interface. Excellent adhesion is obtained on metals, polymers, and ceramics, without the need for excessively high temperatures. Compounds such as zirconium oxide and diamond-like carbon (DLC) can be grown by introducing reactive-gas ion beams concurrently with the evaporated species.

In figure 24 (see page 28), is shown a schematic representation of a dual IBAD system, and in table 9 (see page 38), is listed the salient features of this technique. When producing high-ductility, high-temperature tribological coatings, like alumina, zirconia, silicon nitride and boron nitride, the use of dual-IBAD also substantially reduces impurity content, by eliminating the porous, columnar microstructure commonly seen in low-temperature depositions.

Some of the successful dual-IBAD coating recommendations are listed in table 10 (see page 38). Two typical examples of the improved wear resistance imparted by such dual-IBAD coatings, are illustrated in figure 25 (see page 28).

To engineer high-quality dual-IBAD surfaces, several key components are required for in-process control, such as in situ thickness, evaporation rate, ion energy/current, and residual gas analyser (RGA) monitoring systems. The advantages are that there is a higher probability of achieving the precise stoichiometry in the first run, eliminating costly trial and error.

12. Chemical vapour deposition processes

Chemical vapour deposition (CVD) is a process whereby a solid material is deposited from the vapour by a chemical reaction occuring on or in the vicinity of a normally heated substrate surface. Historically, it antedates the vacuum evaporation-condensation aspect of PVD, to which it is closely related. The CVD technique combines a high throwing power of the process with a large, controllable variation in the properties of the materials produced, to provide the possibility to coat even complex shaped substrates with materials having a unique combination of properties.

CVD is employed to prepare wear and corrosion resistant coatings, semiconducting materials, optical fibres, fibres for composites, coatings for optical and solar energy applications, etc. Further, it can be also used to prepare single crystals, powders with well-defined particle sizes, high-temperature composite materials and overlay coatings on small particles.

The principle of CVD is the reaction of reactant gas mixture proceeding on or in the vicinity of a normally heated substrate surface, as illustrated in figure 26 (see page 29). Gaseous reactants react to form solid materials and gaseous products. The solid material is obtained as a powder, a coating layer or a single crystal.

The type and geometry of the CVD reactors used depend on the process selected and the size, shape and number of substrates. In general, two main types can be distinguished, i.e., hot wall and cold wall reactors.

In the hot wall reactor, the reactor tube is surrounded by a tube furnace. This means that the substrate and the wall of the reactor will have the same temperature. In this type many substrates can be coated in the same run. However, due to the high wall temperature, the deposition occurs not only on the substrate, but also on the reactor walls. This may result in a depletion of the vapour with respect to the reactants. There is also a risk of introducing contaminants in the system, from chemical reactions between the reactor wall and the vapour, and also from particles loosened from the reactor walls. A typical vertical hot wall reactor is shown in figure 27 (see page 29).

In the cold wall reactors, the substrates have a higher temperature than the reactor wall, which means that the deposition occurs only on the substrates. While the risk of contamination and vapour depletion with respect to the reactants is very much reduced, severe natural convections can arise due to the steep temperature gradients around the substrate. A typical RF-cold wall reactor is shown in figure 28 (see page 29).

In a CVD process various sequential reaction steps occur (see figure 29 on page 30). Each of these steps may be rate limiting in the absence of thermodynamic limitations. Plausible rate-limiting steps in a CVD process are listed below:

(a) Transport of the gaseous reactants to the boundary layer surrounding the substrate (free and forced convection).

(b) Transport of the gaseous reactants across the boundry layer to the surface of the substrate (diffusion and convection flows).

(c) Homogenous reactions in the vapour during the transport to the substrate surface.

(d) Adsorption of the reactants on the surface of the substrate.

(e) Chemical reactions (surface reactions) between adsorbed reactants and reactants in the vapour.

(f) Nucleation.

(g) Desorption of some reaction products from the substrate surface.

(h) Transport of the reaction products across the boundary layer to the gas phase.

(i) Transport of the reaction product away from the boundary layer.

Steps (a), (b), (h) and (i), concern the material transport in the vapour. Processes whose rates are limited by any of these four steps are described as being controlled by mass transport. Steps (c) to (g) proceed on the substrate surface. Processes whose rates are determined by one of these steps are described as chemically, kinetically or surface controlled. The slowest step among them may determine the overall rate of the deposition process.

Even though several rate-limiting steps can be identified in a CVD process only four main categories of control are normally discussed.

(1) Thermodynamic control: Here the deposition rate is equal to mass input rate into the reactor. In this case a near equilibrium state exists and the thermodynamic control is valid. The deposition rate will increase with increasing gas velocity due to the increase in the mass input of the reactants. The deposition rate will have a temperature dependence which can be predicted by thermodynamics.

(2) Surface kinetics control: If the deposition rate is lower than the mass input rate into the reactor as well as the mass transport rate in the vapour to the substrate the process is said to be surface controlled or nucleation controlled. The surface control kinetics are favourable for obtaining coating of uniform thickness on more complicated substrate shapes.

(3) Mass transport control: A process may also be controlled by the mass transport in the vapour in the reactor to or from the substrate surface. This occurs frequently at high pressures and high temperatures and when very instable compounds are used as reactants.

(4) Nucleation control: At low super saturation the deposition rate may be controlled by nucleation.

In addition to the above four types of control, homogenous reactions in the vapour also play an important role in CVD as they may control the deposition rate. Thus, homogenous reaction controls should also be introduced.

CVD is today being used for a number of commercial coatings as it is suitable for high-volume production at low cost, after process conditions are determined. High temperature and coating adhesion are common concerns.

Diamond-like films produced by such processes as CVD are becoming increasingly popular because of their superior hardness, excellent lubricity and strong bonding capacity.

For centuries diamonds have been appreciated for their extraordinary hardness and beauty and have been used to create jewellery of highest value. Today due to its numerous outstanding properties, unique in the world of materials, diamond is also regarded as a first-rate tool.

Its properties range from extremes in hardness and brilliance to extremes in heat conductivity, melting point and chemical inertness, to name only a few. Until now diamond was known and available exclusively as more or less bulky crystals. With the advent of low-pressure diamond synthesis, it can be prepared in shapes that have previously been inacessable to man, namely as thin films, coatings or even as free-standing thin sheets or ribbons.

Figures 30-32 (see pages 30-32) and table 11 (see page 39) give a short survey of the different methods of low pressure diamond deposition. The principal aim of the new high growth rate methods is to produce the largest possible concentration in a large volume, or locally at very high growth rates. At least one of these two criteria must be fulfilled in order to scale-up the reactors for industrial production. An outstanding interesting new method is the oxygen/acetylene flame. Surprisingly simple, it works at atmospheric pressure and gives high growth rates. However more work still needs to be done to judge its actual economical and technical value.

Application for non-perfect polycrystalline diamonds include:

- Superhard wear-resistant protective coatings for cutting tools and wear parts.

- Abrasive powders.
- Decorative, scratch- or corrosion-resistant surfaces to be used for medical, optical, chemical or other applications.
- Heat sinks for "chips", utilizing diamond's outstanding heat conductivity.
- Components for loudspeakers, utilizing diamond's extraordinary sound transmission capabilities.
- Mechanical supports for crucibles and tubes where chemical inertness, rigidity and a high melting point are necessary.

A few selected tools which utilize diamond's superhard property are shown in figure 33 (see page 33). Another example of CVD-diamond coating application is for micro-drills, shown in figure 34 (see page 33).

An interesting alternative approach to CVD-coated diamond cutting inserts is the use of free-standing diamond films. In this new technique, diamond film is bonded to the surface of the tool after it has been shaped to its final geometry and tolerances. Figure 35 (see page 34) illustrates the principle involved and in figure 36 (see page 34) is shown in typical free-standing diamond sheet.

Applications that require perfect and single crystalline diamonds include gemstones, optical lenses, high-power lasers, and semiconductor applications. A whole generation of high-performance, high-temperature semiconductors, unthinkable until recently, which could in certain applications outperform such well-established materials like gallium arsenide, is within reach.

Alumina is one of the widely used CVD coatings on cemented carbides and is almost always used in combination with titanium carbide. The TiC coating is deposited first on the cemented carbide substrate due to its excellent adherence, followed by the Al_2O_3 coating. Often a TiN layer is deposited on top of the Al_2O_3, partly to give the tool an attractive appearance. The total coating thickness is normally in the range 5-15 μm and the increased wear-resistance will often increase the effective operating lifetime by 3-8 times. More than 50 per cent of cemented carbide tools used in metal cutting applications today are coated.

C. Future trends

Surface engineering has grown dramatically in recent years, due to the development of new processes, widespread applications and economical advantages. Continued developments are expected in surface treatment of metals to improve wear, corrosion and heat resistance, as well as in protective systems for composite materials and compliant coatings for ceramics. In the area of thermal treating, there is continuing progress in vacuum heat treating of metals and ceramics, ion nitriding of aluminium, induction heating of steel, as well as extended use of conventional HIP process for some unique applications.

Thermal spray technology is growing rapidly and is expected to have greater impact in gas turbine applications as designers make use of unsual combinations of coatings and base metals. It is predicted, for instance, by Turbine Metal Technology, an industrial and aerospace coating firm, that thermal spray coatings will be used as intermediate layers for further surface modification by different methods, and that free-standing parts will be made by what is now only a coating process. State University of New York (SUNY) also predicts that spray forming of near-net shapes of difficult-to-process materials can be done using the variety of thermal spraying materials. For example, inter metallic compounds can be vacuum plasma sprayed to achieve dense, high-performance, free-standing forms. Likewise, thermal sprayed composites such as alumina or dye boride-reinforced disilicides or aluminites, can be considered in several applications.

Tafa Inc. recently has introduced several innovations for improved thermal-spray processing, including the new Arc Jet electric-gun system, which produces a concentrated spray stream having 49 per cent higher velocity than standard arc-spray guns, a unique pencil-shape contour, and very tight focus. Also introduced is their new 95 MXC micro matrix-composite, high chromium alloy arc-spray wire, which produces corrosion and abrasion resistant coatings having hardness approaching WC that can operate in service environments up to 930°C.

Tafa Inc. and its parent firm Hobart also offer a robotic thermal spray cell that provides simpler control, enhanced coating quality, consistency, and productivity, and lower cost operation of plasma, wire-arc, HVOF, or combustion spray processes.

Improvements are also being made in masking materials, with special emphasis on masking tapes for HVOF processing. The challenge is to design and produce masking tapes that will resist particles impacting at pressures over 31 MPa and temperatures up to 2,760°C and replace the costly metal mask and elastomer moulds now in use.

Databases now are being applied in the engineering of thermal spray coatings. A new comprehensive interactive and menu-driven PC-based program is now capable of leading a user from an application problem to standard and recommended process and materials, and even to the name of the material supplier.

Advanced ceramic coatings are also being used to fight wear. Ceramic coatings are capable of drawing up water. Nippon Steel, Akiyama Printing Corp., and Tokyo Keseihin Company Limited, all of Japan, have jointly developed a ceramic roller in a continuous water-dampening system used in offset printing machines that lowers printing costs. The roller, which replaces a chromium plated model is plasma sprayed with a highly hydrophilic ceramic material, followed by a special surface treatment. The coating ensures that the water adheres uniformly to the roller surface, thus allowing it to supply a uniform film of water to the printing plate.

Thermal-barrier ceramic coatings have been introduced recently in the hot sections of some new gas turbine engines. The abradable ceramic coatings produce significantly higher performance by minimizing bypass flows in that section of the engines.

Improvements are also continuing in many other types of coatings besides thermal spraying. For example, Thermoclad Company has developed Duravin ES series of PVC formulations specifically designed for electrostatic spray coating of such parts as welded-wire fencing, expanded metal, springs, castings, and stampings. Previously available vinyl powders were suitable only for fluidized-bed coatings, and electrostatic spraying of thin films had largely been dominated by epoxy and polyester products.

Metal plating has taken a new twist with the introduction of a formulation that provides low friction together with high corrosion resistance on a wide range of ferrous and nonferrous substrates. Nimet Industries has developed TiCoTef coating, which consists of a uniform dispersion of sub-micron-size particles of PTFE throughout an autocatalytically applied matrix of a Ni-P alloy. The nonelectrolytic process ensures uniform coating of internal surfaces and complex parts that would be difficult to protect and lubricate, while the uniform dispersion of Teflon in the coating ensures that lubricity is maintained throughout the life of the coating.

Diamond-like films produced by such processes as CVD will become increasingly popular due to their superior hardness, excellent lubricity, and strong bonding capacity. Unlike other DLC, Implant Science Corp's. Black Diamond is produced by a combination of ion implantation and plasma CVD. This results in a carbon coating and an intermixed near-surface region where carbon atoms become embedded in the atomic structure of the substrate, creating an extra-strong bond.

The various forms of vapour deposition are expected to expand their capabilities. For example, ion vapour deposition (IVD, of pure aluminium on high-strength alumunium-alloy parts is replacing anodizing, hard anodizing, and conversion coating treatments of such parts, which can be adversely affected by some of the alloying elements. Scientists at the Naval Research Laboratory report success in depositing high quality coatings and thin films using two of the newer techniques - IBAD and PLD. Typical examples are improved hardness and wear resistance of titanium nitride films grown by IBAD and diamond-like films and films of metals and dielectrics deposited by PLD. Further, superconductor films deposited by PLD have been reported to show consistently superior transport properties compared to those produced by other techniques. Existing ion plating systems for producing hard-surface wear films on parts such as cutting tools and gas-turbine blades can now be upgraded by the addition of a steered-arc source from Vacuum Inc. Typical deposition rates for steered-arc cathodes are significantly higher than for planar magnetron cathodes.

Surface treating using white light from a high power arc lamp offers several advantages over the traditional methods and electron beam techniques. For example, the Vortek arc lamp (Canada), using only an arc lamp and reflector, can reach an input power as high as 300 kW using an arc length of only 100 mm. An arc current up to 1.2 kA is achieved at the applied DC-voltage. Using this arc lamp, a consistent surface layer hardness of 900 HV has been reported to have been achieved in 10 mm thick 90 Mn 5V tool steel to a depth of 2 mm using a feed rate of 0.64 m/min. While arc-lamp treatments overcome some of the shortcomings of alternate methods, it does not combine all the benefits of the other techniques. It is expected that this technique can be applied in situations where the alternate methods cannot be used due to technological or economical reasons.

Established but still-growing markets for HIP (hot-isostatic pressing) include densifying of investment-cast parts for aircraft gas-turbine engines, and consolidation powder metallurgy tool steels for rerolling into various cutting-tool forms. New applications reported for HIPed silicon nitride include ball bearings, textile industry thread guides and diesel engine parts. HIP-bonding and densifying of clad composites is another relatively new growth market.

Sunlight has been studied for many years as a relatively low cost, clean energy source for bulk processing of materials. Today, however, it is believed that the greatest potential for solar energy in materials processing may lie in surface modification, via use of a concentrated (1 MW/m^3), directed energy beam. This budding solar-furnace technology, called solar-induced surface transformation of materials (SISTM), would compete with other directed-energy methods such as ion, laser and electron-beam processing. Potential applications include transformation hardening of steel, cladding/coating, self-propagating high-temperature synthesis, thin-film deposition, and electronic-material processing.

Duplex- or multiple-surface treatments are also becoming popular in recent years. The scope for duplex- or multiple-surface treatments, to provide an array of novel surface engineered products is virtually unlimited, and there can be no doubt that they will play a predominant role in the next decade.

D. Conclusion

We have but taken a glimpse into this fascinating area of surface engineering. As far as possible, the newer and more important techniques in surface engineering have been covered. It is well-nigh impossible to cover the entire spectrum of surface engineering in so few pages or words. Nevertheless, an attempt has been made, and it is hoped this article provides an impetus for further studies in this field. The combinations of surface treatments that are today available to the designer are unlimited and their application is limited only by one's imagination. The next decades will witness further growth in this important area of engineering.

References

1. Homer, "The Odyssey", c 850 B.C.
2. T. Bell, Surface Engineering, 6,1, 31-40, 1990.
3. T. Bell, Metals and Materials, 8, 478-85, 1991.
4. A. Einstein, "Sources in quantum mechanics", 1967.
5. T. H. Maiman, Physics Rev. Lett., 5, 103, 1960.
6. W. Crookes, Phil Trans Roy Soc., Part I, 135; Part II, 641, 1879.
7. J. J. Thompson, Phil Mag, 1897.
8. M. von Pirani, US Patent No. 848, 600; 1906.
9. BRITE EUREM, Project No. 1555.

10. D. Tyler, Metals and Materials, 11, 672-3, 1988.

11. W. M. Steen, Metals and Materials, 12, 730-6, 1985.

12. D. Apelian and C. H. Entrekin, Int. Metals Reviews, V. 31, 2, 77-90, 1986.

13. C. W. Draper and J. M. Poate, Int. Metals Reviews, V. 30, 2, 85-107, 1985.

14. A. Matthews, Metals and Materials, 3, 150-3, 1991.

15. J. R. Nicholls and D. J. Stephenson, ibid., 156-63, 1991.

16. B. Garside and R. Sanderson, ibid., 165-8, 1991.

17. R. K. Singh and J. Narayan, Jl. of Metals, 3, 13-20, 1991.

18. E. J. Kubel Jr., Adv. Matrls. and Processes, 3, 41-8, 1990.

19. A. M. Staines, Metals and Materials, 12, 739-44, 1985.

20. A. M. Guthrie, Metals and Materials, 1, 30-5, 1987.

21. F. A. Smidt, Int. Matrls. Reviews, V. 35, 2, 61-128, 1990.

22. S. E. Vanes, Metals and Materials, 4, 238-43, 1985.

23. J. J. Kaiser and R. A. Miller, Adv. Matrls. and Processes, 12, 37-40, 1989

24. Technical spotlight, ibid., 12, 49-50, 1989.

25. D. W. Parker and G. L. Kutner, ibid., 4, 68-74, 1991.

26. J. T. Stanley et al., ibid., 12, 16-21, 1990.

27. B. Haywood, ibid., 12, 35-40, 1990.

28. Hiroshi Iyoshi, Ph.D. thesis, TU-Wien, 1987.

29. B. Lux and R. Haubner, Proc. 12 Int. Plansee Seminar, 615-60, 1989.

30. A. R. Poeton, Metals and Materials, 11, 702-4, 1988.

31. C. J. McHargue, Int. Metals Reviews, V. 31, 2, 49-76, 1986.

32. B. J. Sealy, Int. Metal Reviews, V. 33, 1, 38-52, 1988.

33. Adv. Matrls. and Processes, 1, 59-68, 1991.

34. H. Herman, Adv. Matrls. and Processes, 1, 59-60; 84-85, 1990.

35. F. A. Smidt, Adv. Matrls. and Processes, 1, 61-2, 1990.

36. Adv. Matrls. and Processes, 9, 37-41, 1990.

37. C. G. S. Saunders, Metals and Materials, 11, 678-82, 1988.

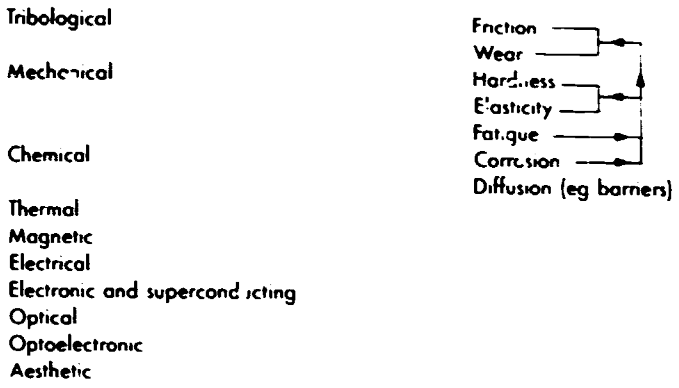


Fig. 1: Properties influenced by surface engineering.

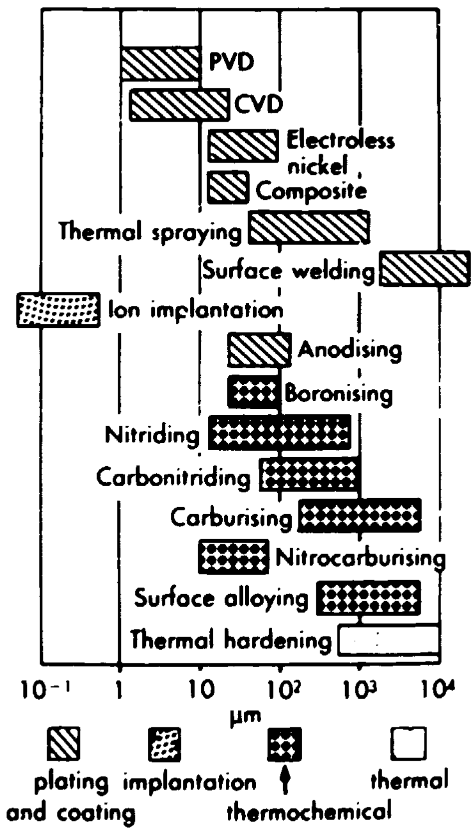


Fig. 2: Typical thickness of surface engineered layers.

Coating

Hardness, low coefficiency of friction, chemical inertness

Interface

Adhesion, bonding, mechanical strength

Substrate

Toughness, strength, lightness, shape

Fig. 3: The properties required in the three effective zones of the tool or component that dictate the choice of materials and treatments.

Laser treatment of thermal and plama spray coatings

Ion beam mixing and ion assisted coatings

Hot isosatatic pressing of overlay coatings

Thermochemical treatment of pre-carburised steels

Thermochemical treatment of pre-laser hardened steels

CVD treatment of pre-carburised steels

PVD treatment of pre-nitrided steels

Ion implantation of pre-nitrided steels

Fig. 4: Typical duplex surface engineering design.

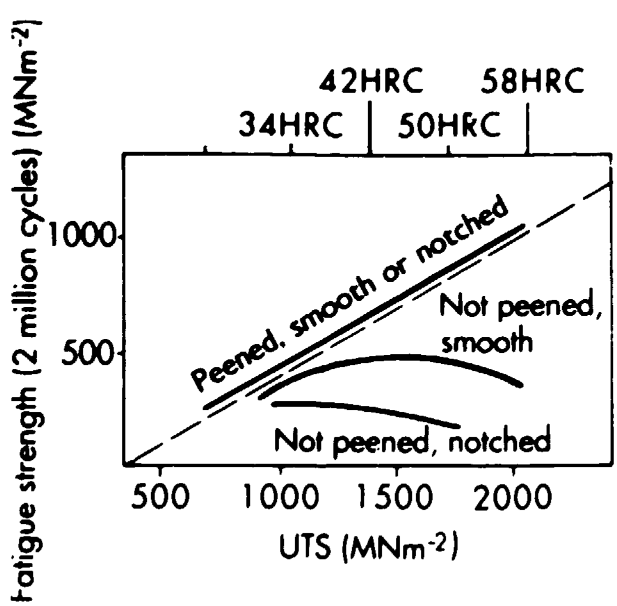


Fig. 5: Comparison of peened and unpeened fatigue limits for smooth

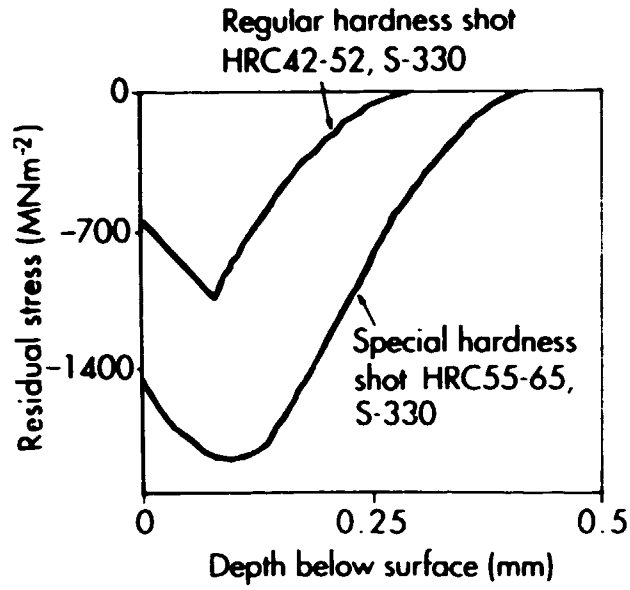


Fig. 6: Substrate stress profiles of 4030 steel peened with two different hardness of shot.

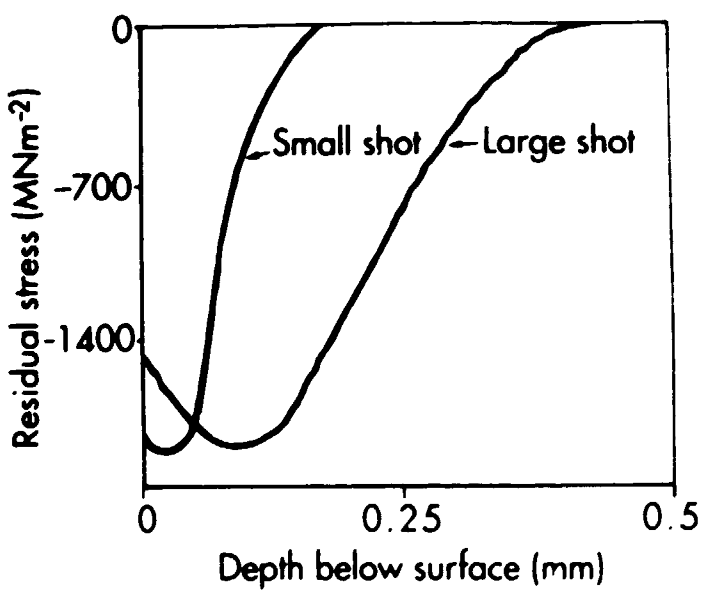


Fig. 7: Variation of substrate stress profile with different sizes of shot.

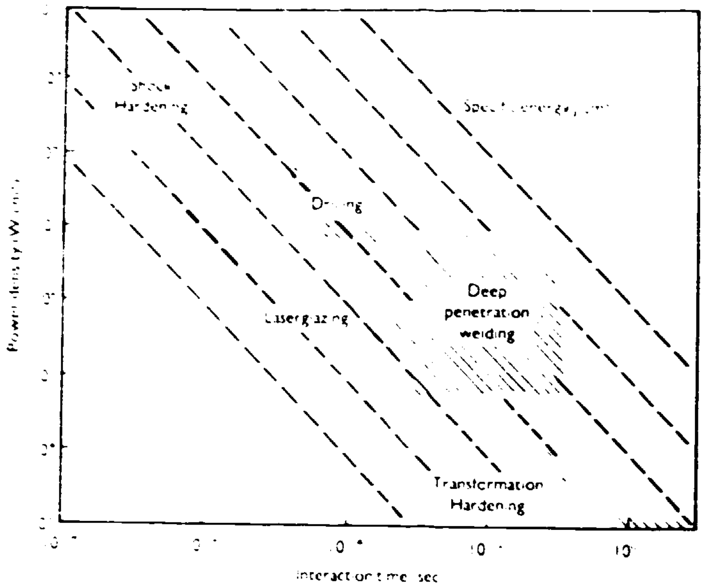


Fig. 8: Operational regimes for various materials processing techniques.

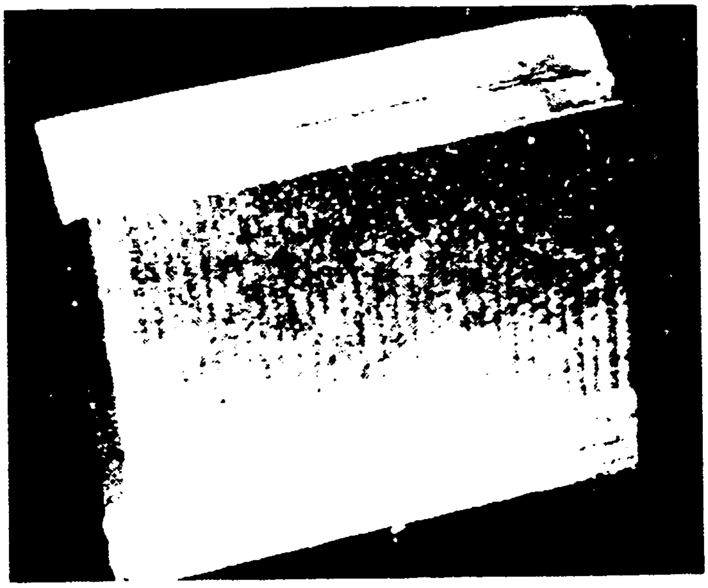


Fig. 9: A laser surface-clad of 316 stainless steel on mild steel.

Fig. 10: [illegible]

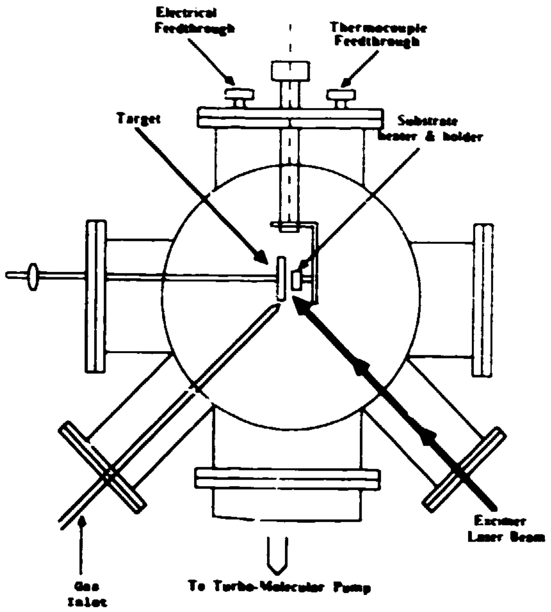


Fig. 11: A schematic diagram showing the set up for deposition of superconducting thin films by PLE.

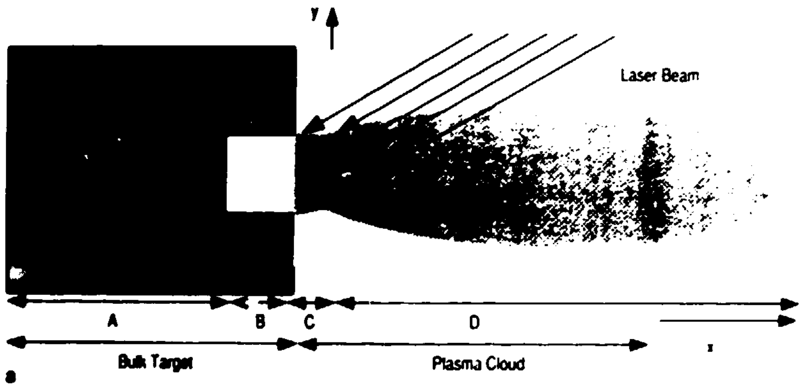


Fig. 12: The nature of laser-solid-plasma interaction during PLE.

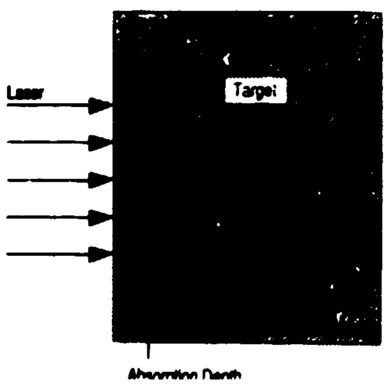


Fig. 13: The absorption of the laser beam by the target material.

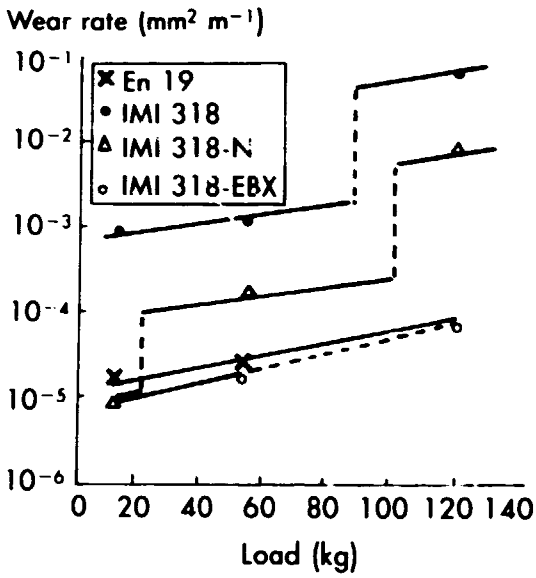


Fig. 14: Steady state wear rate in Amsler tests with 30% slip. All specimens tested against EN 19 counterface, oil lubricated: IMI 318- untreated alloy; IMI 318 N- laser nitrided surface; IMI 318 EBX-EBX coated surface.

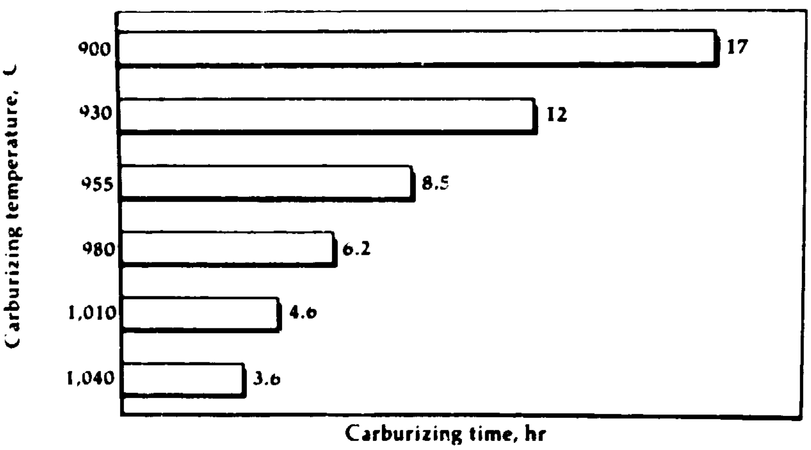


Fig. 15: Increasing the carburising temperature from 900°C to 955°C cuts the time required to achieve a case depth of 1.5 mm in an SAE 8690 steel by half, and cuts the time by almost half again in going from 955 to 1010°C.

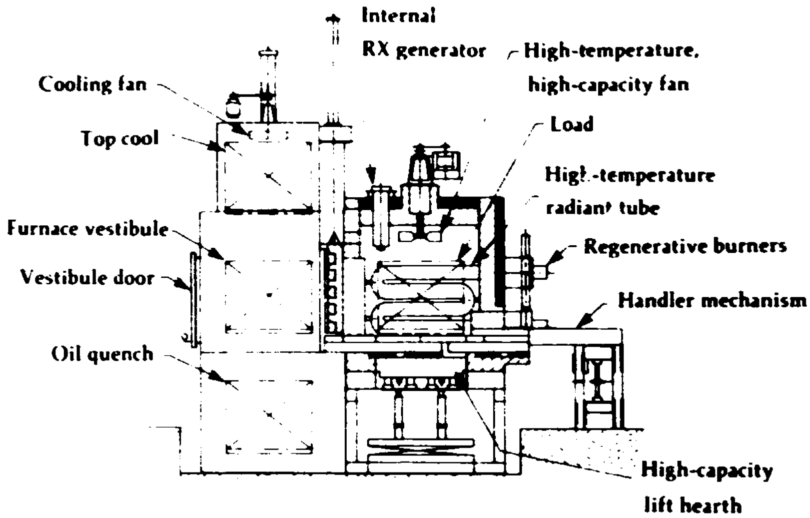


Fig.16: High-productivity gas-fired integral-quench furnace developed by Surface Combustion Inc. and Gas Research Inst.

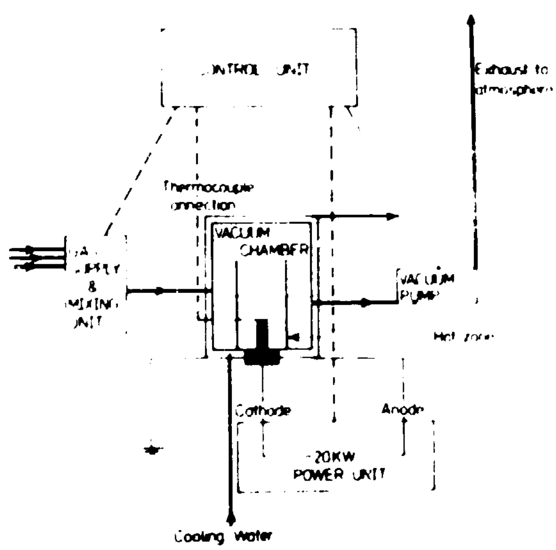


Fig.17: Schematic diagram of a plasma processing unit.

The friable nature of the compound layer

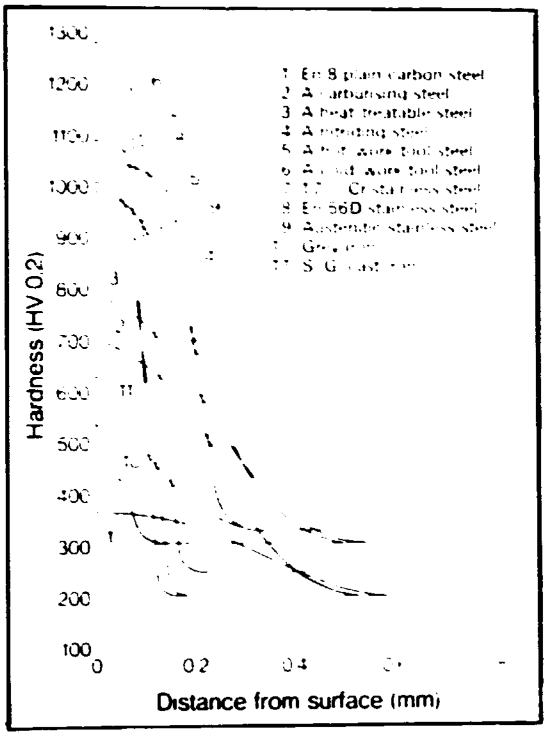


Fig. 18: Typical hardness profiles from a range of plasma nitrided materials.

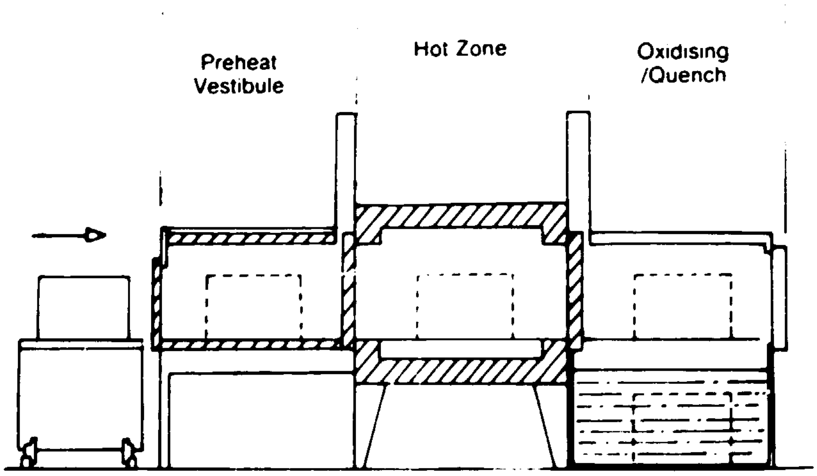


Fig. 19: Schematic diagram of modified sealed quench furnace used in the Nitrotec process.

Fig. 20: Progressive tooth-by-tooth induction hardening of a large gear (TEE, Letchworth)

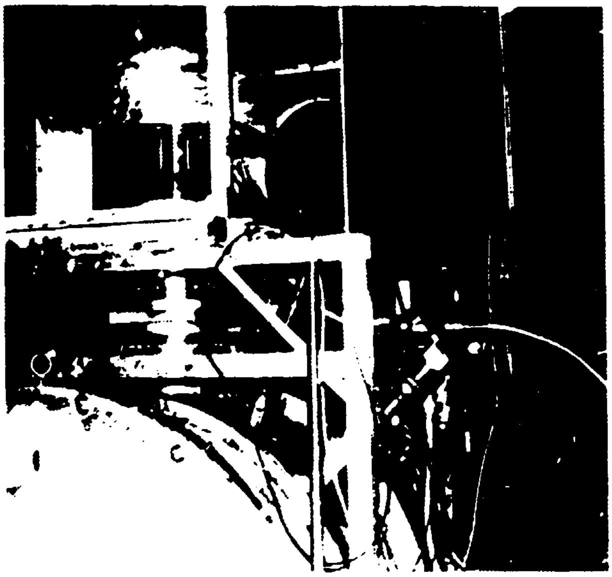
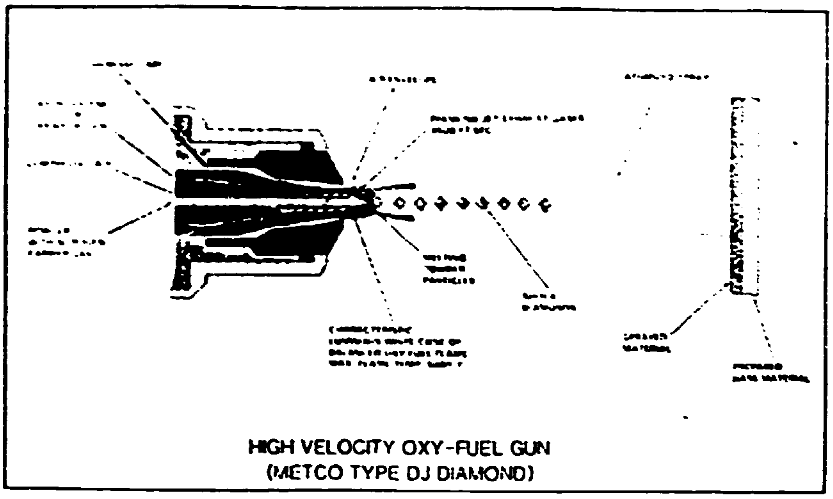


Fig. 21: The Mevva IV multicathode metal ion implantation system.



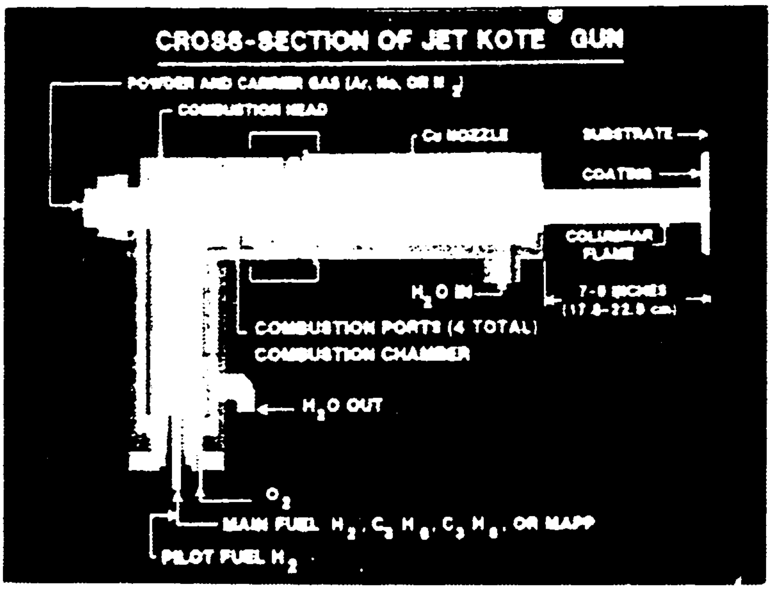


Fig. 22: Two examples of HVOF thermal-spray guns.

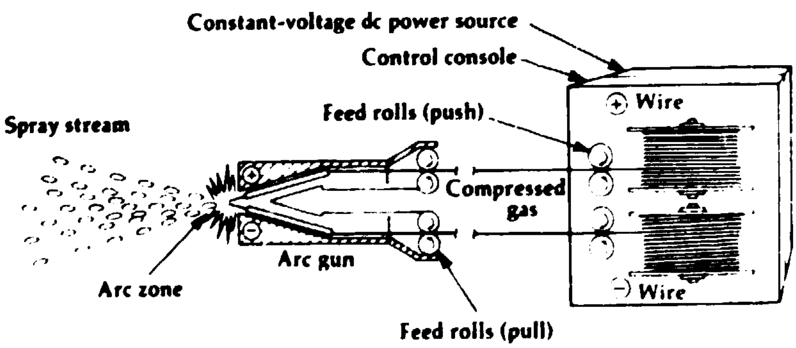


Fig. 23: A typical electric arc system.

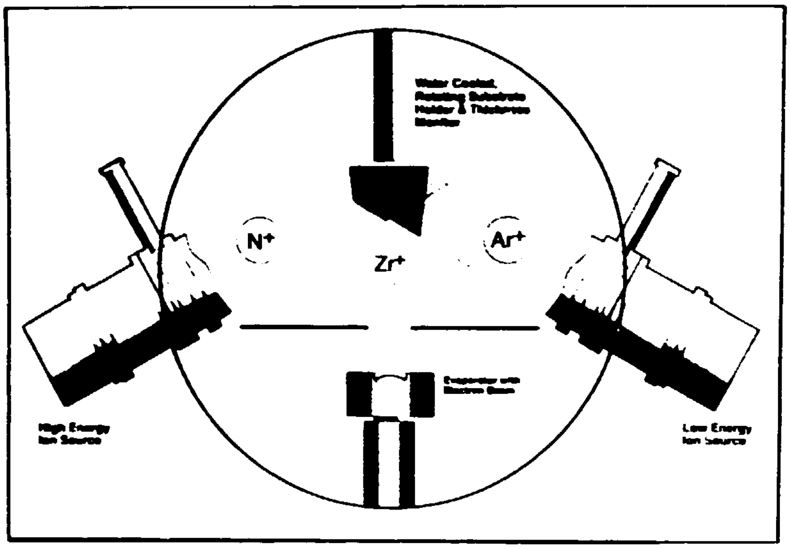
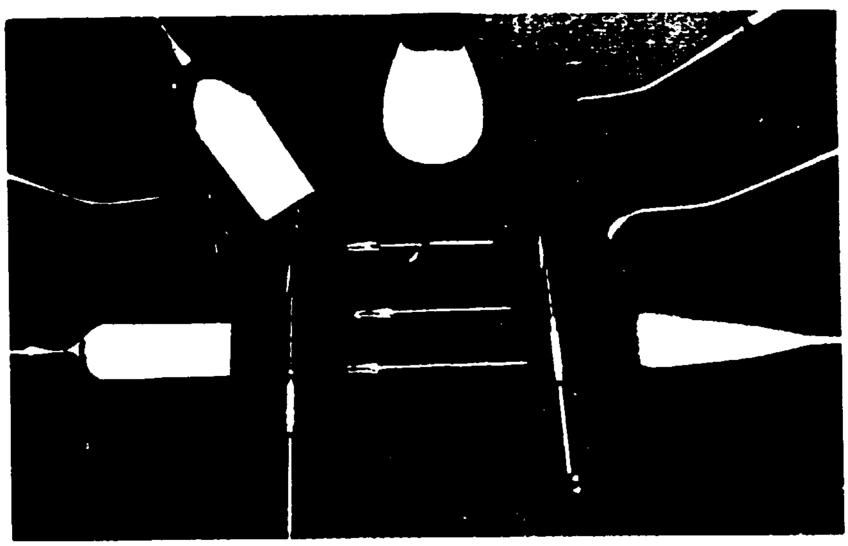


Fig. 24: Schematic representation of a dual-IBAD system.



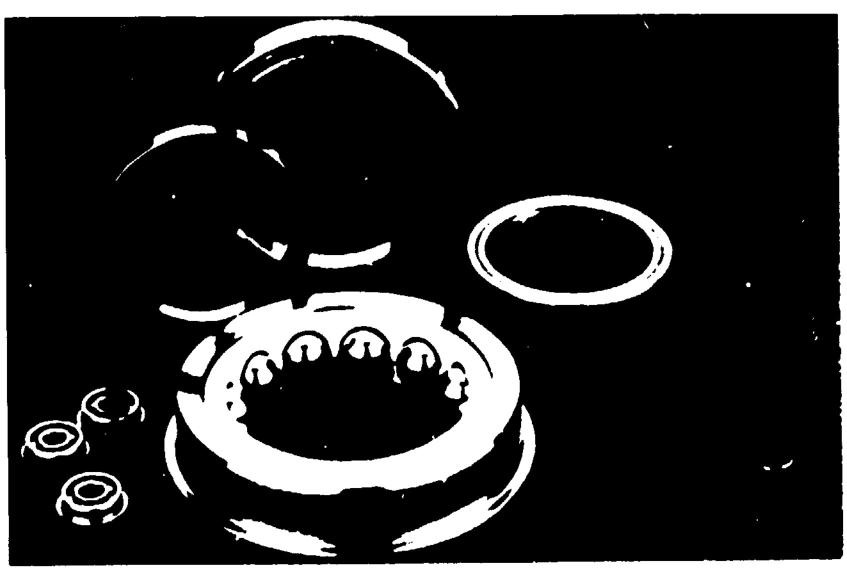


Fig. 25: Dental instruments (a) and ceramic bearings - two typical examples of Dual IBAD coating applications.

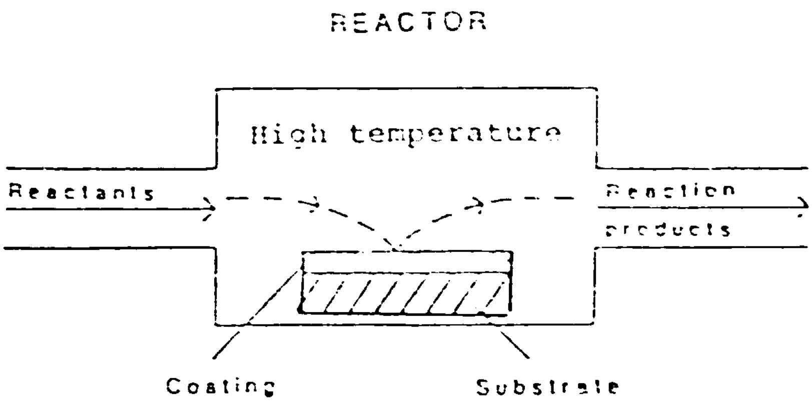


Fig. 26: Principle of CVD.

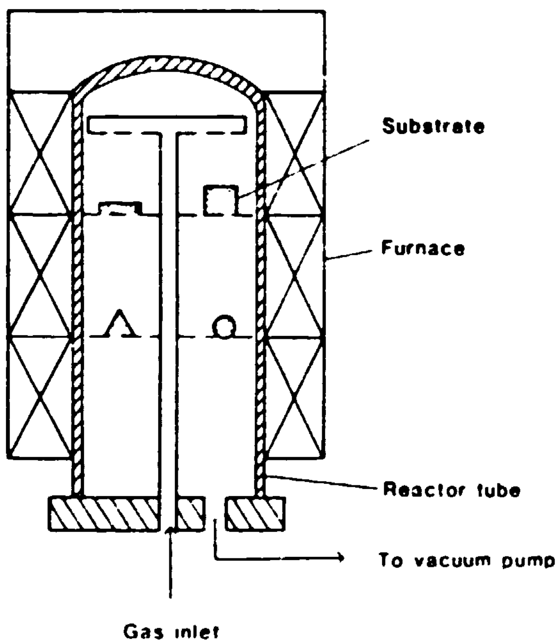


Fig. 27: Vertical hot wll reactor.

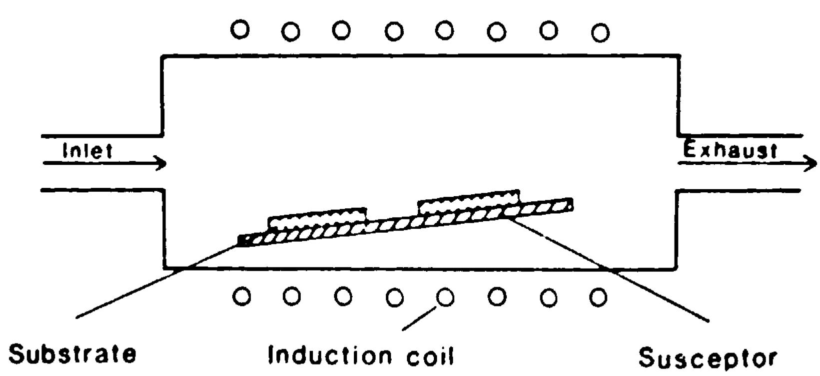


Fig. 28: RF-heated cold wall reactor.

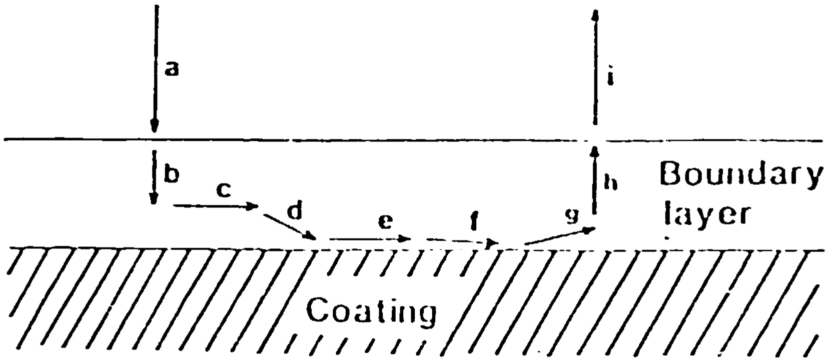


Fig. 29: The sequential steps in CVD.

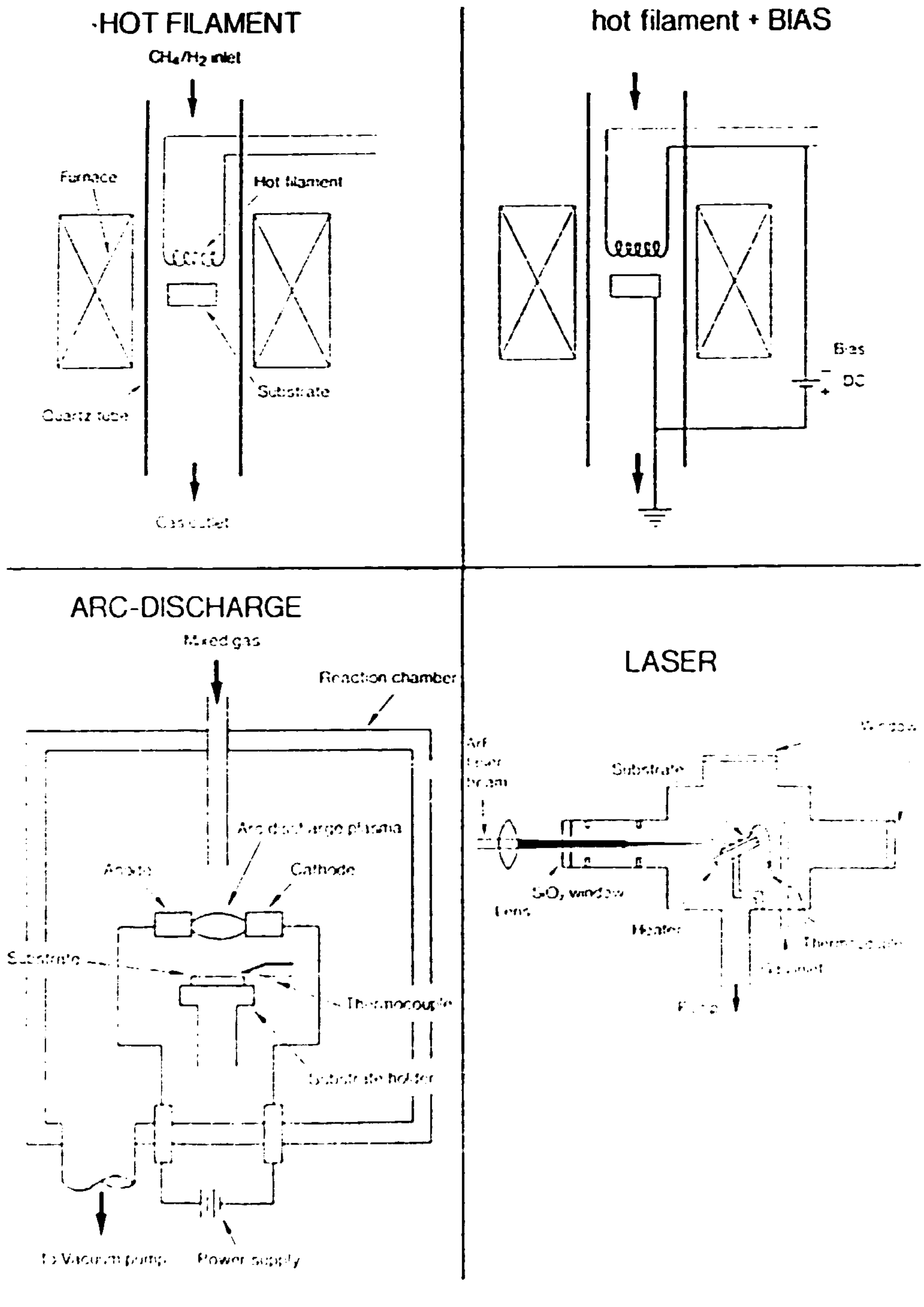


Fig. 30: Methods of gas activation during diamond synthesis: High temperatures.

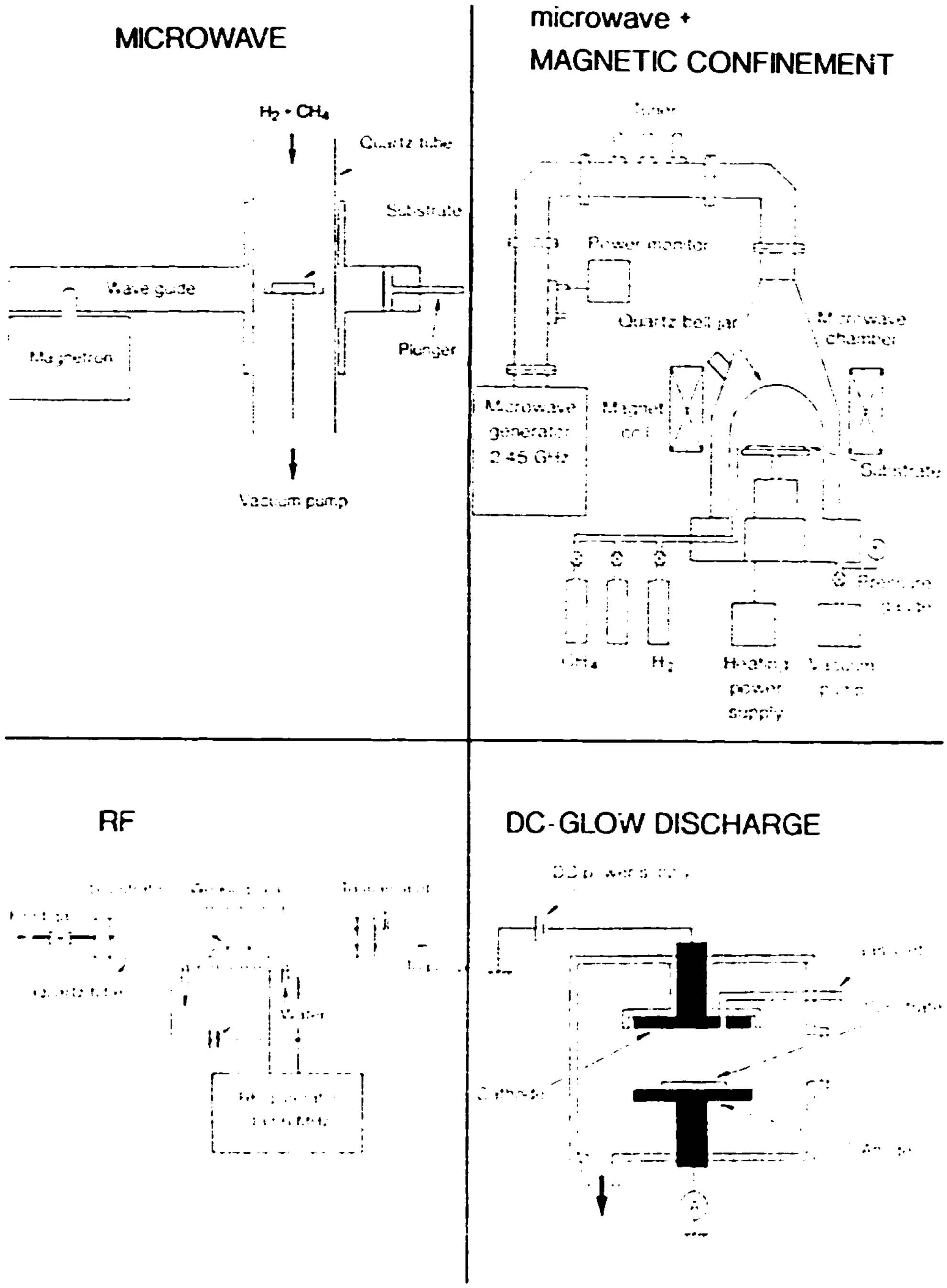


Fig. 31: Methods of gas activation during diamond synthesis: Electric and electromagnetic gas discharges.

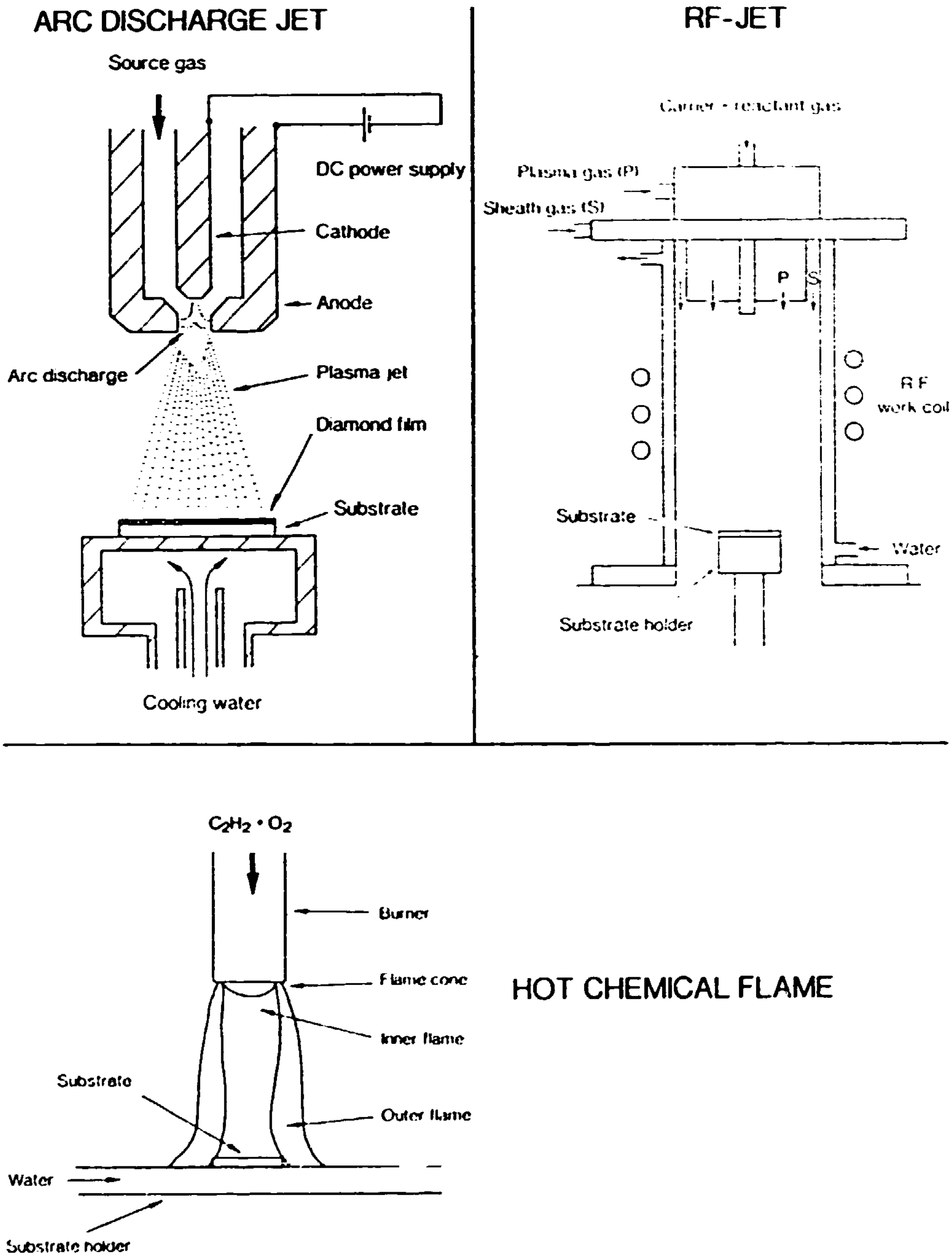
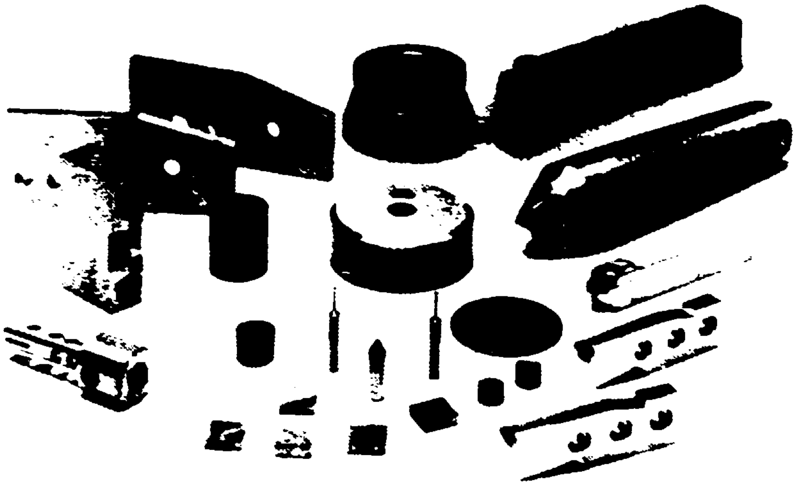


Fig. 32: Methods of diamond synthesis: Use of activated gas jet.




Edge

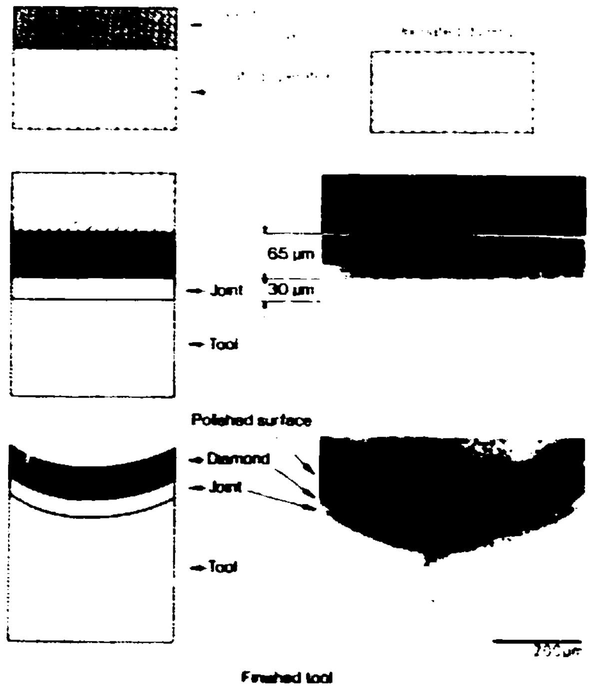


Fig. 35: Principles of bonding a free-standing diamond layer to a substrate and microstructure of a cutting edge.

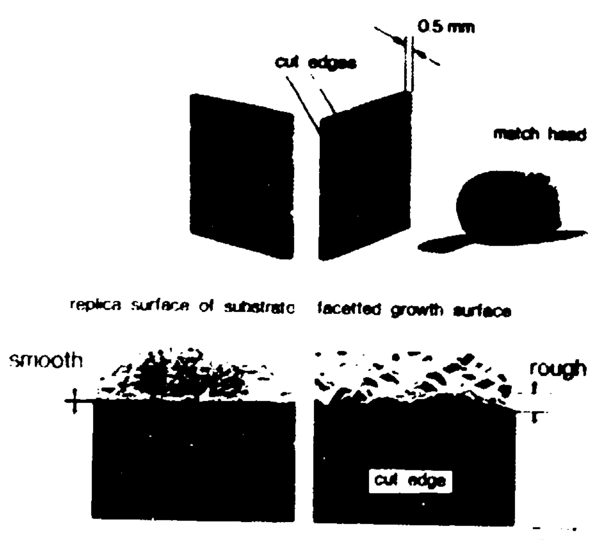


Fig. 36: Thick free-standing diamond layer.

COMPONENT	MATERIAL	COMPANY	POWER	DEPTH
Crankshaft	Nodular cast iron	AVCO		1 mm
Valve guide	Grey cast iron	Ford		
Steering gear housing (Time pt 20s)	Ferritic malleable castings	GM	500W 1000W	0 5 mm
Diesel engine liner	Cast iron	GM	5 kW	
Rivets, clutch				
Springs				
Bushes				
Camshafts	Cast iron			1 27 mm
Typewriters, interpolar bars				
Electric shavers				
Cut out cams, naval guns	4340 steel	US Navy	1 2 kW	0 38 mm
Corrugated paper rolls		Krait	1 2 kW	1 0 mm
Engine air intake ports				
Spline gear root	1050 steel		500 W	0 38 mm
Track guides M1-M60 combat vehicles			4 kW	0 3-0 5 mm
Diesel engine piston grooves	0 4% C steel		5 kW	0 6 mm
	S g cast iron			
Spacers	Cast iron			
Shafts				
Cutting edges				0 61 mm
Parking brake bracket				
Piston rings				

Table 1: Current applications of laser transformation hardening.

SUBSTRATE	SURFACE ALLOYING INGREDIENT	DELIVERY SYSTEM
Ti	N	Gas
Ti alloys	C	Paint
Cast irons	Cr, Si, C	Paint Blown powder
Steel	Cr Mo B Ni	Electroplate Paint Diffusion Plating
Stainless steel	C	Blown, painted
Al	Si, C, Fe	Paint
Superalloys	Cr	Plated

Table 2: A selection of material systems for which LSA has been investigated.

COMPANY	COMPONENT	COMMENT
Rolls Royce	Turbine blade shroud interlock	Triballoy nimonic powder feed
Pratt & Whitney	Turbine blade	PWA 694 nimonic preplaced chips
G E	Proprietory	Reverse machining with Ti powder feed
Quantum Laser Corp	Various	Coating and welding services

Table 3: Representative laser cladding efforts at production stage.

Coating properties vs spray system

	Plasma	HVOF
Powder composition	60% Al, 40% PE	70% Al, 30% PE
Hardness (HR15Y)	70	78
Bond strength, psi	1,010	1,295
Coating metallic constituent, %	46-47	36-50
Hot-erosion, cm³/1,000 gm[a]		
20° angle of attack	5.56	5.08
45° angle attack	10.32	8.50
90° angle attack	9.35	8.06
Deposit efficiency, %	60	82

[a]Volume removed, cm³ for each 1,000 gm of erosion media. Hot erosion test performed at University of Cincinnati, Cincinnati, Ohio

Table 4: Coating properties v/s spray system.

[illegible] characteristics

	HVOF	D-Gun	Standard plasma	High-velocity plasma
Flame temperature, °C (°F)	2,760 (5,000)	2,760 (5,000)	11,100 (20,000)	11,100 (20,000)
Gas velocity	Mach 4	Mach 3	Subsonic	Mach 1
DPH300	1,050	1,050	750	930
Porosity, %	0	<1	<2	<1
Oxide content, %	<1	<1	<3	<1
Typical bond strength, psi	10,000	10,000	8,000	10,000
Thickness limitation, in.	0.060	0.030	0.025	0.015

[illegible] tungsten carbide, 12% cobalt.

Table 5· Spray system / WC-Co characteristics.

	Spray system	
	HVOF	Plasma
Lap-shear bond strength, psi	7,300	6,200
Tensile bond strength, psi	5,200	4,400
Microstructure		
Oxide content, %	12	23
Porosity, %	<0.5	<0.5
Hardness		
Macro HR15T	80	83
Micro DPH300	230	160
Deposit efficiency, %	75	45

[1]Copper-nickel-indium.

Table 6: Cu-Ni-In coating/spray-system characteristics.

Attributes of PVD titanium nitride coating
Excellent adhesion due to the high arrival energy of the coating material and the ability to clean the surface prior to coating very thoroughly by a sputtering stage in the cycle
Uniform thickness due to gas scattering and the ability to rotate the component
Surface finish that in the better systems equals that of the substrate, eliminating finish machining
No effluents or pollutants as a result of the process
No hydrogen embrittlement
Dense structures
Controllable and repeatable stoichiometry and crystallographic structure
Wide range of coatings and substrate materials, including metals, alloys and ceramics
Multiple coating can be used
Low temperature (less than 500°)
Greater productivity and major cost savings

Table 7: Attributes of PVD titanium nitride coatings.

Features combined by dual IBAD process

Feature	From ion implantation	From PVD
Thickness	<1 μm	Several μm
Concentration	40 at. %	0-100 at. %
Cost	High	Low
Adhesion	Excellent	Poor
Density	High (bulk)	Low (below bulk)
Stress	Controllable	High
Control	Excellent	Fair
Reproducibility	Excellent	Fair
Substrate Temp.	Low	High (for best film properties)

Table 8: Combined features of dual-IBAD process

Benefits of IBAD

- Coatings can be "grown" from within the substrate, imparting extreme adhesion and eliminating discrete interfaces
- Not only low-temperature process, but temperature controllable
- Energetic ion beams will ensure high-density, pin-hole-free films, yet varying ion energy and species can produce a porous, textured surface
- Unusual metals and compounds can be applied economically
- IBAD is a dry coating process, ensuring environmental safety with no chemical residues
- Process is extremely reliable due to a high degree of *in situ* control associated with ion energy, deposition rate, thickness, and composition
- Quality and repeatability is ensured by built-in sensors/microprocessors
- Virtually any substrate material can be coated and/or textured
- Sophisticated fixturing allows parts to be articulated with several degrees of freedom
- High-throughput, low-cost production is attainable with larger dual IBAD systems

Table 9: Benefits of dual-IBAD.

Function	Dual IBAD recommendations
Mechanical	
Wear	Hard coatings (TiN, TiC, CrN, Cr_2O_3 i-BN)
Solid lubrication	Ag, Pb, MoS_2, WS_2
Release	PTFE, Ag, MoS_2
Diffusion barrier	Al_2O_3, Pd, Pt, Rh, TiN
Chemical	
Corrosion	Passive film formers (Cr, Ta, Mo)
Oxidation	MCrAlY, Pt, SiC
Catalysis	Pt, Ru, Pd
Electrical	
Conductive coatings	Indium-tin-oxide (visible), VO_2 (IR), Ag, Au, Cu, Al
Magnetic films	Recording media, Permalloy, Ferromagnetics, Rare earth magnets
Insulating films	DLC, SiO_2, TiO_2, Si_3N_4, Al_2O_3, ZrO_2, BN
[illegible]	[illegible]
Decorative films	TiN, TiO_2, TiC, [illegible]

Table 10: Dual-IBAD recommendations.

Methode	Growth rates [µm/h]
I. ACTIVATION BY HIGH TEMERATURES (TA-CVD):	
* Hot filament/surfaces:	
Methane/H_2	0.3-1
Acetone/H_2	10
* Laser-CVD	??
* Arc-discharge CH_4/H_2	200-250
* Hot chemical gas flame (Oxygen/acetylene)	100-200
II. ACTIVATION BY ELECTRIC OR ELECTROMAGNETIC GAS DISCHARGE (PA-CVD):	
* Microwave CH_4/H_2	0.25-1.6
CH_4/O_2	2-8
* RF-CVD CH_4/H_2	0.6-12
* DC-glow discharge Plasma CH_4/H_2	20
III. COMBINED ACTIVATION:	
* Ion-Beam-sputtering	0.3-0.4
Hot filament + BIAS (EA-CVD)	3-5
+ Microwave	10
+ DC discharge	
IV. JET METHODS	
* Plasma jets: - RF	60
- Microwave	30
- Arc-Plasma	180

Table 11: Typical growth rates of the different low pressure diamond synthesis methods.

2. NEW METHODS AND APPLICATIONS

Diamondizing

Diamondizing aptly describes a coating technique that imparts an extremely durable, abrasion-resistant, and clear surface to plastics and metal substrates. In terms of composition and molecular structure, that surface is indeed close to real diamond. Commercialization to date has been limited to such small-area parts as watch crystals and optical lenses. But the future is something else again.

The first large-area plastics applications are anticipated within a year or so, and are expected eventually to include such huge potential uses as giving glasslike abrasion resistance to clear plastics like polycarbonate, acrylic, and polyarylate. It could open up automotive and other glazing markets to these and other polymers.

Another revolutionary potential is application of thin diamond coatings to the surfaces of injection and other tooling, thereby creating the super tool: one with greatly enhanced resistance to abrasion and chemical attack, and improved release characteristics. These are not idle dreams. Diamonex Inc., Allentown, Pennsylvania, USA, a pioneer in diamondizing technology, has formed a partnership with Monsanto Chemical Co.'s Advanced Performance Materials Group, St. Louis, Missouri, USA, to investigate new commercial uses for diamond coating. Until recently, both companies had been working independently on the production of thin (submicron to five micron) films capable of dramatically upgrading the surface performance of plastics, steel, and other tooling. In 1990 Monsanto became a shareholder in Diamonex, signalling the start of a joint marketing effort.

Diamondizing resists abrasion and wear

A thin diamond coating applied to a polymer substrate provides it with greater scratch and wear resistance than any other known coating.

In addition to abrasion resistance, the clear coating also is resistant to chemical attack and yields a non-stick surface with a coefficient of friction similar to that of polytetrafluoroethylene.

Some idea of the hardness of these synthetic diamond coatings is indicated by Vickers hardness ratings. Silicon carbide, one of the hardest of all materials after diamond, rates 2,355 kg/mm^2 on the Vickers scale; quartz registers 1,096 on the same scale. Amorphous diamond is in the 3,000 to 5,000 range.

As a thin film on a comparatively soft material like polycarbonate, diamondizing affords almost as effective a level of abrasion resistance as glass; on a relatively hard material such as steel, it upgrades abrasion strength better than fivefold.

The coating itself consists of carbon atoms bonded in a dense chemical structure similar to diamond. Diamonex produces its coatings using internally developed technology and ion beam technology licensed from the National Aeronautic & Space Administration (NASA). Monsanto takes a proprietary approach based on radio-frequency plasma technology. A substrate is placed in a vacuum chamber and plasma is generated close to it. Hydrocarbon gases are then introduced and high-energy fragments of the hydrocarbons are deposited.

Diamondizing had its beginnings in early work primarily by scientists in the USSR. Then a related technology emerged in the US. Dr. Sol Aisenberg of Whittaker Corp. developed ion-beam-plasma chemistry for producing a variety of materials, including amorphous diamond. Aisenberg constructed a sacrificial cathode ion source that emitted a beam of carbon and argon ions. By controlling ion flux and energy, he was able to produce very thin carbon layers with many of the properties of real diamond. These coatings were extremely hard, electrically insulating, and transparent to visible light. The technology was refined both in Europe and the US, where concentrated work was carried out at the NASA Lewis Research Center in Cleveland, Ohio, USA. A NASA research group developing ion thrusters for space propulsion discovered that the same technology could be used to generate an ion beam for depositing amorphous diamond coatings.

Further research resulted in a new process in 1984, employing two ion beams and yielding films that were closer to true diamond than those made by the original Aisenberg process. Diamonex acquired exclusive licences to both Aisenberg's direct-ion-beam process and the dual-ion-beam NASA technique. In the first - which deposits coatings at room temperature under high vacuum - the energy for coating nucleation and growth is derived from the kinetic energy of an accelerated beam of carbon atoms. In the dual-ion process, two ion sources are focused on the part to be coated. The first produces carbon atoms; the second produces a sputtering beam of argon ions that etches away non-diamond carbon forms.

A breakthrough occurred in improved coatings adhesion, which until then had been only marginally acceptable. Diamonex says it is now able to achieve adhesion values to 62 MPa on glass and metal, and in excess of the polymer strength on plastics.

Neither Diamonex nor Monsanto are quite there with large-area coating yet. Ongoing development work includes scale-up of the technology for large-volume, large-area coating as well as reduction of the slight yellowish tint of current diamond coatings. (Source: Modern Plastics International, June 1991)

* * * * *

Diamond coating process safeguards infrared optics

A diamond coating process developed at the Westinghouse Science and Technology Center, Pittsburgh, Pennsylvania, USA, makes it possible to protect the soft windows of infrared sensors in high-speed aircraft from erosion by rain, dust, or sand.

The soft window materials, zinc sulphide and zinc selenide, are used because they are transparent to the infrared wavelengths most effective in tracking hot engine exhausts or aircraft surfaces. Standard, hard optical materials such as glass are not useful because they block these wavelengths.

So far, Westinghouse has produced small diamond-coated windows only about an inch and a half in diameter, but work on larger windows is under way. Field tests may be possible next year.

A technique called optical brazing overcomes the problem of severe chemical and mechanized incompatibility of diamond on zinc compounds and reduces image distortion created by the uneven growth surface. The diamond coating is predeposited on a silicon wafer, then the diamond side of the wafer is moored to a glass bonding layer, and this sandwich is fixed to the zinc compound window. Finally, the silicon outer layer is removed, exposing the highly transmitting, optical-quality diamond nucleation surface. The bonding medium is a chalcogenide glass, selected for its excellent mechanical and optical compatibility with the two materials. The diamond layer is produced by microwave plasma-enhanced chemical vapour deposition.

Immediate application calls for protection of infrared optics, important for military and commercial aircraft, the space programme, and even drug interdiction. Future uses could include visible-spectrum windows in advanced missiles and spacecraft, protection of photovoltaic cells in space, and more down-to-earth applications like shatter-proof plastic eyeglasses, watch crystals, or scratch-free mirrors. Presently, however, the visual range has a slight residual fuzziness caused by scattering, which will require further research. (Source: MRS Bulletin, June 1991)

* * * * *

Diamond coatings technologies

Monsanto and Diamonex (Allentown, Pennsylvania, USA) are cooperating in the development of their diamond coatings technologies, which rival glass for abrasion and scratch resistance. The processes create diamond layers from a carbon-rich gas in a high-energy environment. Monsanto's plasma-based process has a faster build rate but is limited to simple shapes and generates more heat, while Diamonex's ion beam-based process is compatible with contours and is more accurate. The processes are suitable on metal, glass and plastics. The technique already protects polycarbonate lenses of premium sunglasses, and automotive and aerospace applications are being explored. (Source: Plastics World, February 1991)

* * * * *

What is PE-CVD?

Even coating specialists and surface scientists have trouble identifying certain acronyms. "PE-CVD" stands for "Plasma-Enhanced Chemical Vapour Deposition" processing methods, based on a new "Elongated Microwave Plasma" (EMP) source employing the electron cyclotron resonance (ECR) effect.

In contrast to conventional vacuum coating methods, the materials deposited in PE-CVD processes are introduced not in solid form, but in the gas phase. Processing is straightforward and reliable. Transparent, corrosion-resistant, protective coatings can be deposited at high deposition rates. For plastic components, coating deposition can immediately follow vacuum metallization. The coatings deposited pass, for example, environmental tests, the automotive industry's corrosion-resistance, aging, abrasion-resistance, and wash test.

Coating deposited using PE-CVD methods can be used as substitutes for traditional lacquers and other types of protective coatings and in many cases, with major reductions in environmental impact.

PE-CVD methods can be used to apply barrier layers, as well as to improve the adhesions of metal films to the surfaces of plastic components. (Source: Popular Plastics, February 1991)

* * * * *

Novel low-temperature CVD process for TiN coatings

Injection moulding dies for plastics are one of the major industrial applications of a novel patented process for the low temperature chemical vapour deposition (LTCVD) of titanium nitride (TiN) coatings developed by the Canadian company, Liburdi Engineering. The lubricity of the TiN coating improves plastic flow and reduces sticking during the injection moulding process. An important advantage of this process is the ability to infiltrate and evenly coat complex shapes, deep crevices, and runner passages in the dies. An advantage of the low coating temperature (500°C-650°C) is that tool hardness is maintained (no postcoating heat treatment is needed) and tool distortion, which can occur with conventional CVD at 1,000°C, is minimized.

The low coating temperature is achieved by using a subchloride of titanium, $TiCl_3$, to produce the TiN. The $TiCl_3$ is generated in the reaction chamber by chlorination of Ti pellets in a reducing atmosphere. In the first step, HCl is introduced into a chlorinator containing pellets of Ti under temperature and pressure conditions selected to ensure $TiCl_3$ as the main reaction product along with H_2. The gaseous $TiCl_3$ is then conveyed to the coating chamber where NH_3 is introduced. By carefully controlling the coating parameters, good quality, oxygen-free, films, 1 μm to 10 μm thick, can be deposited at temperatures as low as 450°C. The coatings can be made more adherent as well as more corrosion or wear resistant to suit the application by controlling the gas flow rates, the total pressure, the reactant concentration, and the chlorinator and coating temperatures. Typically, coating temperatures range from 450°C to 600°C and pressures from 2 to 15 torr.

Other applications for these adherent and wear resistant coatings are carbide inserts, stainless steel turbine compressor blades, and dies used in metal forming operations. The sliding wear test indicates that the coefficient of friction of TiN coated steel is reduced by more than half compared with uncoated steel. A systematic investigation aimed at establishing correlations between coating parameters, composition, structure, and properties is now ongoing with the objective of improving the tailorability of the coatings for specific applications. The company is interested in providing coating services to the plastic moulding and metal forming industries, as well as in joint development of new applications for these TiN coatings. [For more information on the technology: Alina Agüero, Ph.D., Research Scientist, Liburdi Engineering Limited, 400 Highway 6 North, Hamilton, Ontario, Canada L9J 1E7. Tel.: (416) 689-0734; Fax: (416) 689-0739. For the coating services: Mr. J. Todd Williams, Marketing Representative, Liburdi Engineering Limited, 23565 Outwood Drive, Southfield, Michigan 48034, USA. Tel. and Fax: (313) 353-1188.] (Source: Materials and Processing Report, April 1991)

CVD SiC for optical applications

Recently there has been growing interest in producing bulk silicon carbide by chemical vapour deposition (CVD). This technology allows for the production of material which is theoretically dense, possesses superior mechanical and thermal properties, and has high polishability. CVD SiC's high stiffness-to-weight ratio, strength, thermal conductivity, hardness, and low thermal expansion coefficient make it an excellent material for optical substrates. After more than two years of work in this area, Morton International Advanced Materials (Woburn, Massachusetts) has developed a scalable, low-pressure CVD process to produce large monolithic pieces of polycrystalline β-SiC for optical applications. The process allows for the production of up to 500 mm diameter, up to 8 mm thick monolith blanks; larger and thicker blanks are possible in the near future. The material's properties make it a candidate for optical components for LIDAR mirrors, solar collectors and concentrators, and astronomical telescopes. [Morton International Advanced Materials, 185 New Boston Street, Woburn, Massachusetts 01801 USA.] (Source: Ceramic Bulletin, Vol. 70, No. 4, 1991)

* * * * *

New environmentally-sound process forms thin and thick films

A new, nonpolluting process for depositing a wide variety of coatings, from 0.1 µm to several microns in thickness (depending on the coating time), has been invented at the University of Colorado. The patented process, called supercritical fluid transport-chemical deposition, can coat large and complex-shaped parts and uses environmentally safe coating materials. Supercritical fluids, which are intermediate between gases and liquids, are better solvents than ordinary liquids at relatively low temperatures, thus can much more readily dissolve polymers and other high molecular weight compounds. The resulting solutions have low viscosities.

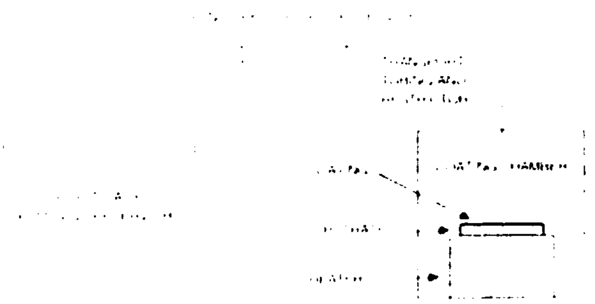
As shown schematically in the figure below, a solution of one or more precursor compounds dissolved in a supercritical fluid, such as carbon dioxide (CO_2) at a pressure of 138 MPa (2,000 psi), is sprayed onto the surface to be coated. A chemical reaction then occurs near or at this surface forming the desired coating. Anticipated applications for this novel coating process include thin films of electronic materials, protective coatings, barrier layers on polymers, and reflective coatings. Although this process resembles metal organic vapour deposition (MOCVD) in some respects, unlike MOCVD it can use starting materials that are not volatile and that are thermally unstable.

In a typical coating process, a metal precursor compound, such as copper (II) dipivaloylmethanate, is dissolved in CO_2 at 138 MPa and 40°C. When this supercritical fluid solution is sprayed on a substrate, such as a single crystal of silicon heated at 500°C, a thin film of copper is deposited rapidly. If nitrous oxide (N_2O) is used as the solvent for the same precursor compound, and the solution sprayed into a radio frequency plasma, a copper oxide film can be formed without heating the sustrate. By dissolving a mixture of the copper compound with corresponding compounds in which yttrium and barium replace the copper (metal organic compounds known as chelates) in the hydrocarbon, n-pentane (C_5H_{12}), in the ratio 3:1:2, a thin film of the high-temperature superconductor, $YBa_2Cu_3O_7$, is formed after oxidation. Because all of the precursors are weighed in the same reservoir before being dissolved, their stoichiometry can be precisely controlled.

Coatings of a variety of metals including aluminium, chromium, indium, nickel, palladium, and zirconium can be deposited on all sorts of unusual shapes. For example, a fused silica fibre can be completely coated using a single nozzle. The coating process is usually carried out at atmospheric pressure. A vacuum is required only when plasmas are used to facilitate chemical deposition.

Because the rapid expansion of supercritical fluid solutions facilitates the vaporization of the dissolved precursors, this process differs from spray pyrolysis of ordinary solutions. The aerosol particles that form when supercritical fluids expand are much smaller (usually <1 µm) than the droplets formed by the atomization of ordinary liquids.

The University of Colorado researchers suggest that an added environmental benefit of using CO_2 as a solvent instead of volatile organics would be the reduction of emissions from painting and other coating processes that adversely affect the ozone layer. Polymeric coatings can be formed by spraying supercritical fluid mixtures of low molecular weight polymer or monomer organic precursors dissolved in CO_2 onto surfaces where the resins react to produce the coatings. [Department of Chemistry and Biochemistry, University of Colorado, Campus Box 215, Boulder, Colorado, USA, 80309. Tel.: (303) 492-7943. Fax: (303) 392-1149.]



Schematic diagram of the supercritical fluid transport-chemical deposition process for applying thin films and coatings. Carbon dioxide or nitrous oxide is compressed to form a supercritical fluid, in which the coating precursors in the reservoir are dissolved. The solution is transported to the coating chamber where it passes through a restrictor nozzle and is decompressed. The resulting vapour contacts the heated surface of the object to be coated. A chemical reaction occurs at or near this surface, forming the coating. (Source: Materials and Processing Report, May 1991)

CVD cluster tool

The integrity chemical vapour deposition (CVD) system is an integrated system that permits the simultaneous deposition, flow and anneal of films in a single chamber. Each of the variables governing the quality of the deposition is optimized through the hardware design. The integrity platform addresses a variety of CVD films with products tailored for each film type. The Integrity/BPSG (borophosphosilicate glass) system permits the simultaneous deposition, flow and anneal of thermal CVD BPSG films. This process, termed "flow as you go", eliminates voids which can be created when the sidewall deposition encloses the top of the trench before deposition in the centre can be completed. The process ensures void free trenches and planar topography on lines as small as 0.3 µm. Film uniformity is routinely ±2 per cent at 1 sigma, with defect densities on a 150 mm wafer of $<0.1/cm^2$, 0.3 µm in size. Operating parameters such as flux, temperature, gas concentration and pressure are all hardware controlled. High throughput rates enable processing of up to 48, 150 mm wafers/hr. In situ cleaning factors further enhance productivity. [Lam Research Corp., Fremont, California, USA.] (Source: Semiconductor International, January 1991)

* * * * *

Superconducting wire by CVD

Using a new chemical vapour deposition (CVD) process to coat flexible fibres within a thin film of high-temperature superconducting material, researchers at the Georgia Institute of Technology have increased deposition rates considerably while achieving promising critical temperatures and maximum current capacity. Existing CVD technology for thin-film superconductors yields a coating just one or two microns thick during a one-hour deposition run. The new process yields 50 to 200 microns per hour, depending on production conditions.

In the past, carrier gas has been used to transport metal sources into a CVD reactor. Since the flow rate, temperature and pressure must be controlled for each vaporizer the process has often been delicate and time-consuming. To make matters even more difficult, reagent sources for the commonly-used 1-2-3 superconductor (yttrium, barium and copper) provide low vapour pressure. If heat levels are increased to speed vaporization, these metal sources undergo chemical reactions and form unwanted compounds.

To improve this situation, the vaporizers were replaced with a powder feeder. A combination of finely-ground yttrium, barium and copper metal-organic powders are mixed with argon gas before flowing into the horizontal reactor, thus eliminating the need for complex controls. During a 5-30 minute period, the team fed between two and 10 grams of powder into the reactor.

Thus far, the technique has mostly been demonstrated using rectangular, single-crystal magnesium-oxide substrates, but several types of flexible, thin fibres also have been coated. Ultimately, the team plans to coat ceramic or metal fibres, possibly made of aluminium oxide and/or silicon dioxide. Other possible substrate materials include silicon carbide and carbon coated with a layer of an oxidation-protective material. A coating barrier between the fibre and the superconductor should eliminate any undesirable chemical reactions. (Source: Electronics World & Wireless World, March 1990)

* * * * *

X-ray window first CVD-diamond product

Windows for the X-ray detectors used in spectroscopes and other analytical instruments are now being made from CVD polycrystalline diamond by Crystallume, Menlo Park, California. This is believed to be the first diamond-coated industrial product made using plasma-enhanced CVD.

Unlike conventional beryllium windows, the diamond devices also transmit low-energy X-rays from light elements such as carbon, boron, and oxygen. A typical window consists of a grid-supported, free-standing diamond film measuring less than 0.5 µm thick. It supports a pressure higher than 100 kPa (1 atm), and has been tested to 400 kPa (4 atm) without failure. It also is leak-tight to helium.

From an optical-transmissivity standpoint, diamond is the material of choice for low-energy X-ray applications. Natural diamond is not suitable because it reportedly cannot be made thin enough to be transmissive in the energy range of interest. (Source: Advanced Materials & Processing, March 1990)

* * * * *

Rapid thermal CVD

The Jetlight 200 system allows the development of new processes based on the combination of low pressure chemical vapour deposition and rapid thermal processing. An 8 in. water coooled stainless steel processing chamber and customized gas and vacuum configuration enable selective processing through full control of the process parameters (temperature, pressure, gas flow). Thermal budget of the wafer is drastically reduced due to rapid heating and cooling of the substrate. Wafer temperature (monitored by an infrared pyrometer) is hot only during deposition. The system also offers: a high flow primary pumping unit and a high vacuum turbomolecular pumping unit with reactive gas processing capability for rapid thermal epitaxy (RTE) processes. Development of selective silicon epitaxy, SiGe epitaxy, and dielectric deposition processes are possible. [Jipelec, Grenoble, France.] (Source: Semiconductor International, June 1991)

* * * * *

Diamond-like carbon coatings

Battelle has developed a technique for depositing what is known as diamond-like carbon coatings (a-c:H). These coatings are produced by a plasma-assisted CVD process, practically at room temperature. They are closely related to diamond coatings and are reported to consist of pure, low-hydrogen carbon, part of which is available in diamond modification. The coatings are very hard (more than 4,000 kg/mm^2) and are characterized by very low friction and extremely good chemical resistance. Typical coating thicknesses range from fractions of micrometres to some 10 micrometres. This property profile makes diamond-like carbon very useful for wear and corrosion protection and for all applications requiring low friction without abrasion. Examples include bearings, guides, cutting tools and other mechanical engineering components that are subject to wear. [Doris Jessen, Battelle Europe, Am Römerhof 35, D-6000 Frankfurt 90, Germany. Tel.: 69/7908-2214.] (Source: New Materials World, February 1990)

* * * * *

Liquid CVD source

LTO-410 is a non-pyrophoric, high purity liquid source material that offers significant improvement over silane for SiO_2 CVD applications between 340°C and 480°C. The liquid provides low film stress, coating conformality and safer handling. [Schumacher, Carlsbad, California, USA.] (Source: Semiconductor International, June 1990)

* * * * *

Plasma-CVD coats steel-cutting tools

Carbide indexable inserts are being coated with titanium carbide, titanium nitride, and aluminium oxide by plasma chemical-vapour deposition (CVD) at Krupp Widia GmbH, Essen, Germany.

CVD can coat parts of complex shape on all sides with layers of uniform thickness. The conventional process, however, is performed at about 1,000°C (1,830°F), a temperature that can reduce the toughness of the carbide substrate and lead to shortened tool life in high-impact steel-machining operations such as milling and turning with interrupted cuts. Plasma CVD, on the other hand, is performed at just 450 to 650°C (840 to 1,200°F), a temperature range that has no adverse effect on toughness. Compared with conventionally coated inserts, Plasma-CVD tools reportedly last longer at the same speeds and feeds, or can be used at speeds as much as 50 per cent higher with no decrease in life.

Krupp Widia's plasma-CVD facility operates at a pressure of about 100 Pa (0.01 psi). Coating gases are converted into a plasma at the lower temperature under high dc current. Capacity of the computer-controlled, tandem-furnace system is similar to that of a conventional CVD operation. (Source: Advanced Materials & Processes, July 1990)

* * * * *

Silicon atoms "see the light"

Plasma-enhanced chemical-vapour deposition (CVD) is a process commonly used to deposit silicon and silicon-dioxide films in the manufacture of advanced semiconductor devices and optical fibres. However, according to a research scientist in the Electromagnetics Laboratory at Georgia Institute of Technology (Georgia Tech), Atlanta, the mechanisms of silicon and silicon-dioxide deposition are not well understood at the atomic and molecular scales, despite the commercial importance of the process. Instead, researchers in these fields currently rely on an empirical approach to study plasma-enhanced CVD. The approach involves trying to relate different flow rates of the chemicals used and microwave field-power levels to the end result of the deposition process, even though the detailed chemical reactions occuring are not understood. The capability to observe silicon atoms and silicon monoxide in the plasmas and flames used to manufacture semiconductors and optical fibres could lead to a better understanding of the complex chemical reactions involved, and thus lead to improvements in manufacturing techniques. For example, if the reactions can be determined and the process modelled, process temperatures possibly could be lowered.

Existing methods for studying such reactions involve sampling steps that can disturb the ongoing reaction. Use of laser-induced fluorescence (LIF), however, can produce accurate measurements without disturbing the reaction. LIF uses tunable (adjustable wavelength) lasers to direct light energy at gases having unknown chemical composition. At certain wavelengths, the individual components absorb light energy and then radiate it back - a process called fluorescence. Because every material fluoresces at a specific wavelength, the technique can be used to clearly identify the gaseous constitutents and their concentrations. (Observation of the laser excitation spectrum also allows the determination of the flame temperature.)

While LIF is widely used to identify trace elements and to study both atmospheric and combustion chemistry, its use in analysing chemicals is limited to those that absorb light at the wavelength of the particular dye laser. Silicon atoms absorb light at about 250 nanometers, and silicon monoxide absorbs light at about 230 nanometers.

Until recently, however, it was difficult to produce wavelengths shorter than 260 nanometers. To overcome this problem, the LIF operating range is expanded using a technique called frequency doubling, in which the laser beams are passed through certain crystals that double their frequency. By passing the laser beam through a beta barium-borate crystal (available only in the People's Republic of China), it is now possible to produce wavelengths shorter than 205 nanometers; this allows the use of LIF to analyse a wider range of materials, including silicon and silicon monoxide.

Researchers at Georgia Tech have successfully used such a LIF technique to detect and measure both silicon and silicon monoxide gas-phase species. In situ laser diagnostics of this type, which allow the direct study of the chemical reactions occuring in a reactor to obtain information such as chemical species involved, their concentrations, and where the reaction is occuring physically, should not only lead to a better understanding of plasma-enhanced CVD, but of similar gas-phase processes. (Source: Advanced Material & Processes, November 1990)

* * * * *

Low-temp CVD merits attention

Low-temperature CVD - chemical vapour deposition at 325-525°C - is an effective means of applying erosion-resistant tungsten-carbide coatings to AM-350 stainless steel and Ti-6Al-4V titanium alloy. The process combines the advantages of physical vapour deposition (PVD) and conventional, or high-temperature, CVD.

As with PVD, the low deposition temperatures reduce degradation of mechanical properties. In many cases, the temperature is sufficiently low so that fully heat-treated parts can be coated without loss of properties. On the other hand, because CVD is not a line-of-sight process, like PVD, complex parts can be readily coated without sophisticated part-manipulation equipment.

Typical reaction conditions for this low-temp CVD process are a temperature of less than 500°C, 40 to 100 Torr pressure, and the following gas-flow rates: about 300 sccm (standard cu-cm per minute) tungsten hexafluoride (WF_6), about 3,000 sccm hydrogen, 40-90 sccm dimethyl ether, and 300-2,000 sccm diluent argon.

The coatings, which were applied to nickel-plated samples of the stainless steel and titanium alloy to protect them from attack by the hot corrosive gases, are a mixture of tungsten and tungsten-carbide phases, the latter W_2C, W_3C or W_2C and W_3C, depending on the partial pressure of the dimethyl ether.

They are very dense coatings, free of voids, with good adherence, and comprise two distinct layers: columnar tungsten on the inside and a fine-grain, non-columnar, lamellar top face of tungsten and the various tungsten-carbide phases. The top face is quite smooth, ranges in hardness from Hv 2,400-3,000, and resists erosion under both mild (low-impingement angle) and harsh (high-impingement angle) conditions.

Others also have reported on tungsten-carbide coatings applied at 325-525°C, the researchers noted. However, although these coatings are also quite hard (Hv 2,000-2,500) and provide good general wear resistance, they are rather poor in terms of resistance to erosion.

Erosion resistance was determined using a miniature sandblast unit, impingement angles of 22.5° and 90°, and two media: angular silica (crushed glass) and alumina. Use of silica, prevalent in topsoil, simulated a real erosive environment, whereas alumina provided a harsher and accelerated test environment.

Not only were the coated samples far more erosion resistant than the uncoated ones - by factors of five to over 100 - but also than samples coated with titanium nitride deposited by cathodic-arc discharge PVD. (Extracted from American Machinist, November 1990)

* * * * *

Surface treatment with lasers

Inductoheat is a small independent UK company which specializes in induction heat treatment services. One technique, induction hardening, is used to improve surface hardness whilst leaving the core material unchanged, thus giving maximum toughness. It became clear to the company that laser beam heating could offer more finesse and versatility in this process than induction and so a flexible laser processing facility was installed. The equipment had to allow for a wide range of operations and production volumes to be capable of development, pilot batch and full-scale production on a subcontract basis.

The system uses a control laser - the 2.5 kw CO_2 laser - which is static and mounted to one side of an enclosed working area. The beam is targeted through a mirror assembly which also aligns the beam to the major axis of the CNC workhandling device which can handle workpieces up to 2.1 X 3.5 X 1 m.

For hardening applications a special optical device is used to produce an enlarged beam which allows tracks up to 15 mm wide to be produced. Both the amplitude and frequency of the spot movement can be changed in both directions which gives flexibility in use.

For steel components, the intense heat of the laser beam focussed on the surface transforms this layer to austenite in a fraction of a second. Quenching is normally by self cooling with beam size, power, surface absorption and interaction time as the controlling factors for hardness pattern and case depth. Maximum hardness is achieved at relatively high scan rates. As heating times are short only short-range carbon diffusion occurs so that coarse grained or cast structures can give a sluggish response.

The use of increased surface temperatures may help here and with high alloy steels. Apart from this all medium carbon and alloy steels, martensitic stainless, tool steels and pearlitic iron castings are readily hardenable. Lower carbon steels can be treated to improve wear resistance because of microscopic variations in carbon content. Fully ferritic ductile SG iron castings can be melt hardened to give a surface layer of fine white iron.

Because cold steel is over 90 per cent reflective to the CO_2 laser beam a coating which absorbs the wavelength of light is normally applied to the surface before hardening. This may be paint, graphite, or a phosphate or metal oxide coating.

The laser's clearest role is in achieving results where other methods prove difficult or impossible. With a large circular or non-uniform component, induction heating cannot be applied to the required area in one pass, or easily scanned around or along it. In other cases induction is unable to concentrate power into the small or inaccessible area requiring heating. The controlled heat of the laser beam can gain line-of-sight access to produce hardened surface layers up to 1 mm deep without the risk of distortion or cracking.

Components can range from a few grams of several tons in weight, typical areas of application for high volume production being in the automotive, consumer of related industries. The first industrial application of laser hardening was at General Motors, Saginaw Steering Gear Division, Michigan, in 1973 where five wear tracks were formed on the internal bore of a power steering casting. This could not be carried out by conventional means because of induced distortion.

An example of the type of subcontract work carried out by Inductoheat is the handle casting used in a compact valve system for hydraulic roof supports manufactured by Dowty Mining Equipment Ltd. The case depth is thickened over the peak of each cam profile to advantage. To produce a uniform pattern over a progressive curve one handle is held at such an angle that static dwell at the lip produces an initial heat line which is then progressed through the profile by scanning. As the handle must be failsafe in operation the pattern must be controlled and kept away from pivot lugs etc. For the second handle, both sides of the lever end 5 mm thick are treated in turn without back temper or risk of embrittlement.

The company has shown that laser hardening at the 2.5 kW level can compete with induction for treating small areas, complex geometries and pieces liable to cracking or distortion. It cannot yet compete directly on larger areas, but higher power lasers may compete in terms of cycle time although high capital and running costs may make this difficult in dedicated applications. However, in terms of flexibility, a clear benefit may be seen. (Source: International Licencing, Ma 1991)

* * * * *

Research on the laser optochemical process in reactions

Objective

Advanced future industries such as electronics, chemical, medical therapy, aircraft and space development require the development of advanced materials to create new substances based on new bonding concepts and for the development of advanced technology to control the compositions and structures of new substances on the atomic and molecular levels.

The objective of this research project is to use lasers with high quality and energy for substance transformation and to combine special reaction environments such as magnetic fields, cryogenic temperatures and surface adsorption phenomena to develop atom and molecule manipulation technologies based on advanced chemical reaction control to create new substances and materials with complex functions.

Contents

Laser chemical reaction allows new kinds of reactions for forming highly reactive activated molecules and reactions at high-energy states, which are impossible with conventional methods.

The aim of this research project is to search for these laser chemical reactions and to promote special reaction environments by combining magnetic fields, cryogenic temperatures and surface adsorption phenomena to control highly reactive activated molecules most effectively and to advance these new types of reactions, to develop processes for the creation of new high-function substances and materials.

In fiscal year 1990, the following research projects were scheduled:

(1) Design and synthesis of reactive raw materials by the multiphoton process relying on light intensity of lasers and other conditions;

(2) Generation of magnetic fields with multi-layer winding coils and the design and manufacture of magnetic field effect chemical reaction containers;

(3) Design and synthesis of laser-reactive raw materials at cryogenic temperatures or on the surfaces of solids. (Source: JETRO, May 1991)

* * * * *

Laser surface hardening of AISI 01 tool steel and its microstructure

The most widely used methods of increasing surface hardness, wear resistance, fatigue resistance, and, in some cases, corrosion resistance of ferrous engineering components through heat treatments fall into two categories:

(i) Thermochemical processes, in which elements such as carbon and/or nitrogen are introduced into the surface at elevated temperatures, such as carburizing, carbonitriding, and nitriding; and

(ii) Thermal processes in which heat alone is applied selectively to austenitize the surface, followed by quenching to produce a martensitic case. Induction or flame hardening are typical examples of these processes. Lasers are also being used increasingly as a finely controllable heat source for surface hardening of steels.

Laser surface hardening has been used in diesel engine parts and components made of cast iron, such as cylinder liners, ring grooves on pistons, automobile camshafts, and gear teeth, to improve their wear resistance and fatigue properties. Investigation of cylindrical specimens of medium carbon steels with 1 wt-per cent Cr has shown that the number of loading cycles was increased 10-20 times by laser melting of the surface. Laser hardening has also been used to increase the wear resistance of the cutting edges of tools, such as milling cutters, drills, and reamers, made of low alloy tool steels and high speed steels, by factors of 1.5-4.

The main advantages of using lasers for surface hardening applications are as follows:

(i) Very little or no distortion of the workpiece occurs;

(ii) Rapid production rates are possible and the process is suitable for automation;

(iii) Usually no external quenchant is required to form martensite;

(iv) Selective surface treatment on a complex shape is also possible;

(v) Residual compressive stresses are induced at the surface.

The beam from a carbon dioxide laser, having a 10.6 µm wavelength, falls within the infrared spectrum and as such can be considered as pure heat energy. If the beam used has sufficient intensity, the surface of a ferrous material can achieve austenitizing temperatures after a very short interaction time (a fraction of a second), while the bulk remains unaffected. Thus, a very steep temperature gradient is created between the surface and the bulk of the material. Consequently, when the heat source is removed, there is no requirement for an external quenchant to bring about the martensitic transformation of the surface, because the bulk of the material provides an adequate heat sink.

For transformation hardening applications, high power lasers usually are used. A high power laser allows the beam to be defocused to a larger spot to cover a larger area in a single pass. On the other hand, if a lower power laser is used to obtain a high power density, the spot size will be comparatively small. However, the incident power density is usually kept less than about 100 W mm^{-2} for surface hardening applications. Generally, higher power densities are used in combination with higher traversing speeds, and lower power densities with lower traversing speeds. Higher power densities with higher scan rates tend to promote smaller case depths, and lower power densities in combination with lower speeds produce greater case depths.

For an effective coupling of the laser energy to the workpiece, an absorbent coating usually is required, because at room temperature polished steel surfaces are about 85-90 per cent reflective to carbon dioxide lasers. The three most commonly used coatings to improve coupling are manganese or zinc phosphate, powdered graphite suspension, and spray paint (flat black). Of these, phosphates are the best absorbers, but are also the most costly and time consuming to apply. Graphite suspension is the poorest absorber and is more difficult to apply than spray paint. In the authors' experience, flat black paint provides adequate absorptive characteristics, is easy to apply, and, furthermore, the laser hardening response of steel coated in this way has been found to be relatively insensitive to the paint thickness.

The aim of this study was to investigate the effect of the laser process parameters and the initial microstructure on the microstructure and hardness of AISI 01 tool steel. In particular, a detailed microstructural investigation of the laser hardened layer was carried out to elucidate the hardening mechanisms.

Material and experimental details

The chemical composition of the AISI 01 tool steel used in this study is (in wt-per cent): 0.9 per cent C, 1.0-1.2 per cent Mn, 0.5 per cent Cr, 0.5 per cent W, 0.3 per cent Si, Fe (bal.). Table 1 gives the heat treatment conditions, the hardness values, and the microstructure of the steel before laser treatment. Treatment HT1 refers to the as received material in the spheroidized condition and HT2, HT3 and HT4 conditions refer to specimens that were hardened and tempered at 621°C, 537°C, and 426°C, respectively. The samples were hardened and tempered at different temperatures to determine the effects of the initial microstructure on the laser hardening response. The heat treated specimens were then ground flat to 600 grit and painted black to improve the laser absorption characteristics.

All laser treatments were applied using a 600 W (nominal) carbon dioxide laser. A special heat treatment lens (Zn Se), with a focal length of about 63 mm, was used. With this lens, the laser beam is focused in the form of a rectangle about 1 X 7 mm rather than a circular spot.

For the laser treatment the specimen was mounted on a computer controlled X-Y table, and a single laser pass with a normal beam impingement angle (90°) was used. The laser power, incident power density, and traversing speeds used are given in table 2. After laser treatments, all specimens were sectioned, polished, and etched for metallographic examination. Measurements of microhardness across the laser hardened track were taken using a microhardness tester with a 200 g load. These diamond pyramid hardness values were then converted to Rockwell C hardness values using a conventional conversion table.

Microstructural characterization was carried out using X-ray diffractometry (XRD) and analytical transmission electron microscopy (ATEM). The XRD of both the laser hardened surface and the bulk material was carried out on a Philips diffractometer using Cu $K\alpha$ radiation. Thin foils were obtained by diamond cutting 0.4 mm thick discs from 3 mm diameter machined bars of both laser treated and untreated material. The discs were ground on 600 grit silicon carbide paper to a thickness of ~0.2 mm and then polished electrochemically using a Tenupol jet polishing unit. Electropolishing was performed at 45 V with a current density of about 25 mA mm^{-2} in an electrolyte of 94 per cent acetic acid and 6 per cent perchloric acid. All foils were examined at 120 kV on a JEOL 100CX TEM, with a double tilt stage for imaging and diffraction or an analytical single tilt carbon stage for energy dispersive X-ray spectrometry (EDS) microanalysis. Some observations were carried out in a JEOL 840 scanning electron microscope (SEM), also equipped with an EDS system.

Conclusions

The following conclusions can be drawn from the results of this investigation.

1. AISI 01 tool steel can be laser surface hardened with an effective case depth of 0.3-0.6 mm using a 600 W (nominal) carbon dioxide laser. The maximum hardness values obtained in the laser hardened zone were in the range 62-68 HRC.

2. Prior microstructure did not have a significant influence on the hardened depth, but it had a pronounced effect on the microstructure of the laser hardened zone. The quenched and tempered microstructure (finer) produced, in general, a more homogeneous laser hardened zone than the as received spheroidized microstructure.

3. The microstructure of the laser hardened zone consists primarily of lath martensite, some carbides, and some retained austenite. A decrease in the amount of retained austenite, together with an increase in the amount of undissolved carbides and a change in the morphology of martensite from plate to lath and to tempered martensite, is observed from the hardened surface onwards. The formation of plate and lath martensite and the dissolution of carbides contribute primarily to surface hardening through transformation hardening and substitutional strengthening mechanisms, respectively.

4. An increase in the lattice parameter of the α-iron (martensite) occurs in the hardened layer through the supersaturation of martensite with carbon. This increase in the lattice parameter, together with the volume increase associated with the martensite reaction, is suggested to lead to the development of compressive residual stresses in the laser-hardened surfaces.

Table 1. Heat treatments carried out before laser treating AISI O1 tool steel

Heat treatment	Tempering* temperature, °C	Rockwell hardness HRC	Microstructure obtained
HT1	As received	16-20	Spheroidized
HT2	621	28-30	Tempered martensite
HT3	537	38-40	Tempered martensite
HT4	426	48-50	Tempered martensite

* Heat treated initially at 787°C, oil quenched, and tempered at three different temperatures.

Table 2. Typical laser parameters and results obtained

Heat treatment	Power, W	Power density $W\ mm^{-2}$	Traversing mm^{-1}	Effective case depth, mm	Case hardness HRC
HT1	500	71.42	2.1	0.40	65
HT2	500	71.42	2.1	0.5	65
HT3	500	71.42	2.1	0.5	65
HT4	500	71.42	2.1	0.6	65

(Extracted from Materials Science and Technology, May 1991, Vol. 7. Article written by H. Bande, G. L.'Espérance, M.U. Islam, and A. K. Koul. At the time the work was carried out Dr. Bande and Professor L'Espérance were at the Centre for Characterization and Microscopy of Materials, Ecole polytechnique, Montréal, Quebec, Canada. Mr. Islam was at the Manufacturing Technology Centre, Division of Mechanical Engineering, National Research Council, Ottawa, Ontario, Canada, and Dr. Koul was at the National Aeronautical Establishment, National Research Council, Ottawa, Ontario, Canada. Dr. Bande has now returned to the Harbin Institute of Technology, Harbin, The People's Republic of China, from which he was on leave.)

* * * * *

Surface hardening of SUS304 by irradiation with a KrF excimer laser in SiH_4 gas ambient

Surface modifications of mechanical and chemical properties of metals such as hardness, wear, friction, and corrosion have been widely investigated, since diversified materials with excellent properties are required in mechanical manufacturing. These studies have shown that although metal alloying, oxidation, or nitridation by ion implantation has merit, ion implantation with a dose high enough to modify the surface creates many problems, such as sputtering, defects, and contamination by oxygen and carbon. An alternative method, UV pulsed excimer lasers, has several advantages. Neither sputtering nor defects have been observed [using high-resolution cross-section transmission electron microscopy (HRXTEM)], and contamination is reduced. In addition, selective surface modification can be achieved by limiting the area of the laser beam irradiation by using a mask or a scanning focused beam. However, knowledge is limited as to the mechanical properties of the metal surface treated by laser processing. Deposited metal thin films for laser alloying and liquid phase dopant sources for laser oxidation and nitridation are primarily discussed in the literature, but gas phase dopant sources are also attractive in order to provide a wide variety of laser modifications of the metal surfaces.

In the present study, surface hardening of SUS304 by irradiation with a KrF excimer laser in SiH_4 gas ambient is described, with SiH_4 gas used as a dopant source. In this case, most of the laser energy is deposited at the sample surface and is immediately transformed into heat, since the absorption depth of UV light into metals is of the order of 10 nm. In addition, the SiH_4 gas has no optical absorption and the optical transmission of the window made of synthetic quartz is 93 per cent at the wavelength of KrF excimer laser. By laser heating, the surface might be melted and simultaneously the absorbed gas molecules on the sample surface subjected to thermal dissociation. The dissociated Si atoms distribute rapidly in the molten region by liquid phase diffusion, and then solidification occurs from the liquid-solid interface. Such a rapid thermal reaction including the melting process has been thoroughly discussed in the studies of pulsed laser doping of Si and GaAs. In this case, deposition of Si films was observed under the limited laser irradiation conditions simultaneously with the incorporation of Si. The deposited Si film might have a very high adhesion strength, since the Si atoms distribute continuously from the metal substrate to the films. The specific process is refered to as LID (laser implant-deposition).

Observation of surface morphology and the measurement of depth profiles of Si distributed by LID for the various laser irradiation conditions are carried out in the present work. The dependence of the surface hardness on the laser fluence and the number of laser pulses is also discussed.

Experimental procedure

A. Sample preparation

A sample was transferred into the small gas cell after cleaning with organic solvents. The cell was then filled with 10 per cent SiH_4 gas diluted in 100 torr of He after evacuation down to 3×10^{-3} torr. A KrF excimer laser beam with 248 nm wavelength and 23 ns pulse width was directed nearly perpendicularly to the sample surface. The laser fluence at the sample surface and the number of laser pulses were varied from 330 to 450 mJ/cm^2 and from 5 to 100, respectively. The repetition rate of the laser pulses was chosen to be 1 Hz in order to avoid heat accumulation by preceding laser pulses. The optical transmission of the window made of synthetic quartz is 93 per cent for the wavelength of KrF excimer laser. The energy loss of 7 per cent is mostly due to the surface reflection, and the optical absorption is less than 1 per cent. Therefore, damages of the quartz window by laser irradiation did not occur in the present experimental conditions. Beam-forming optics combining a cylindrical lens and a pyramidal optical device were used. Thus a nonuniform intensity of less than 70 per cent and rectangular laser beam profile were converted to a square beam pattern with a spatial uniformity of better than 96 per cent.

B. Evaluations

Observation of surface morphology by a scanning electron microscope (SEM) and the analysis of surface composition by X-ray photoelectron spectroscopy (XPS) were carried out. Deposited materials on the sample surface were also analysed by XPS and depth profiles of Si were measured by secondary ion mass spectroscopy (SIMS). Variation of the surface hardness of samples prepared with various laser irradiation conditions was evaluated using a Shimadzu ultramicrohardness tester (UMHT). The UMHT consists of four main components: an optical microscope used to adjust a suitable test area on the sample, a diamond indenter and load application mechanism, a displacement transducer and amplifier, and a programmable control console. The programme determined the rate of application of the load and the maximum load. Sample hardness was evaluated from the depth to which the triangular pyramidal diamond indenter penetrates into the sample under a predetermined load condition. During a hardness test, the load is progressively increased at some predefined rate up to a maximum value. The corresponding indentation depth is measured by a displacement transducer; a curve of the penetration depth versus the load is then recorded on a chart recorder. The harder surface decreases the penetration depth of the indenter, under the same loading condition.

Surface hardening of SUS304 by irradiation with a KrF excimer laser beam in SiH_4 gas ambient has been demonstrated. The doping and deposition of Si occurred simultaneously. Complete coverage with Si thin film has been obtained in the case of a laser fluence of 450 mJ/cm^2, 100 pulses, and 100 torr pressure of 10 per cent SiH_4 gas. The deposited films have shown good adhesion to the substrates, and it was demonstrated that the surface hardness is an increasing function of both the number of laser pulses and laser fluence. (Extracted from Journal of Materials Research, Vol. 5, No. 2, February 1990. Article written by: Koji Sugioka, Hideo Tashiro, and Koichi Toyoda, Riken, the Institute of Physical and Chemical Research, Wako, Saitama, 351-01, Japan; Eiichi Tamura and Keigo Nagasaka, Department of Physics, Science University of Tokyo, Kagurazaka, Shinjuku, Tokyo, 162, Japan.)

* * * * *

Laser Cladding Research Centre

Imperial College of Science, Prince Consort Road, London SW7 2BP, has a Laser Cladding Research Centre. Laser is being used for surface heat treatment, cladding, welding, melting, and alloying with titanium, technical ceramics and composites. Laser cladding techniques as thermal carrier coating on gas turbine engines solves a number of the traditional problems, such as corrosion from fuel contaminants, and yields films nearly twice as hard as plasma spray coating. A continuous wave CO_2 laser lays down 0.1 mm to 1.5 mm thick coatings of yttria-partially stabilized zirconia on mild steel under an argon shroud. Use of shroud reduces the curvature and cracking of the coarsely spaced ripples created during deposition, and boosts hardness to 1500 Hv, from the 800-Hv plasma-spray level.

* * * * *

Laser surface treatments for promoting corrosion resistance of a carbon steel

The effect of laser treatment and laser alloying on corrosion resistance of 1045 steel has been studied. Various ways of surface alloying have been investigated by using continuous CO_2 laser beam: (i) irradiation of chromium painted surfaces; (ii) irradiation of Ni and Cr-electroplated surfaces; (iii) direct injection of Ni and Cr powders into the melt pool. A high and uniform level of alloying in the surface layer can be achieved in the cases of electroplated surfaces and direct powder injection. It requires, however, an appropriate choice of irradiation conditions (such as beam power, beam traverse speed, beam defocusing and degree of overlapping) that provide remelted layer of a limited and fairly uniform thickness. It has been found that in order to achieve corrosion behaviour of laser treated surfaces similar to that of austenite type 304 stainless steel chromium and nickel contents in the alloyed layer are to be higher than those of 304 steel. (Abstracted from Materials & Manufacturing Processes, 5(4), 1990. Article was written by: M. Riabkina-Fishman and J. Zahavi, Israel Institute of Metals, Technion - Israel Institute of Technology, Haifa, 32000 Israel.)

* * * * *

CVD system for coating ceramics

A chemical vapour deposition system that can be used to deposit coatings of titanium carbide, titanium oxycarbide, titanium nitride, titanium carbonitride and titanium oxycarbonitride has been introduced by Lindberg.

The Lindberg/Tungaloy CVD system consists of a vertical batch type electric reaction furnace which uses a variety of atmospheres and a maximum operating temperature of 1,100°C to deposit single and multilayered titanium based coatings of uniform thickness. The coatings can be used to increase the service life of moulds, dies, jigs, fixtures and cutting tools.

A programmable controller for automatic operation is standard. Specific time/temperature profiles are preprogrammed into the system computer and are recalled by recipes. (Lindberg, A Unit of General Signal, 304 Hart Street, Watertown, Wisconsin 53094, USA. Tel.: (414) 261 7000. Fax: (414) 261 0925). (Source: New Materials World, August 1990)

* * * * *

Composite ceramic coatings

Plasmadize, a new group of composite coatings from General Magnaplate Corp., Linden, New Jersey, can be applied to virtually any type of metal including aluminium, and is recommended for use on OEM parts, as well as for repair and/or restoration of old parts. The coating is composed of layers of ultrafine particles of ceramic such as tungsten carbide, alumina, and chromium oxide infused with polymers to enhance structural integrity of the coating and impart nonstick properties. (Source: Advanced Materials and Processes, December 1989)

* * * * *

Protective ceramic coatings

Dylon Ceramic Technologies, Berea, Ohio, has developed an easy-to-use ceramic barrier coating. Dylon B-1302 will reduce the degradation of refractory surfaces at elevated temperatures up to 3,000°F. B-1302 is a high quality, single application, zircon based liquid suspension. It has been designed as a viscous compound that creates a ceramic facing when applied to a refractory surface. When thoroughly dry, the facing is impervious to thermal shock while resisting hostile environments.

Dylon B-1302 is best applied with air atomized spraying systems and in many cases the operation can be automated. The coating can be applied to refractory surfaces at a temperature range from ambient to 600°F. It is recommended for use on coke-oven door plugs and refractory runner covers. A typical coke-oven door plug application shows outstanding performance, after 88 days of service.

This protective ceramic coating is conveniently packaged in 65 lb pails and 750 lb drums. (Source: Iron and Steel Engineer, October 1990)

* * * * *

Firing converts polymer into ceramic "whiskers"

Scientists at Southwest Research Institute (SwRI), San Antonio, Texas, reportedly have developed silicon-based polymer binders that can be used to make tough, heat-resistant ceramics. The organometallic polysilazanes have a complex, three-dimensional (3-D) structure consisting of an inorganic backbone with organic appendages. When a ceramic containing a new binder is fired, the polymer decomposes to form silicon-nitride (Si_3N_4) "whiskers", which toughen the overall structure. The US Air Force Office of Scientific Research currently is funding a programme to study the relationship between the preceramic polymer's 3-D structure and that of the derived ceramic.

Other so-called preceramic polymers are commercially available, but, says SwRI, they yield only a small amount of ceramic: typically less than 50 wt per cent. The new polysilazanes, however, have a conversion rate greater than 90 per cent. These high yields mean that the firing operation has little effect on the part's shape and size. As a result, complex-shape parts such as turbine blades become candidates for injection molding. The polymers also can be produced as low-viscosity liquids, which can be used to make fibre-reinforced ceramics and ceramic coatings. (Source: Advanced Materials & Processes, August 1991)

* * * * *

Quasicrystals at home on the range

Little more than a laboratory curiosity since their discovery in the early 1980s by Israeli scientist D. Shechtman while conducting research at the National Institute for Standards and Technology, quasicrystals may have found their first commercial application: as non-stick, abrasion-resistant coatings on cookware. A low coefficient of friction plus other attractive properties of thermal-sprayed quasicrystalline coatings make them good candidates for use in tribological applications. They provide improved performance for parts made of bulk materials that do not have good wear and abrasion resistance. This provided the motivation to apply quasicrystal coatings to cooking utensils, which require frequent cleaning.

The application of aluminium-alloy quasicrystals to cookware is patented by Centre National de la Recherche Scientifique, Nancy, France. The patented process stemmed from research at Laboratoire de Science et Génie des Matériaux Métalliques, Ecole des Mines, in Nancy. Scientists led by Jean-Marie Dubois, along with conducting fundamental studies of quasicrystals, focused their attention on potential applications of two quasicrystalline intermetallic compounds having the nominal compositions, in at.per cent, of $Al_{65}Cu_{20}Fe_{15}$ (designated alloy A) and $Al_{64}Cu_{18}Fe_8Cr_8$ (designated alloy B). Powders were prepared by mechanically grinding ingots to a mesh size ranging from 20 to 75 μm (0.0008 to 0.003 in.), and were thermally sprayed onto "soft" aluminium-alloy, pure-copper, and low-carbon steel substrates using flame, supersonic, and plasma-arc spraying. The deposited materials consist of a mixture of quasicrystals and crystalline phases. Alloy A contains about 70 per cent icosahedral phase, while alloy B contains about 70 per cent quasicrystalline (icosahedral + decagonal) phases. (An icosahedron is a polygon having 20 faces and a decagon is a polygon having ten angles and ten faces.) Phase contents vary depending on the solidification rate achieved during coating deposition.

While bulk quasicrystalline alloys appear to have little usefulness, coatings prove to be very useful. The deposited materials are hard, thermally stable, and corrosion and oxidation resistant. Coating hardness is equal to that of hardened alloy steel (between 500 and 800 HV), and can be increased by heat treatment. In addition, no microstructural changes occur at temperatures to 700°C (1,290°F) - a significant achievement for aluminium alloys - and there is no grain growth up to about 450°C (840°F).

The friction coefficients of the composite systems (substrate + coating) were determined via a commercial scratch-testing device equipped with both acoustic-emission and friction-force sensors for on-line measurement. Friction coefficients for alloys A and B are similar, around 0.2 and 0.3 for a Rockwell C diamond indenter and an AISI 52100 Brinell ball, respectively.

Under progressively higher loading, the critical load necessary to cause coating perforation varies linearly with coating thickness. By comparison, under constant loading for the same coating thickness and a given type of substrate, the dynamic hardness of the composite system is dependent on the amount of porosity in the coating. On the other hand, crack density (as determined by counting the number of cracks/unit length at the bottom of the scratch track) is not dependent on the amount of coating porosity. [Quasicrystalline powder production and thermal-spray coating is commercially handled by Société Nouvelle de Métallisation Industries (SNMI); SNMI, B.P. 966 F-84093 Avignon, France; Tel.: (33) 90-85-85-00; Fax: (3) 90-82-94-52.] (Source: Advanced Materials & Processes, June 1991)

* * * * *

Ultrathin metal coatings yield unique properties

Coating a metal with an ultrathin layer of another metal creates properties not found in either metal.

Materials researchers are investigating the improved mechanical properties of bimetallic laminates, called composition modulated films, having interlayers only a few nanometers thick. Also, attractive properties have been found for similar systems, called nanometer materials, in which the two metals are dispersed in the form of small particles having dimensions in the nanometer range. These examples of the use of ultrathin overlayers have two aspect in common: the microscopic details of the way the bimetallic configuration imparts unique properties is not understood, and these properties involve film thicknesses in the nanometer range.

Overlay strain affects properties

Sandia National Laboratories, Albuquerque, New Mexico, is investigating these materials via a systematic approach that combines both experimental measurements and state-of-the art theoretical calculations correlating behaviour of the structural, electronic, and vibrational properties of ultrathin films as a function of film thickness. The studies also include work on a variety of bimetallic combinations with contrasting elemental bulk properties. The goal is to understand the fundamental nature of the transition region and how it changes with the varying character of the bimetallic constituents.

The system of copper deposited on the close-packed surface of ruthenium illustrates some typical system behaviour. Examination using low-energy electron diffraction (LEED) shows that the interfacial-bonding interaction between copper and ruthenium is stronger than that of the atoms in bulk copper - so strong that the first several atomic monolayers of copper take up the exact structure of the substrate surface. This is called a pseudo-morphic structure. Because the copper atom is smaller than the ruthenium atom, the first subregion of copper monolayers is under a coherent, or uniform, tensile strain of almost 6 per cent with respect to its own close-packed structure. Thus, it is a strained-metal subregion. This strain is one of the principal reasons that the copper overlayer has properties so different from that of bulk copper.

In the second subregion of the overlayer, however, the interaction at the interface between the first and second subregions is no longer strong enough to support this level of strain. As a result, the growing film mitigates the strain by producing a structure that is periodically strained and has a superlattice of defects. The overall effect of this type of growth is a reduction of the average separation of the copper atoms and, thus, an increase in their mutual bonding interaction. Additional monolayers in this subregion show a gradual "healing" of the structure until eventually the film takes on the structure of bulk copper.

The coherently strained subregion, together with the strain-relief subregion, complete the transition between the structures of the two bulk metals. The exact atomic arrangement throughout the healing transition region has not yet been analysed in detail, but the effect is to produce a film whose properties are different from those of the bulk overlay metal. Copper requires approximately 12 monolayers (only 0.3 nm thick) on ruthenium to change to the bulk copper structure.

Copper films one or two monolayers thick are stable during thermal treatment, while thicker films are metastable. That is, they are stable only up to some temperature, above which they coalesce into small three-dimensional islands attached to the two stable monolayers. For example, a five-monolayer copper film is stable only to a temperature of about 600°C (1,110°F). The thicknesses of the coherently strained and transition regions for other bimetallic combinations are different than those for copper/ruthenium system, and they show different degrees of metastability.

Overlay-property studies

An atomic-level mechanical parameter (the thermal mean-square vibrational amplitude for the atoms of the films) for the metal overlayer films also was investigated. This parameter is related to the stiffness of the film's atomic lattice - the more resistant the overlay material is to distortion, the lower will be the amplitude of vibration of its atoms. Two goals of these measurements are to determine if the strong bonding interaction of the metal overlayers has the effect of stiffening the overlayer, and to investigate the way that this stiffening changes through the transition region.

Ruthenium has a very stiff lattice; therefore, its measured vibrational amplitude is low compared with copper, which is considerably softer. This trend can be observed by measuring the amplitude at zero film thickness, i.e., clean ruthenium, and the value approached for thick copper films.

For overlayer materials with coherently strained subregions, the healing effect extends over quite a few monolayers, the number depending upon the level of strain in the first monolayer. In contrast, overlayer materials that show no coherently strained subregion (e.g., the silver/ruthenium system) heal much more rapidly.

Electronic properties of bimetallic overlayer systems are determined using angle-resolved ultraviolet photoemission spectroscopy (ARUPS), which measures the energy distribution of the electrons responsible for the bonding characteristics of solids, and provides a distinctive characteristic, or fingerprint, of the material.

Copper deposited on the close-packed surface of tungsten was studied because, in contrast to the Cu/Ru system, the tungsten surface is unsymmetrical. In addition, while copper again grows pseudomorphically, it is strained by almost 25 per cent along one axis of the surface, but is essentially unstrained along the other.

Energy-distribution curves for the various monolayers of the copper film show that the first monolayer is different than the additional layers; the features of this curve appear as if they originated at the copper/tungsten interface and are simply attenuated by additional copper layers. Advanced theoretical calculations support this observation and show that the electrons occupying these electron-energy states are spatially localized on the first copper monolayer and the outermost tungsten layer of the substrate. Thus, these electron-energy states are unique; they do not exist in either bulk copper or tungsten, but exist at the interface because of the abrupt change in properties found there. A copper film on ruthenium also shows these singular electron-energy-state fingerprints. These experiments on the Cu/Ru and Cu/W systems are the first positive identification of such altered electron states in a metal-overlayer system.

The interface energy states arise because of the strong bonding interaction between the substrate and the first monolayer of copper. Subsequent monolayers produce a prominent, narrow feature in the energy-distribution curve that shifts between about -2.5 and -2.0 eV. This feature appears only after the deposition of the first monolayer and is due to the weaker copper/copper interaction. However, the distinct electronic fingerprint for bulk copper is not approached until many copper monolayers have been deposited. Spectra similar to that for bulk copper are not obtained until approximately 12 monolayers are grown.

As with the structural properties, the electronic behaviour of bimetallic overlayer systems also varies considerably from system to system. However, the electronic fingerprints consistently return to those of the bulk overlay metal at about the same thickness as in the structural studies of the same bimetallic combination. Thus, the exceptional electronic properties found in the first atomic monolayer must result from the strong electronic interaction with the substrate, while those for subsequent monolayers are driven by their characteristic geometric structures.

The work continues

Future work will include the study of new bimetallic constituents to examine an expanded range of interfacial strains and substrate surface-geometric structures, and an examination of a broader contrast in the individual bulk electronic structures. In addition, a more detailed analysis of the film structures in the strain-relieving subregion is under way. Beyond these experimental and theoretical characterization studies, the bimetallic-film mechanical properties will be measured for thicknesses in and beyond the transition region. These studies will include measurements of the residual stress in the films, their elastic properties, and the character and behaviour of defects under thermal and mechanical stress. The goal is to further develop the fundamental understanding of the physics of ultrathin metal-on-metal overlay systems. This will enable prediction of their properties and, eventually, the design of new surfaces with tailored characteristics. [Surface, Interface, and Ion Beam Research Dept.; or Peter Feibelman, Condensed Matter Research Dept., Sandia National Laboratories, Albuquerque, New Mexico, USA 87185, Tel.: (505) 884-8939 and 884-6706.)] (Source: Advanced Materials & Processes, March 1991)

* * * * *

How LEED works

While the low-energy electron diffraction (LEED) technique is used to investigate the crystallography of surfaces and overlayers absorbed on them, the LEED vacuum chamber used by Sandia National Laboratories, Albuquerque, New Mexico, USA, also is capable of angle-resolved ultraviolet photoemission spectroscopy (ARUPS) and other surface-sensitive analysis techniques on the samples. In addition, this versatile equipment is used to clean the samples by bombarding them with a krypton-ion beam and to lay down the ultrathin films.

In the LEED technique, an electron gun projects a narrow beam of monoenergetic (between 20 and 500 eV) electrons through a small hole in a spherical, convex glass shell. A fluorescent coating on the shell glows when bombarded by electrons. The sample to be studied is mounted beyond the spherical shell at its centre, and when the electron beam hits the surface of the sample, the electrons reflect to the coated shell and show up as a pattern of bright spots in the photo. The reflected electrons are diffracted into an array of individual beams that correspond to the constructive interference of electron scattering from the atomic structure of the sample's surface. The nature of this atomic structure can be inferred by analysing the symmetry and dimensions of the LEED pattern for various input-electron energies.

More advanced applications of the LEED technique yield atomic-structure information beyond the two-dimensional surface arrangement. For example, the spacing between atomic layers and the registry between them can be determined by measuring the variation in intensity of the diffracted beams as the electron energy changes. In addition, the average amplitude of the surface atoms' thermal vibrations and, therefore, the stiffness of the atomic lattice can be obtained by measuring the variation in the intensity of the spots with changing sample temperature.

In the ARUPS technique, photons from an ultraviolet light-beam source strike the sample and lose their energy to its valence electrons. When these excited electrons break free from the surface of the sample, their energy and direction of travel are determined by an angle-resolved electron-energy analyser. Information is then obtained concerning the chemical essence of the surface material by analysing the energy distributions of these excited electrons at various angles of emission.

With the facility's hard X-ray source, the binding energies of core electrons of near-surface atoms are probed using X-ray photoelectron spectroscopy and Auger electron spectroscopy. These techniques are used to determine the makeup of the surface of elements and to obtain information on their chemical properties. With its low-energy (0.5 to 40 eV) electron-beam gun, the vibrational energies of surface atoms and absorbed molecules are measured using low-energy electron-loss spectroscopy. (Source: Advanced Materials & Processes, March 1991)

* * * * *

New deposition process for corrosion and oxidation resistant coatings

ERA is launching a project to develop a new process for coating metal components with protective materials able to withstand high-temperature oxidation, attack by corrosive chemicals and erosion from fluids.

Existing surface treatment methods can only be used to provide general environmental protection (as in the case of paints and polymer coatings) or resistance to abrasion and wear (as with titanium nitride). These coatings do not afford sufficient protection against high-temperature oxidation or corrosion, particularly when erosion has occurred - caused, perhaps, by the flow of a hot corrosive fluid through a pipe.

In order to prevent corrosion and oxidation, it is necessary to form a coating that is refractory and chemically inert, which means using materials such as silica and alumina which cannot be applied satisfactorily by existing methods. (It is normally difficult to form these materials into thin layers.) The crystal structure of the protective coating must be dense and impervious with no pin holes or grain boundaries which could provide sites for corrosive attack. The ideal structure for this purpose is glassy and the coating process should be simple; avoiding the need for harsh surface pre-treatment, providing cover for uneven surfaces and, ideally, producing a layer so thin that it will not interfere with normal engineering tolerances.

ERA believes that the new process to be developed will fulfil these conditions and have a number of other advantages over existing coating methods. For example, it will prolong component life and will be suitable as a conformal coating for complex shapes. In addition, it will provide improved control over film composition and microstructure, reduce the need for substrate heating and facilitate higher pressure (low vacuum) operation.

ERA has many years' experience of forming thin films of refractory, inert, inorganic oxides that can be deliberately tailored to have a glassy microstructure. These layers prevent oxidation at temperatures up to at least 1,000°C and repel attack from most strong acids and other reagents. They are also mechanically robust and strain resistant.

ERA has also developed methods of coating irregularly shaped objects using similar processes. These yield dense, highly adherent thin films and do not involve harsh treatment of the surfaces prior to coating.

ERA's process will combine the best features of both areas of expertise. It will be based on the vapour deposition technique of ion plating which traditionally involves evaporating a flux of coating material into a glow discharge plasma around the object to be coated and scattering the molecules to give a fairly uniform covering. The technique is fast, has good "throwing power" and gives excellent film adhesion because when the plasma is used to clean the surface it combines with the coating. However, the disadvantages of the traditional process are that its usefulness is almost entirely limited to coating metals, it generates heat and is difficult to control precisely.

Special techniques

The process which ERA intends to develop will incorporate special radio frequency techniques to increase efficiency, reduce heating, improve control and allow electrical insulators to be sputtered. The entire process will operate at a fairly low vacuum in order to avoid the need for costly pumps and pump-down times. Special service geometries will be used to allow a wide range of differently shaped objects to be coated at a fast rate.

During the project, a variety of different shapes and sizes of object will be coated with glassy inorganic oxide films and then tested for their resistance to elevated temperatures, corrosion and erosion.

The new process will address a number of industrial problems. It will not only help to improve corrosion resistance within the chemical industry, but will provide better coatings for automotive and aerospace applications and erosion resistant components for the textile industry. [Details: ERA Technology Ltd., Cleeve Road, Leatherhead, Surrey, KT22 7SA. Fax: 037 237 4496.] (Source: ERA Technology News, March 1991)

* * * * *

Surface hardening with pure nitrogen

Nitriding with pure nitrogen at high pressures and temperatures is effective for surface-hardening parts made of titanium, titanium alloy, and refractory metals.

Using equipment similar to that for hot isostatic pressing, the process subjects the parts to the gas for several hours at temperatures of 900-1,200°C and pressures as high as 29,000 psi. Once the parts have been loaded in the pressure vessel, it is evacuated of air, the nitrogen is introduced, and pressure is gradually increased by electric heating. Required temperature and pressure are held constant for 1-6 hours, then gradually reduced, and the parts are unloaded.

Nitriding time depends mainly on temperature, pressure, workpiece metal, and the dissociation of nitrogen at the workpiece surface. As for workpiece metals, titanium, titanium-alloy Ti-6Al-4V, and most refractory metals react quickly with pure nitrogen. That is not the case with steel and iron-based alloys, which is why HTM has discontinued tests with these metals.

To 1700 $HV_{0.025}$ for titanium

As indicated by the hardness-versus-nitriding-temperature curves, which pertain to a nitriding pressure of 14,500 psi, the $HV_{0.05}$ hardness of titanium increases from about 250 to 800-900 at nitriding temperatures in the range of 940-1,200°C. Case depths for nitriding temperatures of 940-1,060°C at the same pressure range from about 15-20 µm. Both hardness and case depth increase with increasing temperature. In terms of $HV_{0.025}$ hardness, values as high as 1700 have been achieved for both titanium and Ti-6Al-4V alloy, with case depths of 5-30 µm.

Such surface-hardness levels indicate substantial wear resistance for these relatively soft metals, which pose problems in surface hardening by other methods. Chemical vapour deposition cannot be used because of the detrimental reaction of hydrochloric acid and titanium. With physical vapour deposition, the hardened surface is too thin. And standard nitriding, as performed with cyanide salts, results in a brittle surface prone to cracking.

Case depth is governed by the length of time at pressure and temperature. Care is required, of course, to prevent grain growth and other undesirable structural changes. The change in structure from the case is more uniform for titanium than for Ti-6Al-4V, the presence of aluminium and vanadium inhibiting nitrogen concentration inward so that the alloy's core toughness is retained.

Because of the extremely hard surface layer, however, concerns naturally arise as to the effect of nitrogen on fatigue strength. In this regard, HTM tests indicate that the fatigue strength of nitrided Ti-6Al-4V is less than that of the base alloy at low cycles but approaches that of the base alloy at high cycles. At 2 X 10^7 cycles, for example, the fatigue strengths of the nitrided alloy and that of the base alloy are about the same.

This demonstrates that the nitrided case can withstand dynamic loads to a certain extent. This case does not tend to chip off, and it is apparently well-rooted so that stresses can be transmitted to the base alloy.

Of the refractory metals, chromium and molybdenum react quickly with nitrogen, surface hardness ($HV_{0.05}$) increasing to well over 1,500 with nitriding temperatures of 1,050-1,200°C and a pressure of 14,500 psi. In fact, maximum values of 1,800 and 2,500, respectively, have been achieved for these metals. For chromium, case depth increases substantially at nitriding temperatues above 1,060°C or so, from about 30 µm at 1,060°C to about 360 µm at 1,200°C. The case depth for molybdenum is much thinner, the nitrogen being more confined to the outer region.

The other refractory metals that were assessed harden to a lesser degree under these conditions. Zirconium exhibits a substantial hardness increase, tungsten the least. Columbium and tantalum require nitriding temperatures greater than 1,060°C to harden appreciably. Tantalum attains substantial case depths, the other metals thin case depths. Stoichiometric compounds of these metals have much greater hardness, indicating that nitriding under test conditions did not achieve maximum values. (Extracted from American Machinist, April 1990)

* * * * *

Rinse type surface treatment

Surface treatment coatings include iron oxide/phosphate, chromate/oxide, complex metal oxide and zinc phosphate.

Iron oxide/phosphate amorphous coatings are produced from an acidic solution containing phosphoric acid and alkali metal phosphates and various accelerators. They are used on cold rolled steel.

Chromate/oxide amorphous coatings are produced from an acidic solution containing chromic acid and accelerators and are used on zinc/aluminium alloy coated steel.

Complex metal oxide coatings are the most commonly used amorphous conversion coatings. They are used on hot dipped galvanized and electrogalvanized surfaces that are attacked by both acids and alkalis. The alkaline attack of the zinc surface initiates the reaction that produces a complex heavy metal oxide coating from a process solution containing heavy metals.

Zinc phosphate coatings on hot dipped galvanized and electrogalvanized material are crystalline and, as a consequence, are thicker than those previously mentioned. They also have higher corrosion resistance properties and are usually used on strip for domestic appliances. The process solution is acidic and contains phosphoric acid, zinc phosphate and accelerators. To control crystal size, it is necessary to activate the zinc surface with a crystal refining agent before it enters the zinc phosphate stage. This is done by adding the refining agent to an additional water rinse prior to the conversion coating stage. A recently developed phosphating process using a zinc-nickel phosphate base is presently being used and is receiving favourable reports for treating galvanized surfaces.

The amorphous conversion coatings need a final passivating rinse to achieve maximum corrosion resistance. Most lines use a chromic acid based process which produces large molecules of chromium chromate which fill any holes in the surface coating. A conversion in the surface coating of oxides to chromate also takes place which increases corrosion resistance.

All of these treatments can be applied by spray (typically at 40 psi) or a reaction cell. The cell is a simple, shallow tray, containing treatment solution through which the strip is passed in a contradirection to the pumped flow of the liquid. The purpose is to constantly present fresh liquid to the strip surface. It has an advantage over spray application because sludge is a by-product of some of the processes and spray nozzles are more susceptible to blockage and subsequent maintenance problems. This problem is still prevalent, even though steps are taken to continuously desludge the pumped circulation system. Plate coils heated by steam or hot water are usually used to heat the hot sections.

The alkaline cleaner and water of the rinse are conserved by counter flowing, to the strip direction, a controlled quantity of cleaner to cleaner, or rinse to rinse. A considerable water saving is achieved by using double rather than single rinses. The quantity of fresh water required to achieve a given contamination ratio across a single rinse is approximately the square of that required across a double-rinse stage.

The used chemicals and rinse waters are discharged to an effluent treatment plant. The degree of treatment required depends on the ultimate discharge limits imposed by the local authorities.

Nonrinse surface treatment

An effluent problem can be reduced by eliminating the conversion coating stages (spray or reaction trays) and also their associated water rinses and passivating rinse. This is possible by using a nonrinse surface treatment system.

This treatment is a multimetal process based on chromates which is usually applied by a two-roll horizontal chemical coater. It is similar in concept to the coaters later used to apply paint. It applies a precisely controlled quantity of aqueous solution to both sides of the strip. The water is then removed in a short oven, leaving a controlled dry coating film on the strip surfaces. There is 100 per cent usage of the process chemical and, hence, the effluent problem at this stage is eliminated. Cleaning/degreasing and its associated rinses are still necessary. Ideally, the use of chromate white rust protection of the incoming substrate should be avoided so that the design of the effluent treatment is not, unnecessarily, further complicated.

Increasing numbers of users are adopting the nonrinse surface treatment. (Extracted from Iron and Steel Engineer, October 1990)

* * * * *

Metal surface inroad disclosed

A new method of calculating how atoms and molecules interact when they are attached to metal surfaces, which holds potential importance to the future development of "designer catalysts" used in applications ranging from auto exhaust control devices to petrochemical processing was developed at the Sandia National Laboratories in Albuquerque, New Mexico, USA.

Molecular interactions on surfaces determine the efficiency of catalytic conversion of noxious gas in auto exhaust to acceptable ones and of catalytic synthesis of petrochemicals. They also are the key to corrosion inhibition and to hydrogen uptake by metals.

The new calculation differs from previous approaches since it does away with mathematical assumptions, such as assuming that a metal surface acts in the same way as a very small cluster of metal atoms.

Since these artifices distort the nature of the results in a way that is difficult to control, the new method represents an important improvement in the ability to predict the behaviour of atoms on surfaces.

Temperatures at which chemical reactions occur on solid surfaces must be below the solid's melting point, corresponding to rather small energies compared with typical chemical bond strengths. Therefore, researchers must try to predict and explain the small energy differences that correspond to different arrangements of surface atoms. (Extracted from American Metal Market, 24 January 1990)

* * * * *

Method of surface preparation of difficult-to-form metals

This method enables intensifying the process of plastic deformation of stainless steels, excluding the operations of intermediate annealing, performing deep drawing of sheets with the aim of producing flasks and other hollow articles. It makes it possible to use cold strain for producing articles from the difficult-to-form metal, for producing the fasteners from the stainless steel of the austenitic class by cold upsetting of heads and also for rolling thread in place of turning and hot upsetting.

Realized also is the multiple-pass plug drawing of pipes without intermediate heat treatment at high rate.

The preparation of the surface consists in preliminary application of the lubricant coating thereon. This enables reducing the number of operations in the deformation of the metals, increasing the metal utilization coefficient to 95-98 per cent, the drawing coefficient amounting to 0.32. [For information refer to: 123223, Moscow, USSR, Prospect Mira, VDNH. Tel.: 2815717; Telex: 411043, ZENIT SU; Fax: 1816231.]

* * * * *

Method of hardening surface of steel articles

This method is used for hardening the surface of tools and parts of machines. It enables considerable elongation of their service life and also replacement of the high-alloy steels by structural plain steels. This method is most effective for hardening the stamping tools and machine parts working under friction and abrasive wear conditions.

The process consists in applying a layer of iron-boron alloy having increased hardness on the surface of steel articles in the molten salt medium. The thickness of the layer, its structure and composition depend on the steel grade and conditions of obtaining the coating. The borating process is compatible with the warming-up process for heat treatment. The operating temperature of the process is equal to 850-950°C.

In comparison with the composition of the "Degussa AG" firm, the Soviet-made composition has some advantages. This analogue can be used for borating in the metal crucibles and it is impossible to use it in the salt electrode baths lined with refractory bricks since the melt interacts with the lining.

The melt used by the firm comprises sodium fluoride and barium chloride that are harmful substances and produce adverse effects on the health of the people. [For information refer to: 123223, Moscow, USSR, Prospect Mira, VDNH. Tel. 2815717; Telex: 411043, ZENIT SU; Fax: 1816231.]

* * * * *

Surface treatment smoothes the way

Tool life of tube-bending mandrels coated with Kro-lon surface treatment is extended 70 per cent over mandrels with standard chromium plating and 120 per cent over those made of aluminium bronze.

The patented in-house process, developed by Tools For Bending Inc., Denver USA, consists of impregnating a hard chromium surface with DuPont Teflon to form a hard and durable surface with a coefficient of friction one fifth that of a standard hard-chromium plating. The reduction in friction and antigalling properties are retained throughout the life of the coating, after which Kro-lon can be reapplied. Although developed for bending tools, the new coating can be applied to any size or shape of wearing surface. (Source: Advanced Materials & Processes, December 1989)

* * * * *

Silicone provides a coating in difficult-to-reach areas

The Metal Protective Coating is a dry, transparent, waxlike veneer of silicone material that is applied as a corrosion barrier and lubricating film to metal parts. The material protects ferrous substrates from rust, zinc-coated parts from white blister, and aluminium parts from effluorescence. This metal protector also has good creep properties, making it possible to treat hard-to-reach areas, such as folds, threaded holes, and sheet-metal overlaps. The product can be applied to clean, dry surfaces - without pretreatment by spray, dip or brush methods. [Dow Corning Corp., Midland, Michigan, USA.] (Source: Chemical Engineering, May 1991)

* * * * *

Aluminium-coated chip for steel processing

Sumitomo Electric has developed a new aluminium-coated Ace-Coat AC15, a general-purpose chip claimed to improve efficiency in a broad range of steel processing applications.

Coated chips comprise a superhard alloy base material and a film coating. Some characteristics of conventional base materials seem to inhibit cutting performance. Specifically, soft base materials do not chip easily, but suffer from wear, while hard base materials are more wear-resistant, but chip more easily. Researchers say these problems were resolved by developing the Ace-Coat series chips which incorporate a base material that is softer on the surface and harder towards the centre. The latest addition to the series, Ace-Coat 15, was developed with the use of new technology to control alloy composition. The composition of the base material of the Ace-Coat 15 gradually changes from the surface to the inside, resulting in an even softer surface and a harder core.

Ace-Coat 15 has the same wear-resistance yet far higher chip-resistance than conventional products. These features make it suitable for steel processing applications in areas ranging from fine to rough cutting, and for improving processing efficiency. Because it can be applied to inserts with highly economical groove type chip breakers, it is stated to help lower production costs. [Sumitomo Electric Industries Ltd., Public Relations Section, 5-33 Kitahama 4-Chome, Chuo-ku, Osaka 541, Japan. Tel.: (06) 220-4119. Fax: 222-3380 or Hard-metal Division, Fax: (0727) 71-0088.] (Source: New Materials World, February 1990)

* * * * *

Cr + N_2 beats Cr or N_2 alone

Both hard-chromium plating and ion implantation of nitrogen can prolong the life of tools, dies, moulds and parts subject to wear. Combine the two, that is, implant the nitrogen in the chromium, and the benefits can be greater still.

The nitrogen seals microcracks in the chromium and, also, forms hard chromium nitrides, increasing wear and corrosion resistance. Lubricity is also enhanced, increasing resistance to galling.

The life of draw punches made of A2 and D2 tool steel and used to form casings of rocket and shell grenades from 0.125-in.-thick 4140 hot-rolled steel increased from 10,000-12,000 parts to 60,000 with nitrogen implantation alone, and to 120,000 after plating and the nitrogen treatment. Combining the treatments also increased the life of the coining punches used in this application, from 12,000 to 40,000 parts, or more than that provided by titanium-nitride coating.

For moulds and mould elements, gains have been quite startling. Sprue bushings made of P20 tool steel and used in an injection mould for a 20 per cent-glass-reinforced-polyester auto part, had to be replated every 2,500 parts. After the double treatment, the bushings were good for a run of some 55,000 parts.

And in the case of rubber-mold cavities made of A2 tool steel and used to compression-mould fluorocarbon valve seals, parts count between cleanings required for good mould release went from a few hundred to about 100,000.

* * * * *

Surface treating with sunbeams

Solar energy is being developed as a direct heat source for surface hardening, cladding, and other applications.

Sunlight has been studied for years as a relatively low-cost, clean energy source for bulk processing of materials. Today, however, it is believed that the greatest potential for solar energy in materials processing may lie in surface modification via use of a concentrated (1 MW/m^2 minimum), directed energy beam. This budding "solar-furnace" technology, called solar-induced surface transformation of materials (SISTM), would compete with other directed-energy methods such as ion-, laser-, and electron-beam processing. Potential applications include transformation hardening of steel, cladding/coating, self-propagating high-temperature synthesis, thin-film deposition, and processing of electronic materials.

Advantages of solar processing

Materials processing is energy intensive, and often requires multiple conversions of resources. Conventional surface-heating methods, for example, require the conversion of chemical energy (fossil fuels) to heat, heat to electricity, and electricity back to heat. Some methods require an additional step of converting electricity to a form of radiant energy that can be applied to the surface of the material. In conventional processing, generation and transmission losses account for a substantial amount of the original energy resource and can contribute significantly to operating costs. There also are environmental considerations associated with producing energy from fossil fuels. These liabilities can largely be overcome in surface-treating applications by processing in a solar furnace.

All solar furnaces direct the sun's radiation to a focus. Flexibility is provided by varying system optics. For example, the beam pattern can be altered to accommodate irregular part shapes, focal lengths can be adjusted to reduce damage to optical elements by sputtering or outgassing of target materials, and the configuration of the secondary concentrator can be chosen to provide the flux range most suitable for a particular application. Solar radiation can be concentrated to about 16 MW/m^2 with a single imaging concentrator, and to 100 MW/m^2 non-imaging concentrators in media having an index of refraction larger than one. Scaling up to very large power levels also is possible. In general, SISTM processes are inherently clean and efficient, there is no need for auxiliary cooling at the optical source, and reaction chambers can be of "cold-wall" design.

SISTM uses terrestrial solar radiation, which basically covers the wavelength spectrum from the near ultraviolet (about 305 nm), through the visible (700 nm max), and into the near infrared (about 2.500 nm). Because many materials absorb visible radiation better than infrared radiation, they often can be efficiently solar processed without the use of special coatings or other techniques. Concentrated sunlight impinging upon the surface of a low-thermal-diffusivity material causes extremely rapid heating. For example, it takes just 0.014 seconds at an absorbed flux of 20 MW/m^2 to heat the surface of a silica (SiO_2) sample to its melting point of 1,720°C (3,130°F). Surface heating is so rapid that the bulk of the sample does not reach the melting temperature.

Transformation hardening of steel

Steels containing 0.4 to 1.2 per cent C are transformation hardened by heating to above the austenite transformation temperature (about 720°C, or 1,300°F) and then rapidly quenching to form martensite. Often, a hard, wear-resistant surface layer surrounding a softer, tougher core is sought. To achieve this goal, it is necessary to preferentially heat the surface using a method such as flame, induction, or laser-beam heating. The relatively recent adoption by the automotive industry of laser transformation hardening for engine and other drive-train components has helped encourage the development of data on solar hardening of steel. Experimental confirmation that steel can be surface hardened using concentrated solar radiation, combined with a favourable economic comparison between a laser and a solar furnace, provide strong evidence that SISTM can compete with conventional methods.

Researchers in China, the Soviet Union, and the United States have studied surface hardening by solar energy for seven years. The Chinese, for example, are using a solar furnace with a 1.56 m (61 in.) in diameter parabolic concentrator having a focal length of 663 mm (26 in.) and a 6.2 mm (0.25 in.) in diameter image at the focal point. A calculated peak flux of 30 MW/m^2 and a maximum temperature of about 3,000°C (5,430°F), which is high enough to melt zirconium diboride (ZrB_2), are reported. When a steel plate was exposed to this flux, a hardened spot almost 5 mm (0.2 in.) in diameter was obtained after a 1 second exposure. Its microstructure was fully martensitic. Longer exposures enlarged and deepened the hardened region. They also coated the surface of some samples with carbon to increase the rate of heat absorpotion, and they used a scanning process to harden relatively complex surfaces, such as the cutting edges of reamers and drill bits.

Transformation hardening of steels also has been studied using the small furnace at Sandia National Laboratories, Albuquerque, New Mexico. Samples of AISI 4340 steel measuring 610 X 150 X 13 mm (24 X 6 X 0.5 in.) were mounted in frames, which were clamped to a positioning table. During solar-beam treating in air, the sample was translated in the z-direction to obtain a strip of hardened material. The translation rate was held constant while the incident solar flux was varied as a linear function of position. Disks of 4,340, measuring 50 mm in diameter X 1.6 mm thick (2 X 0.06 in.), also were exposed to the solar beam after being mounted in a steel holder that could be cooled by either forced water or air. In addition, 90 mm in diameter X 6.4 mm thick (3.5 X 0.25 in.) samples of a nitriding steel were exposed to the solar beam in a controlled atmosphere of nitrogen or argon. These samples were water-cooled on their back sides to increase the temperature gradient and to decrease quenching time.

Selective hardening of 4,340 occurred at a solar flux of about 2 MW/m^2 and a scan speed of about 0.5 mm/sec (0.02 in./sec). The fully hardened region is 1 to 2 mm (0.04 to 0.08 in.) deep and approximately 20 mm (0.8 in.) in diameter, with a heat-affected zone extending for another 4 to 5 mm (0.15 to 0.20 in.) into the plate. Hardness decreases smoothly from fully hardened to unhardened. Mathematical models of the process indicate that scan rate can be increased and depth of hardening can be reduced by increasing the solar-beam intensity by a factor of five. The shape of the hardened region mimics the Gaussian distribution of the incident flux. A flat beam, however, would be expected to produce a more uniform hardened region. Modelling work at the Solar Energy Research Institute (SERI), Golden, Colorado, has demonstrated that solar furnaces can be modified to provide a flatter beam.

The nitriding-steel disk samples were exposed to solar fluxes up to 1.85 MW/m^2. Nonuniform hardening occurred. The treated layer consists of fully hardened dendrites extending for 2 mm (0.08 in.) into the specimen. The interdendritic regions are partially hardened. By using a more intense solar beam to raise the surface temperature, it may be possible to produce a completely hardened surface region in the nitriding steel.

Post-treating of films and coatings

Coatings applied by methods such as plasma spraying and shock cladding often must be post-treated to improve their adherence to the substrate, to eliminate or reduce porosity, and/or to promote solid-state reactions that form specific beneficial microstructures. Post-coating applications for solar energy that have been explored include melting and fusing of slip (or slurry) coatings, melting or fusing of powders applied by other techniques, densification of plasma-sprayed coatings, reaction of layered materials to form ordered intermetallic compounds, and reaction of plasma-sprayed coatings.

Preplaced powders

Soviet scientists have demonstrated that TiC-Ni-B and WC-Ni-B powders entrained in slips can be melted onto steel and titanium-alloy substrates in a solar furnace. The fine powders are strong absorbers of solar radiation, which helps increase process efficiency. A 2 m (6.6 ft) in diameter solar furnace was used to expose samples to solar fluxes of 6 to 12 MW/m^2. The wear- and corrosion-resistant diffusion coatings that resulted are 50 to 150 μm (0.002 to 0.006 in.) thick, and have satisfactory surface quality, good density, and good bond strength between coating and substrate. SERI's work in this area is intended to expand on the Soviet experiment, which was considered a proof-of-concept demonstration. In one experiment, layers of several different alloy powders were clad onto AISI 4340 alloy steel and 1040 carbon steel. The powders were first impregnated with a solution of poly(methyl-methacrylate), or PMMA, dissolved in methyl ethyl ketone (MEK). Fluxes of about 1 MW/m^2 were found to produce the best coatings. The solar-melted powders form dense coatings and excellent metallurgical bonds with the substrate X-ray studies confirm that the coatings contain the required metallic and intermetallic compounds.

The results of our studies and those in the Soviet Union suggest other potential coating applications of solar energy, such as post-treating of heat-dissipating coatings for high-temperature systems in the metals, refractories, aerospace, and other industries. Candidate coating materials have high thermal emissivities, and include SiC, SiB_4, and $MoSi_2$. In the aerospace industry, for example, carbon/carbon (C/C) composites are used for heat shields on the space shuttle's nose cap and wing leading edges, and are being considered for exhaust nozzles and other aircraft gas-turbine engine parts. High heat dissipation and decreased oxidation are important considerations in C/C applications. Consequently, much attention is being paid to silicon-base coatings such as SiC (high thermal emissivity) and SiO_2 (high oxidation resistance). In one instance, slurries of aluminium and silicon powders in a nitro-cellulose lacquer vehicle have been fused onto carbon by heating in a conventional furnace for as long as two hours at temperatures near 1,300°C (2,370°F). Problems noted include vaporization of aluminium, porosity in the coating, and thinning of the coating due to infiltration into pores in the C/C substrate. Use of SISTM to post-process the coatings may offer a solution to these problems. Similar coatings also are being studied for use on an aero-assisted orbital transfer vehicle. Concentrated solar energy has been used to react layered Si_3N_4-C and BN-C systems to form SiC and B_4C between the layers, demonstrating the feasibility of this approach.

Exothermic reactions

Some powder mixtures react with a release of energy. Once started, the exothermic reaction becomes self-sustaining and propagates through the mixture. The process, which is called self-propagating high-temperature synthesis (SHS), can be initiated in a solar furnace. During SHS, the powder mixture's heat of reaction supplements the heat provided by the solar beam, enabling temperatures to rise as high as the melting points of refractory metals and ceramics. This suggests that SISTM-based SHS methods could be used to apply innovative ceramic coatings.

Thermal spray

Plasma- and flame-sprayed coatings are widely used to protect metal components. However, these coatings often contain porosity that adversely affects corrosion resistance and can serve as crack-initiation sites and crack-propagation paths. Laser post-treatment of thermal-sprayed coatings has had some success, but poses a cracking problem of its own. Preliminary studies of the use of solar-beam treating have yielded encouraging results.

PVD films

Physical vapour-deposition (PVD) methods can be used to produce films of selected materials on various substrates. Subsequent heating of these thin layers creates the required coating, either by solid-state diffusion and reaction or by melting and liquid diffusion and reaction. One application is the formation of compound semiconductor films by direct synthesis from layers of the constituent elements that have been deposited on insulator substrates. Laser radiation is a typical energy source for the process. The small spot size of the focused laser beam enables the melting of only small portions of the sample at a time. This is a useful feature for producing electronic devices, but makes the laser hard to justify for treating larger, structural parts. A solar furnace with its high level of deliverable energy and relatively wide spot diameter may prove to be a more efficient alternative for these applications.

The formation of nickel aluminides by solar-beam treating of various combinations of aluminium and nickel layers applied by sputtering (a PVD method) also is being studied at SERI. A solar-based diffusion-bonding/SHS method is used. In one experiment, the nickel and aluminium layers were sputtered onto 4340 steel and pure-iron targets using a dc magnetron-sputtering unit. The outer layers were aluminium to increase oxidation resistance during the test; however, the metal's high reflectance reduced the efficiency of energy transfer. A surface coating of carbon helped reduce exposure time. The reactions were tracked using optical pyrometry, and by visual monitoring of the sample surface with a remote video system. X-ray diffraction studies of samples exposed to solar radiation demonstrate conclusively that SISTM can be used to form these compounds.

Electronic-materials processing

The electronics industry has developed sophisticated surface-modification techniques. Among those being considered for SISTM applications are chemical vapour deposition (CVD) and its variations, rapid thermal annealing (RTA), and zone-melting recrystallization (ZMR).

CVD

In chemical vapour deposition, coatings are formed on nearby surfaces via chemical reactions among various gaseous species. All reactions are initiated by heat and/or light. CVD reactors can be of either hot- or cold-wall design. Hot-wall reactors can be visualized as furnaces that have been modified to allow for the passage of reactant gases. These systems are inefficient because chemical reactions occur on other heated surfaces in addition to the sample. Cold-wall units, on the other hand, concentrate the reaction activation energy on or near the surface to be coated by using induction heating or radiant energy supplied by sources such as lasers and arc lamps. Solar furnaces fitted with reaction chambers also make very good cold-wall CVD reactor systems. The sun's radiant energy can easily be controlled to deliver prescribed amounts of heat for predetermined times. Production of TiN, TiB_2, SiC, and hard carbon films using a solar furnace is being explored. An early conclusion is that relatively small solar fluxes are sufficient to produce CVD films.

The solar furnace also may be used for rapid thermal-chemical vapour deposition (RTCVD), a process that conventionally combines radiant-heating lamps with a CVD chamber to deposit thin films in very short times. RTCVD systems are being developed by the electronics industry for the production of high-quality films of silicon, SiC, Si_3N_4, and other materials.

RTA

Semiconductor manufacturers like ion implantation because of its ability to precisely control dopant profiles. However, the process also causes damage to the crystal. The defects introduced by ion implantation traditionally are annealed out in furnaces by heating for 15 to 30 minutes at temperatures of 900 to 1,200°C (1,650 to 2,190°F) for silicon, and 800 to 1,000°C (1,470 to 1,830°F) for GaAs. Unfortunately, these time-temperature conditions can cause extensive redistribution of the implanted dopants, which makes it difficult to fabricate shallow junctions and small devices for very-large-scale-integration (VLSI) circuits. To reduce heating time, three transient-annealing techniques have been developed: pulsed laser or electron beam, scanned laser or electron beam, and rapid thermal annealing (RTA) with incoherent light. The RTA method, which is the best of the three, uses radiant-heat sources such as tungsten-halogen lamps and annealing times of 1 to 10 seconds. The conditions for successful RTA are very similar to those found in the high-flux region of a solar furnace.

SERI's solar furnace also is being used to produce films of high-temperature superconductors on substrates such as $SrTiO_3$, ZrO_2, and MgO. The films are produced by metal-organic deposition and then RTA-processed in a solar furnace to produce the superconducting phase.

ZMR

Graphite heaters or lamps are used to scan across multilayer coatings on substrates such as silicon, germanium, or sapphire. The heating of an intervening layer, usually a fine-grained silicon film, causes it to slowly recrystallize. A typical scan rate is 1 mm/sec (0.04 in./sec). This technique, called zone-melting recrystallization (ZMR), creates large-area films that may provide excellent substrates for epitaxial growth of GaAs. It may be possible to use solar energy as the heat source. [Article written by James T. Stanley, Clark L. Fields, and J. Roland Pitts, Solar Energy Research Institute, Golden, Colorado.] (Source: Advanced Materials & Processes, December 1990)

* * * * *

Sample chambers

SERI researchers have designed a variety of sample chambers and related equipment specifically for materials processing using a concentrated solar beam. Among the SERI-built sample chambers are designs for maximizing temperature gradients by cooling the back side of the sample with forced air or water, and chambers that allow use of controlled atmospheres. The most sophisticated chamber to date includes a four-gas mass-flow control system, and a residual-gas analyser for reaction diagnostics.

Other features of SERI's solar-furnace facility include long-focal-length primary mirrors that enhance flexibility in choosing experiment size and orientation; remote video monitors with colour cameras for flux mapping and real-time viewing of the target zone; more than 100 channels for data acquisition from thermocouples, pyrometers, weather instruments, and incident-sunlight monitors; and an x-y-z platform for translating specimens. Recent acquisitions include an optical-laser pyrometer to measure and control sample surface temperature, and a nonimaging secondary concentrator that has produced peak fluxes higher than 20 MW/m^2. On SERI's shopping list are a turning mirror to redirect the solar beam onto horizontal surfaces, a lower-power laser-alignment system, and a refractive, nonimaging secondary concentrator that will push peak flux past the 50 MW/m^2 mark.

Some high-flux solar facilities

Location	Total Power, kW	Peak Flux, MW/m^2
Albuquerque, N. Mex		
CRTF[1]	5,000	2.4
Furnace	22	3.0
Atlanta, Ga		
Furnace	1.3	9.5
Golden, Colo	10	2.5 20[2]
White Sands, N. Mex	30	3.6
Odeillo, France		
Horizontal furnace	1,000	16.0
Vertical furnace	6.5	15.0
Rehovot, Israel		
CRRF[3]	2,900	-
Furnace	16	11.0
Uzbek, USSR	1,000	17.0

[1]Central Receiver Test Facility [2]Measured using nonimaging secondary concentrator [3]Central Receiver Research Facility

(Extracted from Advanced Materials & Processes, December 1990)

* * * * *

Electrochemical surface treatment of carbon fibres

The role of the interface in composite integrity is of considerable importance. The transmission of stress between fibre and matrix depends on a strong interfacial bond which resists failure. The poor shear strength of carbon fibre reinforced polymer is generally attributed to a lack of bonding between the matrix and the filaments.

Extensive work has been devoted to surface treatments of carbon fibres in order to improve their bonding to the resins. Surface treatments that improve the ILSS of carbon fibre composites by a factor of two to three are available. These include wet and dry oxidation, application of organic or inorganic coatings, whiskering and irradiation. The most effective surface treatment besides whiskerization is the liquid-phase oxidation, i.e. anodic oxidation.

Investigators have correlated changes in the interfacial bonding strength with changes in the area, functionality, roughness and wettability of the fibre surface. Some of them concluded that surface chemical functionality played a more significant role than surface area with regard to shear strength. They explained it by: improving wetting characteristics of carbon fibres; formation of chemical bonds between matrix functional groups and fibre active sites as well as fibre functional groups.

- The most common industrially practical anodic oxidations of carbon fibres are in aqueous electrolytic baths containing acids (such as HNO_3, H_2SO_4), strong bases (such as NaOH) and salts like NH_4HCO_3, NaOCI.

- As a result of the treatment the carbon fibre surface is covered with oxygen containing functional groups and the surface area is increased. Four oxide species have been identified: strongly acidic carboxylic acid, weakly acidic carboxylic acid, phenolic hydroxyl and carbonyl. The carboxylic acid functional groups have the biggest contribution for improvement of the shear strength of a composite.

- The nature of the electrolyte, the pH of the solution, the polarization potential, the reaction time and the electrolyte concentration have significant effects on the type of functional groups, on their amount and on the morphology of the fibres' surface. Acidic solutions (such as nitric acid) give rise to substantial surface oxidation while alkaline solutions lead to less surface oxidation. Electrolytes which tend to release carbon dioxide during electrolysis, such as salts containing bicarbonate or strong bases, inhibit the oxidation of the fibres by forming an envelope of carbon dioxide around the fibres. Increasing the polarization potential, reaction time, or solution concentration causes oxidation to increase considerably. Anodic oxidation leads to topological changes. For example, treatment with nitric acid causes splits or pits along the fibre axis while oxidation in sodium hydroxide forms circular holes on the fibre surface.

- Oxidized carbon fibres, particularly fibres oxidized by nitric acid, lose surface functionality when they are heated. The main weight loss is realized in all cases between 300° and 500°C due to the evolution of carbon dioxide that comes from decomposition of carboxyl groups; additional weight loss above 600°C occurs due to the evolution of carbon monoxide. This suggests that the oxygen on carbon fibre surfaces is present in the form of different functional groups with varying thermal stabilities.

Conclusions

In this research on electrochemical surface treatment of carbon fibres, it was shown that:

1. Anodic oxidation with ammonium nitrate solution changes the surface functionality of the carbon fibres effectively.

2. Ten minutes' treatment is sufficient to get uniformity in oxygen pick-up across the fibre bundle.

3. The functional groups which were added to the surface during the oxidation treatment are hydroxylic and carboxylic groups.

4. No change in surface morphology or mechanical properties of the fibres was realized.

5. The oxygen content on the surface of the fibre remains stable even after exposing them to high temperature. [Excerpts from the 36th International SAMPE Symposium, 15-18 April 1991; Article written by: Aharon Moshonov, Hong Li and John D. Muzzy, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100.]

* * * * *

Painting the town green

To reduce the health and environmental problems associated with surface coatings, industries have been moving towards high-solids formulations, more benign solvents, water-based products and the replacement of toxic additives.

Traditional alkyd paints rely on metal soaps as driers to achieve crosslinking of high molecular weight fatty acids through atmospheric autoxidation. To produce high-solids products, low molecular weight polymers must be used to keep the viscosity of the paint down.

Rhône-Poulenc, UK, describes a new application for aluminium organics in decorative paint. The cross-over of aluminium organic crosslinkers from industrial coatings to the decorative market has been forced by regulations of the type seen in California, where volatile organic compounds (VOCs) in architectural coatings must constitute less than 250 g/litre of product.

Aluminium organics act as the "driers" in these high-solids formulations forming covalent linkages from autoxidation reactions, plus covalent and coordination bonding through the aluminium atoms. This "second tier" of cross linking gives greater hardness and durability.

The use of the modified resins makes possible the formulation of decorative paints with up to 90 per cent solids and similar rheological properties to commercially available gloss paint. Cobalt, calcium, zirconium and lithium organics will be considered increasingly important as the industry moves away from lead and barium. Rhône-Poulenc is now developing water repellents for wood based on zirconium technology and containing almost no VOCs.

Binary polymer systems where one polymer is emulsified and another present in the continuous phase, or where different polymers are present in a core/shell arrangement, are being developed for water-based paints.

Water-borne basecoats for the automotive industry have been introduced in all General Motors plants in Western Europe, and VW and Volvo have also implemented their use at some plants. Although problems still exist in producing water-borne clear topcoats for cars, the technology is now at a pilot stage and trial production lines will be set up in 1992.

Traditional solid colour paint for the average car releases into the atmosphere about 30 g of solvent per square metre of surface covered. Metallic car finishes release around 55 g/m^2. Dietor Plath of Hoechst calculated that water-borne systems could reduce these to 17 and 22 g/m^2, respectively, representing reduction in VOC emissions to German air of over 10,500 t/a. (Extracted from Chemistry & Industry, 15 October 1990)

* * * * *

New material for antistatic paint developed

An electrically conductive composite material of potassium titanate and tin oxide for application as antistatic paint on automobiles and for other industrial uses has been commercially developed by Otsuka Chemical Co., Osaka, Japan, and the Research Institute for Production Development in Kyoto under a commission from the Government's Research and Development Corporation.

The new material is fibreform potassium titanade, as fine as 10 to 20 microns, that is coated with tin oxide. The composite comes in powder form.

The white colour of the conductive material is both unusual and beneficial. Previously available conductive composites using carbon black, metals and other conductive materials were heavily coloured, making their colouration difficult in commercial applications, officials of the Government corporation explained.

Also important is the high strength of the white-coloured potassium titanate, which reinforces the transparent tin oxide. The new composite excels in strength and conductivity as well as in colouration.

The powdered composite material can be mixed with pigments to make electrically conductive paint or used in sheet form in electronic and other advanced materials areas.

In the newly developed process, tin chloride and antimony chloride, after hydrolysis, are applied to fibreform potassium titanate. Then the film-covered potassium titanate powder is baked at high temperatues so that the film turns into a conductive oxide of uniform quality.

The new material will have immediate applications not only in antistatic paint but in housings for electronic equipment and antistatic flooring material for clean rooms, among others. (Extracted from American Metal Market, 31 October 1990)

* * * * *

Surface treatment flying high

Leading aerospace components manufacturer, Aero Structures Hamble Ltd., Southampton, says surface treatment specialist, Abrasive Developments, has helped revolutionize the company's vital paint stripping processes, used in new and refurbished structures for aircraft manufacturers.

Aero Structures uses an Abrasive Developments dry blast cabinet to strip paint from a huge range of military and civil aircraft components.

The 1.5 metre Jupiter machine with JP plastic media recovery system has replaced a laborious and hazardous all-day chemical soaking process which was followed by several hours of hand-scraping.

The company reports that the process is now cleaner, quicker and more efficient, and provides excellent surface finishes. (Source: Metals, Industry News, Vol. 7, No. 2, June 1990)

* * * * *

Below are listed two achievements, inter alia, done by Science and Technology of Shandong Academy, Keyuan Road, Jinan, People's Republic of China.
Tel.: 615102 - 637/620; Eip: 250014.

(1) Adhesive M-876 for heat-shrinkable materials

Heat-shrinkable materials coated with this adhesive are used to bond and seal welded joints of the anticorrosive pipelines which are wrapped with polyethylene plastics to transport petroleum and gases. They are also used to bond and seal joints of electric cable. This adhesive is ideal for bonding polyethylene and polypropylene plastics.

Features and specifications: The product has strong adhesion, high heat and cold resistance and good resistivity against acid, alkali or salt.

- Shear strength (HDPE/HDPE, 20°C)>1.3 MPa;
- Peel strength (HDPE/Heat-shrinkable materials, 20°C)>45 N/cm;
- Peel strength (HDPE/Heat-shrinkable materials, -35°C)>45 N/cm.

(2) Thermostable Polyolefine Hot Melt Adhesives

Features and uses

This adhesive has strong adhesion, high heat and cold resistance, good resistivity to acid, alkali and salt, good thermostability and wide range of service temperature. The difficult adhesion materials of low surface energy (polyethylene, polypropylene) can be bonded easily and efficiently without any special treatment on their surfaces. This adhesive has been successfully used to join polyethylene on steel pipeline in the field of petroleum transportation to improve corrosion resistance. It can also be applied to self-adhesion of PE or PP plastic, adhesion of polypropylene composite weave, polyurethane foam, wood, paper, in wide range of petroleum, chemical industry, electronics, packaging and daily life etc.

Specifications

1. Outward appearance: orange massive solid.

2. Ring and ball softening point: 135-145°C.

3. Bond strength:

   HDPE sheet/steel - shear strength (20°C)>1.5 MPa;

   HDPE film/steel - 180° peel strength (20°C)>30 N/cm.

* * * * *

Foaming coating for sheet steel

Researchers have developed a "post-foaming adhesive sheet" which foams during heating and can be applied as a protective coating to sheet steel. Steel coated with the new material is expected to find applications in the production of automobiles and electric appliances. The foaming sheets are composed of: (1) a special foaming agent that uniformly expands rubber to more than 10 times its original volume; (2) a tackiness agent that reacts with the rubber to impart adhesive properties; and (3) a weather-resistant ethylene-propylene terpolymer (EPT) rubber. With use of an oiling agent, the tackiness can be further improved, allowing the sheets to be used on sheet steel which will be coated with rust-preventative oil during automobile production.

During application, the sheets are first bonded to steel plates, and then foamed in an oven. By controlling the foaming temperature and the area, thickness, and shape of the sheets, the sheets can be formed into various shapes to meet the user's specifications. The sheets are reported to have the following properties: (1) a bonding strength of 1 kg/cm^2; (2) a service life of over 10 years based on UV-based weatherability tests; (3) adequate heat resistance based on tests in which the sheets retained 80 per cent of their adhesive and foaming properties when heated at 100°C for 1 month; and (4) vibration damping properties.

Compared with other techniques in which resins are sandwiched between steel sheets, the use of the foaming sheets is claimed to result in labour cost savings and production at half the cost. The foam can be activated at 160-200°C, and used for filling in gaps between the components of electric home appliances. [Nitto Denko Corporation, 1-1-2 Shimohozumi, Ibaraki City, Osaka Pref. 567, Japan. Tel: 0726-22-2981, Telex: 5332339; Fax: 0726-26-1505.] (Source: New Materials World, February 1990)

* * * * *

Acrylic surface mount adhesive

BP Chemicals, UK has developed a new surface mount adhesive for the electronics industry. Named SMD Adhesive 881, the product is a fast curing flexible acrylic adhesive for bonding surface mounted devices to printed circuit boards. The acrylic adhesive combines the advantages of products already available on the market. It offers dot application reproducibility - an essential feature in an industry which routinely lays down adhesive at the rate of 200 dots per minute. The product, an orange UV or thermally cured acrylic adhesive, is a thixotropic material with a flash point greater than 100°C which can be used on circuit boards populated with all types of components. On a board using only melf components, the adhesive provides a good cure with UV light of high intensity (80 mW/cm^2 and heat (three minutes at 120°C). Using heat alone, melf components can be cured in three-five minutes at 120°-150°. For circuits with flat chips only, best results are obtained from heating for three minutes at 150°C or five minutes at 120°C. All the stated times are exclusive of heat-up rate. According to the company, surface mount devices cured by these methods have a push-off strength in excess of 2 kg. [BP Chemicals Limited, International Information Centre, BP/18, PO Box 6, Bradmore, Nottingham, NG11 6PE.] (Source: Popular Plastics, November 1990)

* * * * *

EC adhesives programme

Adhesives are widely used in manufacturing industries in the US, Japan and elsewhere, but only to a limited extent in Europe, though there is a rapidly growing awareness here of the potential benefits of adhesive technology - not just as alternatives to welding and soldering, but also as complementary techniques which open new possibilities.

There are at present no commercially independent technical centres in the European Community dealing primarily or exclusively with adhesive bonding. This contrasts sharply with the situation in welding technology. Work on adhesives technology tends to be in university departments or in small sections of larger organizations. Few, if any, of such organizations, have the capability and organization to provide the required multidisciplinary based assistance to SMEs.

Against this background the EC Commission has given support within its SPRINT programme to establish a network within the EC which would catalyze the acceptance of adhesive technology by industry, with particular reference to SMEs. This network has already taken shape, and is called REACOL (Reseau européen pour l'assemblage par collage), but the project objectives may take four years to realize. In the first year of the project, which began in early 1990, six countries are participating: UK/The Welding Institute (project co-ordinator); France/Centre Technique de Region Aquitaine (CETRA); Spain/INASMET, Centro Technologia de Materiales; Belgium/CRIF (Matières Plastiques); Portugal/Instituto de la Soldadura; and Ireland/EOLAS.

It is the intention to involve other Community countries on a gradual basis over the four-year project period. At present there are no fixed views on how REACOL will evolve. However, its main aims are:

- To improve the EC's competitive position in industrial manufacture by increasing the rate of acceptance and diffusion of adhesives technology into European industry;
- To provide a network;
- To improve the effectiveness and scope of methods to promote and diffuse information on the opportunities presented by adhesives technology, particularly to SMEs;
- To provide a mechanism for technology and information exchange between specialists and specialist organizations within the EC;
- To initiate and pursue, in appropriate cases, collaborative or coordinative action to establish interfaces with sources of information and data, such as research institutes, universities and industrial laboratories. (Source: Technology Ireland, July/August 1990)

* * * * *

Yttrium-oxide coatings

Zyp Coatings Inc., Oak Ridge, Tennessee USA, introduces three yttirum-oxide formulations for use in titanium-processing applications including high-temperature lubrication for superplastic forming titanium sheet; anti-stick coating during diffusion bonding and hot-press decanning; braze stop-off and weld-spatter release; and core, crucible, and mould coating for titanium melting and casting. Formulations are available for use in all atmospheres to temperatures above 2,000°C (3,630°F). (Source: Advanced Materials and Processes, July 1991)

* * * * *

Sealants and coatings

UV-curing products for bonding, coating, potting, and sealing applications are photo-initiated and cure when exposed to ultraviolet light with/without heat. Products can exhibit a variety of cured properties such as specific substrate adhesion, durability, optical clarity, and chemical and moisture resistance. Range of physical properties and process options include viscosity, thixotropy (sag resistance), and cure conditions. [Emerson & Cuming Inc., 77 Dragon Court, Woburn, Massachusetts 01888, USA.] (Source: Machine Design, 25 July 1991)

* * * * *

Polyimide coating

The Ultradel 1414 coating protects the underlying interconnect system and microcircuitry against moisture, particulate and mechanical damage during wafer handling and assembly operations. Ultradel's low modulus provides significant stress relief for die in overmoulded plastic packages and can increase the life of the device. By relieving film stress during cure - 200°-300°C - the Ultradel coatings have substantially lower levels of residual stress built into the cured film. The coatings are self-priming and adhere to either ceramic or silicon substrates using standard coating techniques. [Amoco Chemical Co., Chicago, Illinois, USA.] (Source: Semiconductor International, July 1991)

* * * * *

New coating system features low VOC emissions

Formulated by crosslinking an acrylic solvent-borne polyhydric alcohol (polyol) with polyisocyanates, this polyurethane coating system offers protection from corrosion and harsh chemicals. Compared to the current level of 3.5 lb/gal of volatile organic compound (VOC) emission from coatings used in chemical and marine environments, this coating material boasts VOC levels ranging from 2.8 lb/gal down to 2.08 lb/gal. In addition to providing abrasion resistance and low-temperature curing, the product is resistant to downglossing and disclouration. [Mobay Corp., Pittsburgh, Pennsylvania, USA.] (Source: Chemical Engineering, May 1991)

* * * * *

PTFE coating service

PROCESSOO engineers manufacture glass-lined vessel spares with MS/CI-PTFE coatings. According to the company, the PFTE coatings offer better replacement of glass, lead, exotic metals and rubber linings. PTFE coatings are said to give good impact and abrasion resistance. Besides ease of repair, complicated shapes can be coated. The coating service is done for vessels, reactors, agitators, thermowell, dip pipe, sparger, top lid, manhole cover, reducing flanges, flush bottom valves, column sections, heat exchangers, pipe and pipe fittings, diaphragm valves, etc. [Processoo Engineers, A-35/208, Yogi Nagar, Eksar Road, Borivli West, Bombay 400 092.] (Source: Popular Plastics, November 1990)

* * * * *

Low-friction coating

A low-friction, corrosion-resistant metal surface treatment, designated as Niflor, has been introduced by Norman Hay International Ltd., Memphis, Tennessee. Niflor combines 18 to 25 per cent polytetrafluoroethylene (PTFE) particles with an electroless nickel plating to provide a solid-lubricant surface. The coating can be applied to any solid surface. (Source: Advanced Materials and Processes, July 1991)

* * * * *

Corrosion-resistant coating

Thermoset elastomer-silicone coating protects ferrous and nonferrous metallic surfaces from corrosion. Temperature range is between -40° and 400°F. Coating cures at ambient temperatures as low as 40°F to form a flexible, hydrophobic film that is well suited for use in corrosive environments such as chemical plants where moisture, humidity, and gases can be problems. [Dow Corning Corp., Box 1593, Midland, Michigan 48641, USA.] (Source: Machine Design, 21 March 1991)

* * * * *

Surface treatment method for architectural concrete

Nihon Cement Co. Ltd. and Asahi Sangyo Co. Ltd., have jointly developed a new concrete durability-improvement method called New Ceracoat for finishing the concrete surfaces of buildings without impairing the sense of mass and material of architectural concrete laid at random.

A high-pressure water jet rotary gun (aqua pulse gun) is used for foundation treatment for removing mould and contaminants from the concrete surface, followed by application of an inorganic foundation strengthening solution (surface tension lower than water), after which the surface is finished with a water repellent inorganic permeable finishing agent.

This surface treatment makes the concrete water-repellent, rain seepage is inhibited, and concrete deterioration prevented. The coating is gas permeable and prevents exfoliation as well as static electricity, so there is hardly any concrete contamination by dust adsorption, and the inherent porosity is not impaired.

It can be applied with conventional working methods and architectural concrete while retaining the inherent sense of mass and material, which was previously difficult. The treatment can also be applied to new concrete structures. [Nihon Cement Co. Ltd., R&D Dept. II, 1-6-1, Otemachi, Chiyoda-ku, Tokyo 100. Tel.: +81-3-3211-1625; Fax: +81-3-3211-1624.] (Source: JETRO, April 1991)

* * * * *

Coating absorbs smells

Swedish company Kefa Hightech has announced a new coating material capable of absorbing noxious airborne odours. The material is described as having a structure similar to plaster and can be sprayed or painted onto the surface to be treated. It contains a high concentration of micropores which can quickly absorb contaminants and then subsequently release them at a much slower rate. Used as a wall covering in conjunction with an effective ventilation system the material can therefore limit the unpleasant environmental effects of processes that generate foul odours

Kefa says that when used in an American tannery, for instance, the material helped reduce the level of hydrogen sulphide in the atmosphere from 6 ppm to 0.25 ppm. (Source: Engineering, Februrary 1991)

* * * * *

Unmanned system for treating concrete joints

Fujita Corp., has developed unmanned system that automates the work of treating the joint surfaces of massive concrete sections used in constructing dams. When laying such concrete sections, it is essential for the concrete surfaces to be scraped by an exfoliation method known as "green cutting" to improve the adhesivity between concrete surfaces.

With the new system called the FALCM System, deposits are removed with a high-pressure water jet nozzle and a travelling vehicle (green-cutting machine) mounting a nozzle suction unit for removing dust. Green-cutting is performed unmanned by using optical distance gauges equipped at the vehicle front and near the green-cutting point in combination with a personal computer.

This method enables 100 m^2 of green-cutting work, usually requiring 8 hours of work by five workers, to be completed within an hour. The first green-cutting system was tried out in the construction of the Tonami Yamadagawa Dam in Toyama Prefecture, and highly satisfactory results were obtained.

FALCM enables deposit removal matched to the concrete hardness by adjusting the water jet pressure, the distance between the concrete surface and nozzles, and the vehicle running speed. When working with relatively soft concrete, the pressure is lowered and the distance between concrete surface and nozzles increased, and the reverse for hard concrete surfaces. The working speed is 100-150 m^2/hr.

The company plans further study on the system to expand to applications such as cleaning airport runways. [Fujita Corporation, Corporate Communications Office, 4-6-15, Sendagaya, Shibuya-ku, Tokyo 150. Tel.: +81-3-3402-1911; Fax: +81-3-3404-8477.] (Source: JETRO, April 1991)

* * * * *

Heat treatment

Plasma technology progress improves options in surface treatment

Moulders and extruders of plastics parts in such widely differing application areas as electronics, automotive and packaging can benefit from a surface treatment technology that enables significant improvements to be made to such characteristics as paintability, adhesion, weather resistance, gas permeability, and others. Part surfaces can be etched, they can be coated with ultra-thin layers of quartz-like materials, or monomers can be polymerized directly onto the surface of the parts. The technology is highly effective and reliable, non-polluting, and is becoming increasingly suitable for production environments.

The biggest market to date for the technology has been electronics. Photo-resists are etched by plasmas, drill holes in circuit boards are cleaned, plastics housings for small components such as resistors and capacitors have their surfaces modified to make them bond better to potting compounds. But now the number of applications in many other markets is beginning to open up. Parts already being plasma treated include products as diverse as pen components, heat-shrink sleeving, car door mirrors, and packaging film.

Plasma treatment makes plastics more wettable

Wettability of plastics - and hence their paintability and bondability - is improved dramatically by exposing them for short periods to low-temperature plasma. The effect is particularly pronounced in such non-polar polymers as polypropylene and polyethylene.

A Plasma Technology PPS 800 plasma treatment unit is used by the Parker Pen Co., Newhaven, England to improve the ink-wettability of flow control mechanisms in its ink pens. The mouldings are extremely complex, with closely-spaced fins less than 1 mm thick. The company uses plasma treatment in preference to liquid acid etching with chromic acid. Although initial investment costs and running costs are higher, plasma treatment is, according to a company spokesman, cleaner and much more controllable. The plasma treatment unit operates at either 13.56 MHz or 2.45 GHz.

The Institut für Kunststoffverarbeitung (IKV) has developed equipment to improve wettability of fibre reinforcements for composites. The fibre passes from an unwind bobbin outside the chamber through a small orifice into the chamber, then round a series of pulleys inside the chamber, before passing through a second orifice to an unwind bobbin also outside the chamber. Although air is able to pass into the chamber through the orifices, the vacuum pump is sufficiently large to retain a sufficient vacuum inside the chamber.

Fibres run continuously through the chamber at a speed of around 0.5 m/sec, depending on the level of activation required. In composites containing treated carbon fibres, interlaminar shear strength is 50 per cent better than composites of untreated fibres. Plasma treatment is much more effective than coupling agents, an IKV researcher, Martin Londschien, claims.

Economics of making PP bumpers paintable

By far the biggest end user for Technics Plasma is the auto industry. One reason is that more motor companies are switching to polypropylene copolymers, blends, and compounds, for large painted exterior and interior parts. And despite all the efforts by materials manufacturers to improve the ability of PP to take paint and adhesives, pretreatment is virtually always necessary.

A bumper generally weighs approximately 5 kilograms. PP costs no more than $2.50/kg, whereas a competitive engineering thermoplastic is over twice that. Plasma treatment costs less than $1.00 for a large part, taking into account equipment amortization.

One material supplier taking an active interest in plasma treatment of PP bumpers is Appryl, a subsidiary of Atochem/BP, France. It is working with machine supplier Balzers. Balzers has a treatment unit designed to fit into a bumper production operation, operating at speeds that fit with the maximum cycle times of the production line. The unit has two treatment chambers, connected to a single high-capacity vacuum pump. Each chamber accepts two bumpers at a time (dimensions 1,800 by 800 by 400 mm). Loading and unloading can be automated, as can the control of the treatment cycle. Estimated treatment cost per bumper is FFr 8.00 (approx. $1.50), taking into account amortization of equipment. Balzers and Appryl have carried out extensive tests with an unidentified French bumper producer.

Wing mirrors on the Mercedes SL luxury sports car are body colour painted after they have been plasma treated in order to improve substrate-paint adhesion. The mirror shells are molded by Zipperle, Wurzburg, Germany, and treated and painted by an independent coating company before being delivered ready for assembly to the vehicles at Mercedes. Mercedes uses plasma treatment owing to the high reliability of the process.

Plasma treatment is highly competitive with corona treatment and with flaming. Plasma produces a higher level of surface energy, and parts can be stored for several weeks before this energy falls below a critical level necessary to ensure paintability. For example, the company can guarantee that a part made in a 30 per cent talc-filled PP will still have a surface energy of 54 mN/m four weeks after treatment (72 mN/m is the level required to make a part wettable by water).

Parts such as dashboard carriers are becoming so complicated that it is virtually impossible to treat them using flaming or corona. Furthermore, one plasma unit can be used to treat a wide range of different parts with only minor modifications to treatment procedures. Unlike flame treatment, there are no robots to reprogramme, for example.

Technics Plasma has built a prototype of a large plasma treatment unit that is capable of treating complete interior fascias and other equally large parts. Electrodes and magnets are fitted to horns that direct the stream of ions into the chamber. The horns are designed to produce the best dispersion of ions in the chamber.

All large motor companies have shown interest in plasma treatment for large parts, for improving adhesion to either paint, or, in the case of fascias, to polyurethane foam. Technics Plasma will supply Deutsche Fibrit, Düsseldorf, with a system to surface treat PP dashboard carriers prior to back foaming. The system will treat 800 fascias a day. The unit has two processing chambers, which each hold two dashboard supports at a time. Berthold Kegel, Managing Director of Technics Plasma, says he has another inquiry for a system to treat 4,000 large parts a day. It would comprise a series of chambers and pumps, working automatically on staggered cycles, feeding a single conveyor. The system would produce one treated bumper every 30 seconds. Chambers would each have a working volume of 3,000 to 5,000 litres, working on four-minute cycles.

Developing treatment systems for on-line use

Technics Plasma has supplied what it believes is the first plasma treatment unit designed to fit into a production/assembly line. It will be used by an unidentified supplier to treat ignition coils. It improves adhesion between the various plastics components and the epoxy potting compound. The specifier has set extremely tough specifications for the treatment system: finished parts were put through vigorous temperature cycles (-40 to +125°C in under 30 seconds, 200 times) to see if any delamination occurred between the epoxy and the highly contoured plastics parts.

Treatment cycle time is between four and five minutes, inclusive of chamber evacuation and replenishing. Preassembled coils pass through the plasma chamber on a custom-designed conveyor. The chamber takes between 10 and 50 parts at a time, depending on their size. The entire unit is 5.2 m long, the chamber itself is just 1.2 m long. Cycle time is 4.5 minutes. The unit will have an annual throughput of 1 million parts.

Continuous treatment of film for packaging, technical applications

If plastics monomers are introduced into a plasma, they form radicals that polymerize on the surface of plastics parts in the plasma, forming a very thin, but perfect, pinhole-free layer. A similar effect is achieved using silicone-based monomers. This form of treatment is called plasma polymerization, or plasma-enhanced chemical vapour deposition (PECVD).

Equipment from Leybold for coating film webs under vacuum, principally used to put thin layers of metal onto plastics substrates, can now be supplied in addition with a PECVD station that handles a vast range of non-metallic materials. Depending on end-use requirement, these materials will enhance chemical resistance, optical clarity, hardness, adhesion, and dielectric strength. A unit at Leybold's production facility, available for contractual development work, is equipped with six coating stations - five for sputtering, one for PECVD - enabling the production of multilayer coatings in a single pass.

Major uses for PECVD coatings are protective and functional layers for data storage media, barrier layers, and surface activating layers for improved adhesion, wettability, printability, and other properties.

PECVD deposition rates are too low for the system to run in tandem with an electron beam evaporation metallizing unit, but they fit very well with sputtering. Maximum web speed is 10 m/minute. Speeds could be increased by using more plasma sources, but this requires more space and more money, Leybold points out.

By combining various processes in a dynamic coating system, within a single vacuum chamber, the cost of producing the vacuum - an expensive element in the process - is ameliorated. Deposition rates also need to be improved: current lay-down rates are up to 10 nm/second, but it should be possible to improve that by a factor of ten.

Making auto glazing parts scratch-resistant

The technology is equally applicable to moulded parts. Plastics have many potential advantages in automobile glazing - safety, weight, design freedom - but they still lack scratch resistance. However, if they are given a permanent coating under plasma, this hurdle could be overcome. Multilayer, multifunctional coatings could be used: for example the sheet could be given a hard coat of silicon dioxide, a translucent solar cell layer of amorphous silicon oxide, an infrared reflecting layer, or even a layer functioning as an "electronic curtain" with selective transparency to electro-magnetic radiation depending on the radiation frequency.

The treatment may also be applied to head-lamp glass, if problems of matching thermal expansion coefficients of substrate and coating can be overcome. Leybold is working with General Electric Plastics, Schenectady, New York, USA, on such a project.

Bosch, Germany is one of the first users of PECVD technology, in the production of car headlamps. A plasma-polymerized surface layer with low surface tension prevents water that enters the headlamp unit from forming droplets that reduce the intensity of the headlamp beam. Reflectors are aluminized, then treated with a very thin (70 nm) layer that provides no interference. In some cases, the moulding also has to be surface treated before it is aluminized. PECVD enhances the adhesion of the metal to the substrate, by preventing the degassing from the polymer surface that normally occurs because of the high vacuum.

The treatment is normally a batch process, but if volumes require, it can be operated continuously. The aluminium sputter coating unit runs continuously for two days before the aluminium target needs replacing. Alternative coating systems use conventional lacquers.

Bosch, which has experience with both systems, says lacquering costs ten times as much as PECVD. The process is also suitable for treating louvres, and reflectors for neon and halogen lamps. The PECVD layer is more stable at high temperatures than conventional lacquers.

Improving gas barriers in blow moulded packaging

Plasma polymerization will soon play an important role in surface coating technology. Researchers at the IKV have developed a system for depositing very thin layers of very dense polyethylene onto the surface of such parts as blow moulded bottles. Coatings are amorphous and highly crosslinked, with high resistance to chemicals and to heat, and show high mechanical stability. Plasma-polymerized PE has a density of 1.6 kg/m^3. Coatings are free of micropores even at thicknesses less than 1 micron. Coating properties can be varied widely by changing processing parameters.

The IKV is developing a system for coating the inner surfaces of plastics bottles. The equipment has three linked chambers, with a high vacuum created in the innermost chamber, enabling the process to run quasi-continuously. Monomer is injected only into the bottle. A 1.2 litre bottle is coated in around 30 seconds. Diffusion of oxygen through polyethylene bottles is reduced by 98 per cent. Londschien says equipment could be used off-line in a blow moulding operation.

Similar technology is now commercially available from Eastapac, a joint venture subsidiary of Airco Coating Technology and Eastman Chemical. The difference is that Eastapac technology is used to apply inorganic coatings. The QLF (quartz-like film) technology is promoted as a means of improving barrier properties of polyethylene terephthalate (PET) packaging film and blow moulded containers, but it is equally applicable to packaging made from other plastics.

Enhanced oxygen barrier properties of QLF-treated PET packaging make it suitable for such oxygen-sensitive food and beverages as ketchup, beer, fruit juices, and baby foods, Airco claims. A coating less than 0.3 micron thick improves barrier properties by 200 per cent.

The Eastapac system deposits the barrier layer on the outside of the bottles. This means that bottle makers will not have to obtain food contact approval for the coatings.

A key advantage of Eastapac's process is that coatings have no colour tint. The process uses a mixture of gaseous organo-silicon compound and oxygen, with helium ionization gas. Substrates become coated with a layer of SiO_x, where x is between 1.7 and 1.9. In other systems, x is about 1.5, which produces a yellow/brown tint.

Eastapac has just finished building its first production-scale machine for treating bottles, which will be used for in-house development work. It is a semi-continuous unit, with three chambers, capable of treating up to 500 bottles/h. There should be no problem in scaling up to such throughput levels as 30,000/h, since the system has a modular construction, and chambers can be joined together to form long cylinders, capable of taking pallet-loads of bottles.

Eastapac will sell equipment, and pass on know-how through licensing agreements. It will also take royalties on finished product sales. QLF-coated bottles should cost not more than 30 per cent more than untreated bottles, and that the process should beat coextrusion on cost-performance grounds and QLF-coated parts are totally recyclable.

Coating benefit: fewer hard-to-recycle resins

Research organization Battelle Europe believes that the growing emphasis on post-consumer recycling will boost development of thin film coatings. It should be possible to reduce the number of different types of plastics required for all the various applications in, for example, a car, by transporting as many properties as possible given by the bulk material to the surface. So the same basic plastics could be used for a wide range of applications, with most of the required properties provided by the plasma-polymerized surface. Coating companies can look to a good future in a plastics recycling world, according to Heinz-Otto Irmler of Battelle.

Battelle first developed a PECVD technique for depositing diamond-like carbon (DLC) wear-resistant coatings on metals and plastics. The coating also provides a barrier to chemical attack. The coatings are produced by introducing a carbon-containing gas - Battelle usually uses acetylene - into the plasma. A research project is also planned into techniques for depositing diamond coatings. These differ from diamond-like coatings in their higher level of crystallinity.

The importance of having a coating that is not only chemically resistant itself, but which is also free of pinholes and which is impermeable, to prevent chemicals reaching the substrate was pointed out.

Battelle has put friction-reducing coatings on rubber windscreen wipers. low-friction coatings on computer disks to reduce the possibility of head crashes, and PTFE coatings (applied under plasma conditions) on floppy disks to reduce the chance of accidental damage to disks left on desks from spilt drinks or other office hazards.

Contact lenses are treated to improve wettability, to control permeability, and to adjust their density. This occurs through a technique called CASING (crosslinking of activated species by inert gases). Using an inert gas in the plasma may cause crosslinking, but without any of the chemical reactions that occur when using plasmas formed from reactive gases. Plasma-polymerized coatings less than one micron thick on the inside of gasoline tanks and other solvent containers reduce permeation to virtually zero.

Technics Plasma has carried out preliminary research on plasma fluorination, a derivative of the conventional fluorination process, but which has the great benefit of being much safer to use. No expensive gas exhaust systems are required. Instead of using fluorine gas, the plasma process uses CF_4 or Sf_6, which produce fluoride ions. In trials reductions of 85 per cent in permeability were achieved.

Irmler admits that such barrier-forming techniques as coextrusion that require no or little additional equipment or processing know-how still stand a greater chance of success in such applications. But he is much more optimistic about applications in the food, biomedical, and pharmaceutical areas. He cites pill coating with tightly-defined permeabilities for controlled release of drugs, as well as linings of plastics tubes and containers that do not degrade biological products. In tests, migration of diethylhexyl phthalate (DEHP) plasticizer from PVC into blood plasma was reduced by a factor of 100 by coating a PVC container with a plasma-polymerized fluorocarbon layer.

Plasma-polymerized membranes can be produced with selective permeability for partial osmosis of spent liquids in various chemical treatment processes. Work is being carried out by the Gesellschaft für Trenntechnik, Germany, as well as by various polymer suppliers and fabricators.

In metallization of plastics, the use of organo-metallic gases will open up new areas of application, Irmler claims. Simply by adjusting processing parameters, it is possible to produce layers that are isolating, partially metallic, or pure metal. [For more information contact: Balzers AG, FL-9496 Balzers, Liechtenstein; Battelle-Institut e V., Am Römerhof 35, D-6000 Frankfurt am Main 90, Germany; Eastapac Co., Eastman Chemical International AG, P.O. Box 3263, CH-6300 Zug 3, Switzerland; Institut für Kunststoffverarbeitung, Pontstrasse 49, D-5100 Aachen, Germany; Leybold AG, Wilhelm-Rohn-Strasse 25, D-6450 Hanau 1, Germany; Plasma Technology (UK) Ltd., North End, Yatton, Bristol BS19 4AP, England; Technics Plasma GmbH, Dieselstrasse 22, D-8011 Kirchheim, Munich, Germany.] (Source: Modern Plastics International, October 1990)

* * * * *

Advances in thermal-spray technology

Thermal spray, while still not a household word, has shown impressive increased recognition in recent years. Variations of thermal-spray techniques and the diversity of sprayable materials, along with advanced spray-control systems, have created new opportunities for the thermal-spray industry. Use of the process has grown well beyond the "band-aid" stage, and while its continuing importance in maintenance and repair is assured, thermal spray has a great deal more to offer. Thermal-spray technology has entered a new phase of development. Largely accepted by the gas-turbine industry, the process is rapidly gaining recognition as a viable process in "front-end" design in other industries.

Plasma spray: taming a complex process

All thermal-spray processes use a device (the gun) to melt and propel a coating material at high velocities onto a substrate where solidification occurs rapidly (one million degrees per second), forming either a protective coating or a bulk shape. There are basically three types of thermal spray guns: plasma, combustion-flame, and two-wire electric arc. The consumable coating material (feedstock) is in the form of powder, wire, or rod, and combustion or electrical power supplies the energy to achieve melting and acceleration.

Plasma-arc spraying uses a thermal plasma (the highest temperature heat source), and is the most versatile thermal-spraying process. The thermal plasma, a dense, highly ionized gas, has a sufficiently high enthalpy density to melt and deposit powders of virtually any metal alloy or refractory ceramic, as well as combinations of materials.

Traditional dc thermal-plasma units can spray powders at high velocities (>200 m/sec, 650 ft/sec), yielding good coating densities, potentially approaching theoretical density. Plasma spraying results in fine, essentially equiaxed grains, without extensive columnar boundaries, of particular advantage in certain ceramics applications (thermal-barrier coatings, for example). Coatings are chemically homogeneous; there is no (or controllable) change in composition with thickness. It is possible, however, to change from depositing a metal, to a continuously varying metal-ceramic mixture, to a ceramic-rich mixture, and finally to a completely ceramic outer layer, using programmed automation without intermediate delays in spraying or in part handling.

Off-the-shelf plasma-spray equipment offers the capability of high coating-feedstock throughput (3 kg/h, 6.5 lb/h), and special high-power guns can achieve a feedstock (e.g., alumina) throughput of over 25 kg/h (55 lb/h). Aside from normally spraying in air, it is possible, and sometimes essential, to plasma spray in a reduced-pressure environment chamber. Underwater spraying also is possible.

The plasma flame is maintained by a steady, continuous-arc discharge of flowing inert gas, generally argon plus a small percentage of an enthalpy-enhancing diatomic gas, such as hydrogen. Feedstock powder (10 to 70-μm diameter) is carried by an inert gas into the emerging plasma flame. The particles melt in transit without vaporizing excessively, are accelerated, and impinge on the substrate where they flatten and solidify at cooling rates similar to those achieved in rapid-solidification processes.

Much of the heat contained within the particles being deposited, as well as the heat of solidification and the heat of the plasma flame, is removed by conduction through the substrate. Consequently, precautions must be taken to prevent thermal degradation of substrate properties, or to prevent a metal substrate and/or coating from becoming excessively oxidized. Both the substrate and coating contract upon cooling, which can generate high residual stresses if a significant difference in coefficients of thermal expansion exists; these stresses can lead to coating delamination.

While there are hundreds of parameters that influence the plasma-arc spraying process, about 12 have been identified as having the strongest influence on coating properties and the survivability of the coating system. Improved control of these parameters was the focus of many developments that have occurred during the past few years, and is the focus of many current developments. These include incorporating empirical or real-time feedback looping, redesigning fundamental gun components and feedstock powders (e.g., chemical composition, size distribution, and shape), and rethinking power-supply design.

There also have been major changes in gas-handling equipment. Mass-flow control and metering are replacing traditional analogue gauges, which enable digital output with feedback potential. Data logging is gaining acceptance: flawed areas within a coating are now attributable to an "event" in gas flow, for example. Similar control schemes have been adopted for the powder-feed operation, including a variety of devices that display instantaneous powder-feed rates. Powder feeders also have changed, with fluidized-bed feeders becoming common; these feeders permit smooth flow (less pulsing) of a wider range of powder types.

In the area of power supply, controlled dc-power supply systems incorporating heat exchangers have been designed specifically for use with plasma guns, and are becoming the standard in the industry. And while not yet commonly practised throughout the industry, monitoring and logging current, voltage, cooling-system temperature at various locations (including the gun), gas parameters, and feed rate is a relatively straightforward task.

A revolutionary development in plasma-spray technology that occurred in the 1980s is reduced-pressure atmosphere chamber spraying. Plasma spraying essentially in the absence of oxygen allows the coating/substrate system to be maintained at a high temperature during processing, resulting in interfacial diffusion, which produces a true metallurgical bond.

The high interest of the aircraft industry in this technique has encouraged further development, and signficiant progress has been made by Electro Plasma Inc., Metco Perkin Elmer, and Sulzer Plasma Technik Inc. Chamber plasma spraying is expected to be capable of producing coatings having unique properties in a wide range of applications. For example, it is possible to chamber spray refractory oxides to obtain fully dense, well-bonded coatings. It also is relatively easy to add a high-temperature metal alloy to the oxide to obtain a composite having good high-temperature wear-resistance. Chamber spraying also can produce good coatings of reactive metals, such as titanium and zirconium.

An extension of the technique involves spraying the interior of large pipes or tanks for handling chemicals, using the vessel itself as a reduced-pressure inert-gas chamber by excluding air during spraying. Enhanced coating characteristics (e.g., density and adhesion strength) and accompanying improved coating properties achieved in chamber spraying are related to increased particle velocity and the high temperature of the coating/substrate system attained during spraying.

Another variation of chamber spraying is reverse-arc sputtering. The technique involves electrically connecting the target substrate to the spray-gun system, which establishes a transferred arc at the surface, thus effecting a highly efficient sputter-cleaning process. This surface pretreatment combined with the high coating/substrate temperature results in excellent coating adhesion.

Versatility through process variety

Combustion-flame spraying generally uses an oxyacetylene flame to melt and spray either powder or wire feedstock. Due to its lower flame temperature and particle velocity compared with plasma spraying, flame spraying produces a less dense coating having lower adhesion strength. However, flame spraying is simpler in principle and operation, and system and production costs are lower than for plasma spraying. An additional consideration is the possible use of less-skilled operators because the process is more forgiving.

Commercially available wire combustion-flame guns can be used to spray virtually any welding wire including composite wires. For example, Alcan Aluminum Corp. recently introduced Duralcan metallizing wire produced from Dural, an alumina-reinforced metal-matrix composite (10 vol per cent alumina/aluminium). Wire-sprayed Duralcan yields a well-bonded corrosion- and wear-resistant coating in applications ranging from nonskid decks to corrosion/erosion-resistant industrial marine use.

A variation of combustion-flame spraying is the spray-and-fuse method of surface hardening. This well-established technique enables flame-spray deposition of a hard-facing material, for example, with subsequent flame fusing. Although the process lacks some control, it is highly effective and is widely used.

The hypervelocity oxyfuel (HVOF) gun represents a major development in thermal-spray technology. Developed by several companies to obtain well-bonded, dense coatings, HVOF guns have in common a method to burn oxygen and fuel and carry the combustion products through a nozzle with subsequent free expansion. This arrangement results in hypersonic flame gas velocities, and by introducing the feedstock powder "up-wind", powder particles attain high heat and supersonic velocities; this permits particle flattening upon striking the substrate, thus forming a dense coating. Special particle-size distributions are required for HVOF spraying, creating challenges and significant opportunities for powder producers.

HVOF-sprayed metallic coatings often have properties superior to those of plasma-sprayed coatings, and equal to or superior to coatings produced using the detonation gun. The aircraft industry is especially interested in the HVOF spraying process for producing wear-resistant coatings. Refinements in the process are expected in the future, which may extend its application into areas traditionally dominated by plasma spraying.

Two-wire, electric-arc spraying represents an important method to achieve low-cost application of metallic coatings. Most welding wires can be electric-arc sprayed at high throughput (from 30 to 50 kg/h, 65 to 110 lb/h). During the process, two consumable wires, through which an electric current is passed, form an electric arc at the point where they intersect. The arc melts the wires and the molten metal is atomized by a continuous flow of either high-velocity compressed air or nonoxidizing gases, such as carbon dioxide, nitrogen, or argon. Coatings formed using air atomization are relatively dense and have good adhesion. Those formed using inert-gas atomization (which can be carried out in a reduced-pressure chamber) are very dense and well-bonded to the substrate.

The Sonarc process combines two-wire, electric-arc and HVOF spraying; molten metal at the arc is atomized and rapidly propelled to the substrate by the HVOF flame. The introduction of hard reinforcement particles (e.g., alumina or silicon carbide) into the flame makes it possible to form either a metal-matrix composite coating or a free-standing bulk shape. The high particle velocities attainable in the Sonarc process result in extremely dense composite materials.

New powders create new opportunities

The enhanced quality and variety of feedstock powders is contributing significantly to the advancement of thermal-spray technology. New processes are being used to economically produce special metal-alloy and ceramic formulations (e.g., cemented chromium and tungsten carbides). For example, GTE Products Corp. has developed a new microatomization process in which metal is melted using a plasma torch and molten droplets are propelled at high velocities against a rapidly rotating substrate. The droplets are fragmented and rapidly solidified resulting in spherical powders tens of micrometers in diameter, which can be used as feedstock for plasma and HVOF spraying. Spherical powders are especially necessary in plasma and HVOF spraying to obtain even, nonpulsing powder injection into the flame.

Metco Perkin Elmer uses a plasma gun to process an agglomerated ceramic powder. This process yields chemically uniform spherical particles. Hollow particles also can be produced, which enables deposition of ceramic coatings having controlled levels of porosity.

Various spherical ceramic powders having uniform composition and fairly uniform size are produced by Alcan using the sol-gel process. Some other techniques used to produce high-quality powders for thermal spraying include chemical precipitation and atomization of ceramics and advanced atomization processing of metals. In addition, mechanofusion powder processing, a variation of mechanical alloying, may contribute significantly to the production of unique thermal-spray powders.

Considerable research by National Aeronautics and Space Administration, aircraft-engine manufacturers, and independent research laboratories has led to the development of optimum coating compositions and spray parameters to produce viable, strain-tolerant ceramic thermal-barrier coatings on hot-section components in gas-turbine engines. These coatings are generally based on partially stabilized zirconia (PSZ) using yttria as the stabilizer. However, there is strong interest in the use of alternative, possibly more effective, rare earths to act as stabilizers for zirconia.

Alumina and alumina-titania are used extensively for wear-resistant coatings, and hydroxyapatite is being evaluated for use in biomedical applications. There also are potential applications for plasma spraying high-T_c ceramics and piezoelectric powders. Metco Perkin Elmer has produced complex high-T_c ceramic superconductor powders using a variation of its hollow spherical powder (HOSP) process. [Article written by Professor Herbert Herman, State University of New York, Stony Brook, New York, USA.] (Source: Advanced Materials & Processes, April 1990)

* * * * *

Continuous, high-energy system treats moulded parts

A new electrical surface treatment uses high voltages (to 56 kV) and high frequencies (from 18 to 25 kHz) for continuous online 3-D treatment of parts. The method changes the surface wettability of polyolefins so they can be bonded to other plastics or metals, or prepared for printing. An advantage of EST, developed by Tantec (Tantec AS, Industrivej 6, DK-6640 Lunderskov, Denmark) is that it provides line speeds twice as fast as regular methods.

EST transforms a nonwettable surface into a workable one by accelerating free electrons, present in the atmosphere, in the presence of the high field. The electrons impact on the surface with energies two to three times those needed to break the molecular bonds of most substrates. The resulting free radicals react rapidly with the oxidizing by-products of the discharge or with adjoining free radicals on the same or different chain, resulting in a crosslink. EST treats parts with geometries as deep as 38 mm, compared with about 6 mm for corona treatment.

An EST system consists of a generator, a high-voltage transformer, and a treating station. Claimed benefits of EST, compared to standard treatments, are:

- Flame treatment. EST can be integrated into production machinery easily because it uses electronic switching. EST provides feedback electronic control for better process uniformity, and is simpler to operate than flaming.

- Plasma treatment. EST offers continuous versus batch heating. Energy costs of plasma are said to be 10 times more than EST.

- Corona treatment. Corona usually is a 2-D process. Treatment is six times longer, due to lower frequency and voltages.

- Chemical treatment. Operating costs are 5-10 times higher.

EST bonding sites at the polymer surface increase bonding characteristics of polymers, eliminating the need for primers. Tests are said to show an enhancement in lap shear strength between surfaces of an EST-treated polymer. The method produces one by-product - ozone, which is eliminated by activated carbon adsorption. (Source: Modern Plastics International, June 1991)

* * * * *

The next two articles tell us about recent developments from Leybold AG, Germany:

Vacuum coating of steel strip

New methods for applying both functional and decorative coatings to flat steel stock have been the subject of studies and development work in various parts of the world within a number of materials science research programmes for nearly ten years. Energy conservation considerations and environmental impact aspects also have become matters of major importance for future coating technologies.

Vacuum coating, a method already well established in the mass production of architectural glass and plastic foils as well as in the semiconductor and electronics industries, has proved to be a valid industrial technology for modifying the surfaces of steel strip stock.

Leybold AG has recently developed and tested specific applications in the field of vacuum coating of steel strip stock. Leybold has engineered a dual purpose coating deposition line with the following coating sources:

- Thermal line evaporators;

- Large area sputtering cathodes;

- Plasma CVD line sources.

There are at present concerted efforts to produce ceramic and oxide coatings employing ion plating methods that specifically address current demands for higher deposition rates and greater operating efficiencies. It is expected that mass production systems will be installed in Europe over the next few years, with special pilot scale installations for "high-tech" products coming on line even earlier.

Leybold envisages vacuum steel strip coating technology competing with existing electroplating and hot dip coating methods across parts of the product spectrum. Its major contribution, however, the company comments, will be that of broadening the variety of available coating processes. (Source: Ironmaking and Steelmaking, 1990, Vol. 17, No. 4)

Laser disk coating

Video disks and other optical disks of 200-mm diameter are usually manufactured from polycarbonate material. The production process used is comparable to that for CD audio disks. Leybold AG of Hanau, Germany has recently introduced its Singulus 200 system for the metallization of such disks. This system can be readily integrated into production lines. It can also be combined with the stand-alone systems used for manufacturing laser disks. According to the company, this system offers high product quality and production rate. Processing cycles take 8 seconds to complete. This corresponds to 450 disks coated per hour of operation. This is fast enough, and often even faster than needed, to allow in-line integration with the injection moulding equipment, says the manufacturer. Targets last long enough to coat 40,000 disks with 55-nm (0.000055-mm) thickness aluminium films. Target replacements interrupt production operations for about 20 minutes. The system's floor-space occupation (excluding control rack and power supply) is one square metre. [Leybold AG, Wilhelm-Rohn Strasse 25, D-6450 Hanau 1, Germany. Tel.: (06181) 34 1690; Telex: 415206-0 lhd; Fax: (06181) 34 4330.] (Source: Popular Plastics, November 1990)

* * * * *

Plastics

New surface treatment method upgrades cheaper plastics for industrial use

A new surface treatment method for plastics has been developed in Sweden by PP Polymer AB, Stockholm, according to the magazine New Scandinavian Technology. Eliminating the need for washing with chlorinated solvents, the new technique is based on a modification of the plastic surface and also allows the painting, glueing and pressing of plastics.

The method calls for the submersion of the plastic in a chemical bath for a few seconds. This is enough to accomplish a permanent change in the plastic surface, but not in the bulk material. The company has not specified the composition of the chemical bath but indicates that hydrogen atoms in the long polymer chain have been replaced by other atoms. This is said to result in steric stability.

The new method will open up very interesting perspectives for manufacturers of such varied products as motor vehicles, plastic carrier bags and composites, New Scandinavian Technology says. They are now obliged to use dangerous solvents to allow their products to be treated with paints, adhesives or printing inks. After use, the non-degradable toxic substances often pollute the environment. In addition to being more environment-friendly, the PP Polymer method will make a number of cheaper plastics - including polyethylene and polypropylene - more interesting for industrial purposes, the magazine adds.

PP Polymer AB has also developed a new environmentally acceptable high-speed filler for use in the woodworking industry. Called PP-Fill, it can be used to mend blemishes or fill surface irregularities in wood or plywood. The substance is applied with an ordinary spatula and is subsequently cured under ultraviolet and infrared light for 10-30 seconds each. The filler can be applied in thick layers and then sanded and painted. It can also be pigmented. It is not tacky and is said to have excellent outdoor durability and storage stability. (Source: SIP, The Swedish International Press Bureau, January 1991)

* * * * *

Weather-resistant hard coating agent

Showa Techno Coat Co., Ltd. has developed the weather-resistant hard coating agent Technocoat A-1000X that is highly resistant to acid rain and salt damage. The weatherability of this coating agent exceeds the 480-hour level as confirmed with a super-UV tester, while the salt damage resistance of about 1,200 hours has been confirmed through tests conducted by the company.

A distinct characteristic of this new hard coating agent is that a film is formed by cross-linking (thermal condensation reaction) of an organic polymer with functional groups and an inorganic polymer of high reactivity. The new agent has excellent adhesivity to metals and glass.

An outstanding advantage of this method is that chemical processing, normally performed for adhesivity improvement, is unnecessary. As compared with fluoride paints of comparatively good weatherability, it has greater transparency and hardness, and can reduce costs by about 50 per cent.

Paints generally use melamine or isocyanate as the cross-linking agent, but the melamine hardening method has inadequate resistance to acid rains and poor weatherability, and the isocyanate method has a toxicity problem. The automotive industry, for example, is looking for a high-performance salt damage resistant coating agent for preventing the corrosion of aluminium wheels, especially for export cars governed by strict controls such as a resistance of 1,200 hours in salt water spray tests. The corrosion problem is also present in the construction industry in the corrosion of aluminium structural members by acid rain and salt damage.

Technocoat A-1000X is a single-liquid coating agent. In contrast to conventional coated film hardening methods, the new coating agent is expected to have various advantages.

For weatherability, the service life has been raised to about 480 hours, compared with about 100 hours for conventional paints. Fluoride paint is a coating material of comparatively good weatherability, but it is expensive and fails to provide a reliable surface hardness. The new coating agent displays a vertical hardness of 4-8 H, so the resistance to scratching, salt damage and chemicals has been improved considerably. [Showa Techno Coat Co., Ltd., 1-4-1, Higashi-Kanda, Chiyoda-ku, Tokyo 101. Tel.: +81-3-3862-0009; Fax: +81-3-3862-0026.] (Source: JETRO, April 1991)

* * * * *

Hard-wearing Soviet floor

A Soviet innovation in flooring could provide a safe and hard-wearing surface for companies handling acids and other corrosive substances.

The Karpol floor comprises an unbreakable plastic sandwich, which is resistant to acids, alkalis and salts.

Developed by the Montazhkhimzashchita Trust in Moscow, and reported by the Novosti Press Agency, the floor has a backing of concrete covered with an epoxy resin and a layer of soil. On top of that is a half-millimetre-thick layer of chemically resistant resins and liquid rubber, which will not crack or peel.

That is covered with a layer of a proprietary material and finished off with a coating of polymer - such as polyurethane or acryl - which can be coloured to the company's choice and makes the surface easy to clean. (Source: Financial Times, 11 January 1991

* * * * *

Protecting surfaces

A revolutionary product claims to protect paintwork and other surfaces for twenty years and eliminates fading, cracking and peeling. Bonacryl, manufactured by Bonacryl International Ltd., Ayr, Scotland, gives a water-borne plastic coating, whose destruction is virtually impossible apart from burning or severe mechanical abrasion. The product contains a two-pack water dispersion acrylic polyurethane lacquer which provides a virtually impregnable barrier between a painted surface and the outside elements with a hard, strong and flexible finish. As it has a highly ceramic-like surface it requires less time, effort and materials to clean than conventional surfaces. Dirt is simply floated off.

When Bonacryl is applied, there is no need for special equipment, specialist skills or training, as it is easily applied to any type of surface and no difficulties are experienced. Bonacryl can be readily applied with a brush or spray painted. Householders and unskilled painters can achieve a superb mark-free finish on both new and used surfaces. Its applications in restoring defaced surfaces are limitless.

Bonacryl has a wide range of applications when it is applied to restore or protect surfaces. These surfaces include copper, stone, brickwork, marble, terrazzo and cement. It can be applied internally and externally to industrial plants, abattoirs, food factories, as well as coating oil storage tanks, machinery, street furniture and cement floors. (Extracted from Technology Ireland, February 1990)

* * * * *

Advanced surface modification in material processing

A recently developed advanced surface modification technology is ion beam technology that (1) is applicable to high-purity materials, and (2) has excellent controllability (control on the atomic and molecular levels), so it is expected to become a basis for technological progress into the twenty-first century.

The objective of this research project is to combine ion beam technology with all types of conventional coating technology such as plating, chemical vapour deposition (CVD), and physical vapour deposition (PVD) processes to develop advanced material surface modification technology.

Figure 1 shows the basic concept of this R&D project. An ion beam is bombarded on the surface and/or the interface between a material and a film to improve the surface function.

Contents

1. Functional Film Formation

(1) Film forming technology

A film is formed to improve a material's inherent functions or to give the material an entirely new function. Here, the aim is to develop material surface cleaning technology and activation technology based on ion beam bombardment to advance film formation technology. In this case, it is essential to prevent the material surface from damage. Therefore, research will improve the performance and durability of cutting tools, superprecision moulds and machinery parts and improve the functions of various materials such as polymer films.

(2) Advanced material-film joining technology

The life expectancy of a film formed on a material is largely influenced by the adhesion strength. Ion beam technology will be used to improve the adhesion, and technology developed to prolong the life expectancy. In particular, a method for improving the adhesivity by an ion injection bombardment at the interface between material and film after film formation will be studied.

2. Material processing technology for film formation

There have been several examples of difficulty in the past when forming films, depending on the combination between materials and films, such as forming a diamond film on a silicon substrate. Ion beam technology will be applied to form films which have new functional properties.

Results

The effects of ion beam bombardment on the surface of materials depend on the energy of the ion beam, and various processing technologies using these effects are being advanced (Fig. 2).

Studies were first conducted on the bombardment effects of ion beams used in combination with other film forming technologies, which revealed that ion beam bombardment is effective in three energy ranges.

Firstly, at the energy range from several hundred to several thousand electron volts (eV), where the material surface sputtering effect is dominant, but surface damage not so pronounced, indicating that the beam is useful for cleaning or activating the surface prior to film forming. Therefore, by forming a film on a surface bombarded with an ion beam of this energy range it is expected to provide a film with good adhesivity and performance without damaging the material's surface [Fig. 3 (1)].

Secondly, in the energy range of several dozen keV, the knock-on effect and ion implantation effect are involved in addition to the sputtering effect. The surface atoms and molecules are partly sputtered away and partly pushed inside the material. A fraction of the ions themselves also penetrate the material. Therefore, if an ion beam of this energy range was bombarded while a film was being formed by physical vapour deposition, for example, a mixed phase consisting of vaporized substance, material substance and ions will be formed in the initial stage of film forming, with the ratio of the material substance being decreased gradually to ultimately form an alloy (compound) film consisting of vaporized substance and ions. Therefore, it was found that using this method and controlling the vaporization beam and ion beam enables a film to be formed without a joint [Fig. 3 (2)]. This method is expected to be useful for forming films of good adhesion on materials which previously resisted films forming.

Thirdly, in the energy range of several hundred keV to several MeV, the ion implantation effect is definitely dominant. Ions penetrating inside the material are stopped at depths determined by the energy level and mix with the material. Therefore, it was found that if an ion beam of this energy range was bombarded on the surface of a film, it will be possible to modify the film selectively depending on the film thickness and the ion beam energy [Fig. 3 (3)], or to improve the adhesion by forming a mixed phase on the interface between the film and material surface [Fig. 3 (4)]. This process is also expected to improve film performance by modifying the material surface with this ion beam beforehand and forming a film [Fig. 3 (5)].

Throughout this project, it was revealed that the common theme for study was the adhesion between the material and the film. Therefore, research is presently in progress to design the estimating apparatus necessary for studying the adhesion from both macroscopic and microscopic aspects.

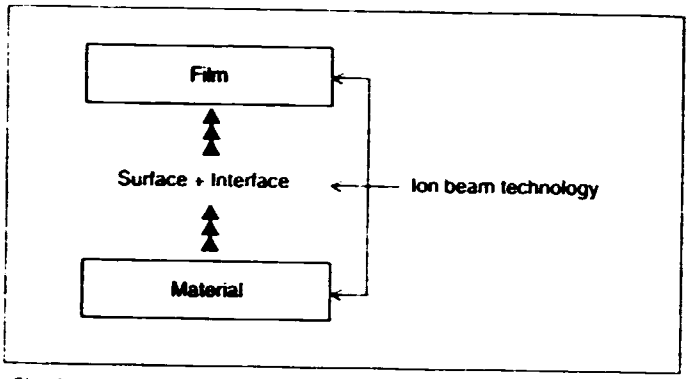


Fig. 1. Basic concept of project

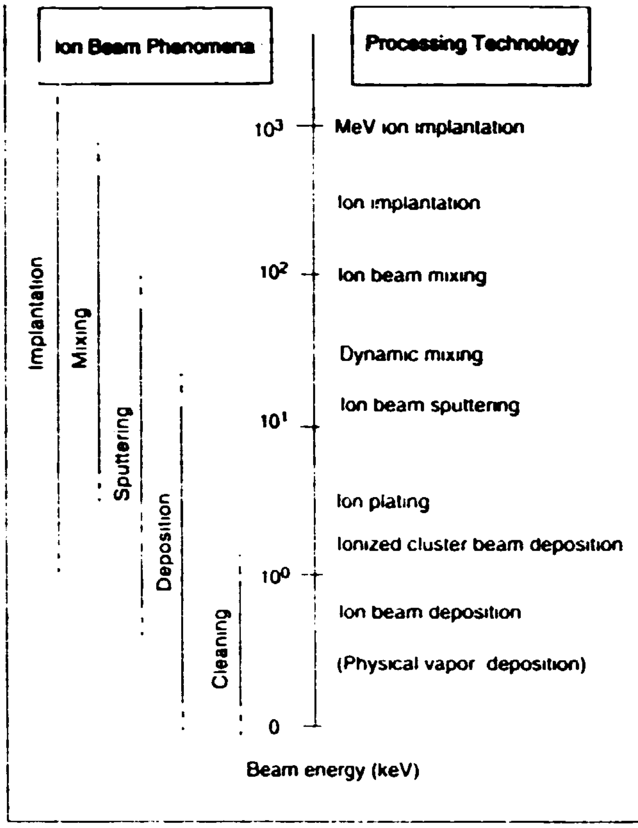
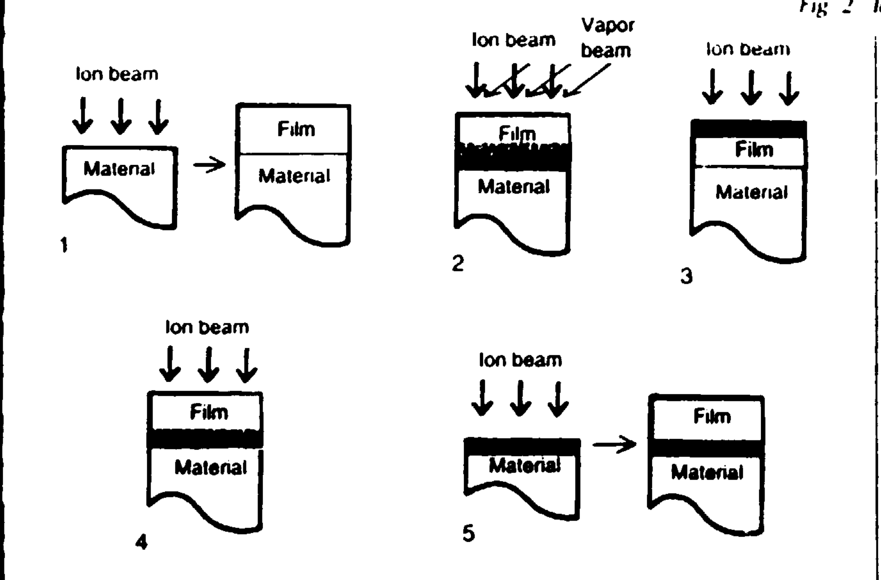


Fig. 2. Ion beam effect and processing technology



g. 3. Example of combination between ion beam technology and film forming technology

(Source: JETRO, February 1991)

* * * * *

3. SURFACE ANALYSIS

Surface analysis: new ways for new materials

Continual development of techniques for coating and treating the surfaces of engineering materials is presenting today's designers with many exciting opportunities, as is evident from the broad range of applications set out in the first table (see page 75). By selecting the material they want for its bulk properties of, say, toughness and weight, engineers can modify its surface to impart many kinds of special qualities that may be required of it. Examples extend from semiconductor manufacture to coating optical lenses, from making bearings to putting magnetic layers on recording tapes. We have come a long way from early applications such as case-hardening mild steel parts to resist wear.

Whenever surfaces are modified, it is vitally important to monitor the formation of the altered layer and the subsequent performance of the engineering component or device. This is necessary for quality control and to give early warning of any failure of the coating.

Some of the most important problems met with are listed in the second table (see page 76). In general, what is needed of the monitor is that it should provide quantitative analysis of all chemical elements, have a high sensitivity (of the order of one part in a million), high spatial resolution (less than one micrometre), an imaging capability so that spatial distribution of chemical species can be seen, and be able to obtain concentration-depth profiles with a resolution also better than one micrometre.

A programme of study, to be carried out at Salford under the UK Department of Trade and Industry's LINK scheme, aims to develop such an analytical technique. The technique is known as Sputtered Neutral Mass Spectrometry (SNMS). With the foregoing characteristics, it will provide an ideal means of studying the surfaces of modern engineering components.

Surface analysis

Many surface analysis techniques are available but only a few give quantitative information and have a high sensitivity. The main contenders for further development are listed in the third table see page 76). They include the well-established, but non-quantitative, Secondary Ion Mass Spectrometry (SIMS). In this, a beam of energetic ions strikes the surface of the sample under analysis and removes (sputters) atoms from the surface layer. A fraction of these ejected particles, typically one in a thousand, leaves in an ionized state. These particles can be steered into a mass analysing device, such as a quadrupole mass spectrometer, which then gives an output signal for every species on the sample surface. It is a relativ ly simple matter to scan the range of masses and discover which impurities are present on a given component.

What SIMS cannot generally do, however, is provide quantitative information on the amount of a given material present. This is because the number of particles ejected as ions critically depends on the nature of the surrounding matrix atoms. So the signal from element B in a mixture of B+A will not usually be the same as that for the same percentage of B in a mixture of B+C. Because many engineering components have sharp changes in composition near their surface, for example the oxides at the surfaces of metals, the SIMS technique is not reliable for any quantitative measurement.

The number of atoms sputtered as neutral species is not as sensitive to surface and matrix conditions. If these atoms can subsequently be ionized in a controlled region, away from the surface, the technique will have all the advantages of SIMS but the added advantage of being quantitative. Several techniques have been proposed for this post-ionization process. In the first, a glow discharge is created at, or near to, the surface under analysis. Atoms characteristic of the material pass into the discharge and are ionized and extracted into a mass analyser device. A second technique proposed is to irradiate sputtered atoms by a pulsed laser which causes ionization, and a third is to irradiate sputtered atoms by an electron beam which ionizes them.

An instrument of the first type has been investigated at the University of Kaiserslauten, in Germany. Its ouptput was seen to be capable of giving quantitative information, but the discharge interacts with the whole sample surface and spatial distributions of species cannot be obtained. Laser techniques are successful but expensive and the pulse repetition rates restrict the practical sensitivity. The electron beam ionization technique appears to combine the advantages of allowing spatial distributions of species to be found and of holding out the promise of high sensitivity, so our aim now is to develop the technique, to calibrate our system against standard samples and to devise techniques for minimizing background signals so that the sensitivity limit may be improved.

The schematic diagram (see page 77) indicates the proposed components of an SNMS system. A primary ion beam, which may be broad or finely focused for detailed spatial analysis, causes sputtering of sample material, a fraction of which passes into the electron beam ionizer region. Particles leaving the surface as ions can be rejected by applying a transverse electric field to ensure that this matrix-dependent part of the secondary signal does not reach the analyser. Some of the neutral species are ionized by the electron beam and are then extracted, passed through an energy filter and mass analysed by the quadrupole mass spectrometer. The output signal depends on the fraction of neutral atoms entering the ionizer region, the ionization efficiency and the transmission efficiency of the secondary-ion optical system. All these quantities are fixed parameters for a given mass and system operating conditions, so the analyser may be calibrated and thereafter used to provide quantitative information.

The difference in performance of the SIMS and SNMS analyses is shown clearly in the second diagram (see page 77), where a sample of chromium oxide on steel is studied. It is clear that the SIMS method gives a spuriously high chromium signal near the surface, resulting from oxygen that is present and which increases the ion yield. But the SNMS technique is not influenced by the matrix. It is significant that, although the oxygen level is extremely small, the SIMS signal for chromium is a factor of twice its normal level; this shows just how serious the quantification problem is when using SIMS.

SNMS, however, has all the advantages of SIMS and can be used in the imaging mode. For this a finely focused primary beam is raster scanned across the sample. When using a liquid metal ion source a beam diameter as low as 50 nanometres is possible. The output from the quadrupole mass analyser is used to modulate the intensity of the electron beam in a TV tube which is swept across the screen in a raster that is synchronized with the probing primary beam. When the analyser is tuned to a particular mass, bright spots appear at image points corresponding to the positions on the sample surface where the concentration of that species is high. Depth profiles of species in the sample can be obtained by sputtering the sample surface with a broad primary beam and monitoring the output as a function of erosion time. Use of a frame store computer allows the distribution of several species to be followed while the spatial distribution is obtained layer by layer as the sample is sputtered away.

Specific tasks

The foregoing account shows that the SNMS technique has tremendous potential for evaluating the detailed condition of surface, near-surface and interface layers of a whole range of engineering materials. Nevertheless, there are several problems to be solved before the new technique has a reasonable sensitivity and can produce reliable results to permit calibration. There are three main areas of study, namely background signals, sample mounting, and the calibration itself.

The sensitivity limit will be determined by the ability to distinguish a true signal, arising from sputtered neutral atoms from the sample, from other signals giving a background "noise". One of the main background signals will arise from the ionization of residual gases by the electron beam in the ionizer chamber. Fortunately the energies of ions created from background gases are typically less than one electronvolt, whereas the majority of those of the ionized sputtered neutrals will be greater than five electronvolts. A suitable voltage bias of the order of five electronvolts should therefore eliminate the residual gas ions; preliminary data shows that this is indeed so. The bias also reduces the level of the true signal, so careful optimization will have to be carried out to attain the best sensitivity.

A second problem is the need to suppress certain other ions that have higher energies arising from electron bombardment of surfaces and charge transfer collisions in the ionizer region. It will be necessary to try various geometrical arrangements, additional biasing and new signal processing techniques to resolve these problems.

In mounting the sample, the main challenge is to devise a way of introducing it that is versatile enough to cater for a range of sample sizes but which places each sample at precisely the same point in space with respect to the analyser. This is necessary to ensure that collection efficiency, and hence calibrations, do not change. To obtain the best sensitivity the whole assembly should be as near as possible to the analyser but it should not, of course, obstruct the primary beam.

A great deal of the calibration can be done with standard samples, but there is a need to prepare special targets with small concentrations of species to enable us to look at any remaining matrix effects and to evaluate detection limits. Such studies will involve the preparation of special, uniform ion implanted samples.

The SNMS technique's capability for quantitative measurement gives it a tremendous lead over other analytical methods for analysing a wide range of modern engineering component surfaces. Our Centre for Thin Film and Surface Research is heavily involved in surface modification processes and sees the availability of such an analysis technique as a vital factor for evaluating the performance of novel surfaces. We foresee that a strong interaction will be generated between CTFSR and engineering firms, research laboratories and other universities so that the information the new technique makes available may be exploited to allow the production of components far superior in durability and performance to those now being made.

Applications of engineering materials with modified surfaces

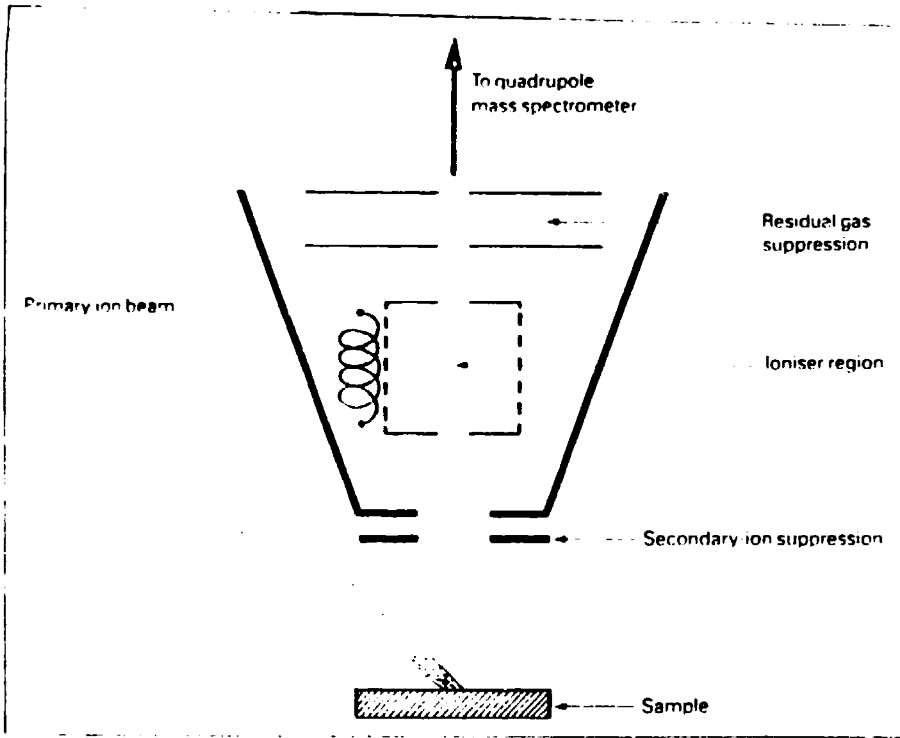
Electronic	Ion implantation for semiconductor devices
	Metal-silicide layers for interconnector strips (interconnects)
	Thermo-junctions
	Superconducting films
	Well-bonded contacts with linear (ohmic) properties
Mechanical	Hard layers for cutting tools/drills
	Low friction layers for bearings
Chemical	Corrosion-resistant layers
	Catalytic layers
	Electrodes for gas sensors
Physical	Magnetic layers for recording tapes and discs
	Diffusion barriers (to protect food for example)
	Coatings for optical lenses

Typical causes of failure of components and devices

Electronic	Contamination by certain impurities
	Diffusion/segregation of materials in semiconductors
Mechanical	Wear, seizure, fusion of surfaces in contact
	Hydrogen diffusion, embrittlement
	Phase change, precipitation, diffusion/segregation of component materials, amorphous/crystalline transition
Chemical	Disappearance of layers into solution
	Pinhole formation (pitting)
	Segregation/diffusion of component materials
	Oxidation and other reactions
	Contamination by active species
Physical	Adhesion failure, flaking, blistering
	Phase changes
	Contamination, such as formation of impurities in optical devices
	Density/refractive index changes
	Diffusion/segregation

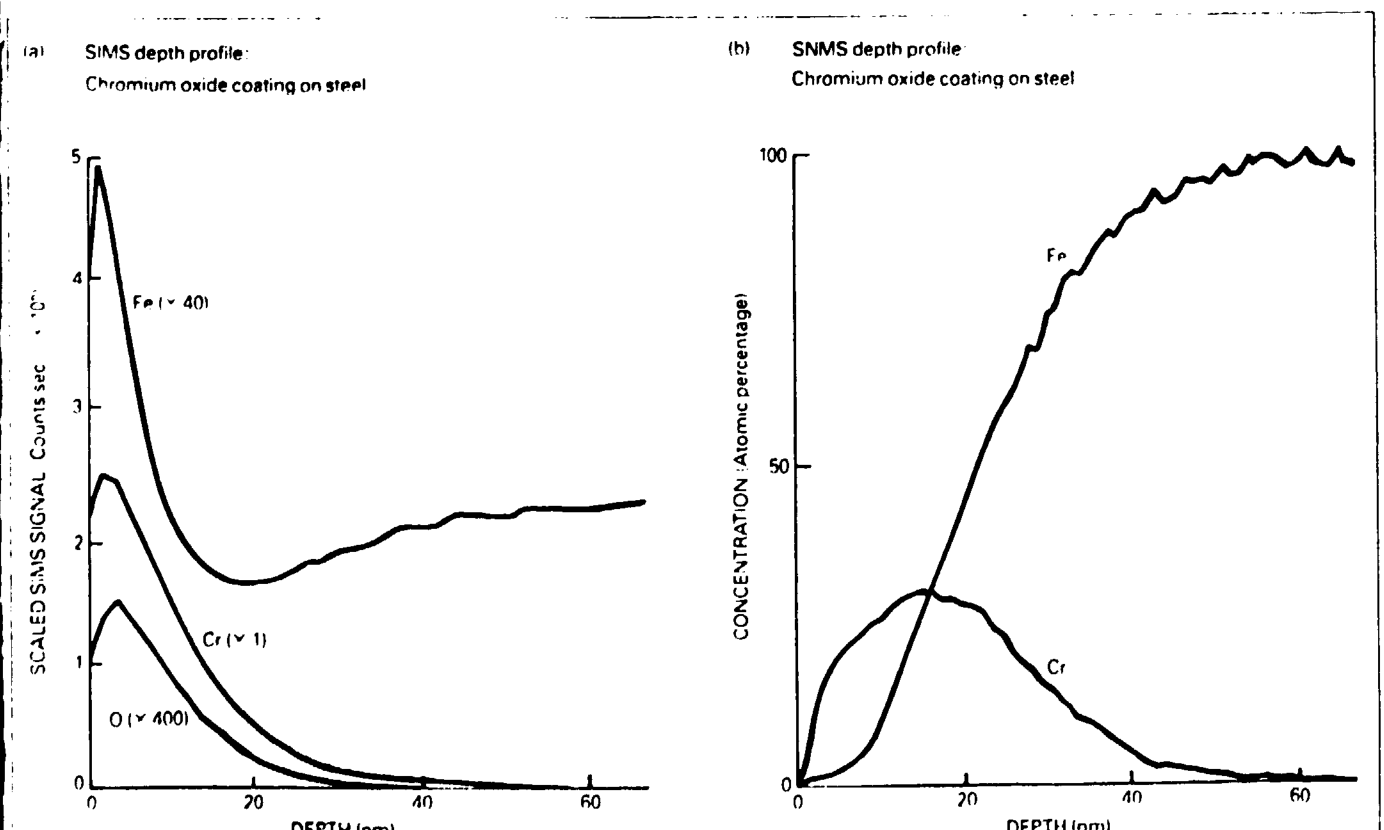
	XPS	AES	SIMS	Electron-beam SNMS
Element range	Z > 2	Z > 2	Z > 1	Z > 1
Sensitivity (per cent)	0.1	0.1	10 [illegible]	0.01
Image resolution	10 µm	20 nm	50 nm	< 1 µm
Typical speed of imaging	10 mins	20 mins	40 secs	1 min
Depth profiling	Poor	Good 2 to 3 orders dynamic range	Good 6 orders dynamic range	Good 3 to 4 orders dynamic range
Isotope sensitivity	No	No	Yes	Yes
Can be used for delicate materials?	Yes	No	Yes	Yes
Chemical information	Yes	Some	Yes	Yes
Quantification (with standards)	10	10	N/A	1

Comparison of techniques for quantitative surface analysis. (XPS denotes X-ray induced photoelectron spectroscopy and AES is electron beam induced Auger electron spectroscopy.)



Outline of an SNMS system. A fraction of material sputtered from the sample by the primary ion beam passes through a transverse electric field that removes particles leaving the surface as ions, and enters the ioniser region. Here, some of the neutral species from the surface are ionised and passes through an energy filter to the quadrupole mass spectrometer for analysis.

Comparison of performances of SIMS and SNMS techniques applied to a sample of chromium oxide on steel. The SIMS method gives a spuriously high chromium signal near the surface, because of oxygen that is present and which increases the ion yield. The second technique is not influenced by the atomic matrix. This comparison reveals the serious quantification problem that arises with SIMS.



(Source: SPECTRUM/8, No. 222/1990. Article written by Dr. John Colligon, Director, Centre for Thin m and Surface Research, University of Salford, UK)

Surface contamination measurement and control by non-destructive techniques

A technique based on photoelectron emission has been employed for non-destructive inspection of the quality of surfaces that can be used for painting, soldering, coating, plating and adhesive bonding. It can be used for quality control of semiconductor surfaces as well as monitoring defects (scratches) on metal surfaces. The experimental unit measures current due to optically stimulated electron emission (OSEE) from the surface and since an electrical signal is produced that is directly related to the surface quality, such a tool can be employed for feedback in the operation of automated processes. Experimental results show that such a technique can be used effectively in measurement of surface contaminations in wafer processing, printed circuit boards and storage media disks in electronic industry.

Introduction

Techniques to more accurately define and describe surface cleanliness levels of a part machined, processed or surface treated have been a fundamental problem in the industry. Over the last few decades, methods developed to study surface contamination problems have to led to extremely sophisticated and elaborate techniques. These techniques, usually referred to as "analytical techniques" include scanning Auger microscopy, energy dispersive X-ray analysis, scanning electron microscopy and secondary ion mass spectroscopy. Although many of these techniques are well qualified for and perform an extensive surface characterization, they are not generally suited for application in most production environments. The encumbrance arising from the inherent nature of the analytical techniques involving high vacuum results in unfavourably long test times, small sample size and high cost of instrumentation and test arrangement.

Since the explosive growth of the electronics industry, the constant need to maintain high cleanliness levels has demanded new methods to provide surface contamination measurement and control. Researchers recently have applied the basic principles used in analytical techniques to result in techniques that can be used in production environments; these techniques include laser interferometry, infrared spectrophotometry and optically stimulated electron emission (OSEE). Another technique that uses electrostatic charge decay measurement has also been attempted and is being investigated for meaningful applications in the electronics industry.

Although these techniques, laser interferometry, infrared spectrophotometry and optically stimulated electron emission offer high resolution and great accuracy, they are better suited for different applications and in a way complement each other. Laser interferometry detects point defects on the surface such as pits, scratches and dust patches precisely and provides information on their size and location on electronic substrates. This technique, however, is not suitable for detecting the presence of either organic or metallized films or their thicknesses. Infrared spectrophotometry also detects particulate contamination on the surface; in addition, this technique uses spectrometry on the contaminant to indicate its elemental composition, thereby identifying the contaminant. However, this technique cannot detect surface defects such as pits and scratches. Laser interferometry and infrared spectrophotometry both suffer from one problem, that is, the small scanning area. Optically stimulated electron emission (OSEE), however, offers large scanning area and flexible design to suit part shapes. It detects not only particulate type contamination but also organic and other metallic thin-film type contamination. In addition, this technique can be used to quantify surface treatments and to provide quality assurance in surface preparation and treatment.

Experimental procedures

Optically stimulated electron emission

The underlying principles in OSEE involve exposing the surface to high energy ultraviolet photons that are absorbed by surface atoms or molecules, resulting in the transfer of excess energy to electrons and thereby stimulating electron emission. Detection of the emitted photocurrent is the basis of the OSEE technique which can be used to characterize relative changes in the surface cleanliness. The electronic structure and the composition of the surface fully determines the OSEE yield. Hence, any contaminant on the surface, depending on its own OSEE characteristics, will either enhance or attenuate the inherent OSEE yield from a clean substrate. Figure 1 on page 79 shows a schematic diagram of the OSEE from the surface. The emitting electrons from the surface are scattered in all directions and are captured by a biased electrode not in contact with the surface. The typical current level is of the order of 10^{-10} to 10^{-12} amperes. The contamination on the surface alters the current from a clean surface by up to four orders of magnitude. Generally metallic particulates retain very high charge due to their shape resulting in large photoelectron emission currents of the order of 10^{-8} to 10^{-10} amperes; thus it is easy to detect submicron level metallic particles. Contamination in the form of organic films down to the angstrom level can easily be detected.

Figure 2 on page 79 shows a schematic diagram of the instrument developed to measure picoampere levels of electronic current from the surface non-contact in the air. A significant amount of specialized electronics is involved in keeping the signal level above the noise and in providing stability to the measurement system in order to make repeatable measurements. The measured signal can be displayed on the instrument in digital format or can be used to compare with standards to perform accept/reject decisions. In the case where a part is scanned by the instrument, photoelectron emission can be displayed in a three-dimensional image that represents the surface chemistry variations therein due to contamination or surface treatment.

Surface contamination measurement

The OSEE technique has been applied to detect contamination in various applications in the electronics industry. In the present work, effort has been targeted in the areas of wafer manufacturing and processing, storage media disk manufacturing for both flexible and hard disks and printed circuit (PC) board manufacturing. In the following section, experimental results will be presented.

Results and discussion

Wafer processing

Figure 3 on page 80 shows the scans obtained from a clean and a contaminated wafer. One should note the difference in the appearance of the two images. The area scanned was approximately 5 cm by 5 cm at a scanning speed of 300 cm min^{-1}. Table 1 on page 80 shows the range of measurements in scanning the wafers from three different batches; wafer group "A" measured consistently between 0.48 and 0.54, while group "B" produced measurements between 0.42 and 0.48 over a 25 cm^2 area. Wafers from group "C" measured in the range from 0.38 to 0.46 over the same scan area. The difference in measured values relates to the change in surface chemistry during various cleaning batch processes.

Further knowledge of the batch processes in these samples is required to interpret the data with respect to the surface chemistry effects; however, the data positively indicate that measurements on any single wafer are reasonably consistent and they do vary from process to process. It was found that typical fingerprint contamination decreased the signal to 50 per cent level on any wafer.

Storage media disk

In a study on Winchester hard disks, photoelectron emission was measured from bare aluminium disk, disk plated with magnetic medium and from plated disk with lubricant coating. The data from these tests are given in table 2 on page 80. Note that the aluminium disk gives a signal in the range from 13.7 to 14.2, which is significantly higher than the signal from the plated disk, 1.3 to 1.4 volts. The lubricant (Montedison) on the plated disk acts as contaminant and reduces photelectron emission consistently as the thickness of lubricant increases to about 40 Å; such lubricant coating will fully attenuate the OSEE signal from the disk.

Printed circuit boards

Tests were conducted on printed circuit boards at various stages of processing and manufacturing in order to determine the contamination evolving during various processes and also to evaluate the ability of the OSEE technique to characterize surface chemistry effects. The typical data are given in table 3 on page 80. Measurements on out-of-crate board vary considerably over the area. The blanking operation which left some oil stains produced a very low level of emission of about 0.05 as compared to 0.35-0.80. The photoelectron emission increased significantly to 1.48 after the board was cleaned. During another stage of water rinse after cupric chloride etch, the emission from clean and spotted areas varied from 0.7 to 0.13, which indicated gross contamination.

In another series of tests where the lubricant coating on the finished PC boards was found to be contaminated, a drastic decrease in the photoelectron emission was observed. The trend reversed when the contact pins were cleaned by simply abrading them.

Conclusions

Data presented clearly show that particulate or film type contamination can be easily detected by measuring photoelectron emission from the surface. On the hard disk, 24 Å contamination produced more than a 50 per cent drop in the measurement level.

The significance of the OSEE technique is in determining very low levels of organic or inorganic contamination. The advantages this technique offers over laser and infrared systems are that this technique is fast, reliable and the OSEE instrument can scan large areas of up to several centimetres simultaneously. (Extracted from Materials Forum (1991) 15. Article written by T. Chandra, Department of Materials Engineering, University of Wollongong, Wollongong, New South Wales, Australia and A. Aurora, Rockwell International Science Center, Thousand Oaks, California, USA)

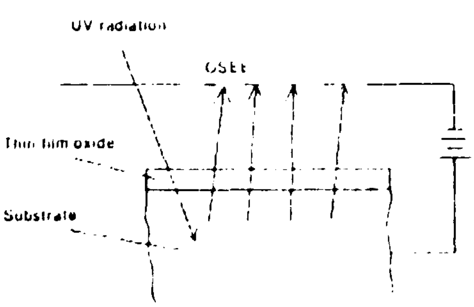


Fig. 1 Schematic diagram of the principles of OSEE

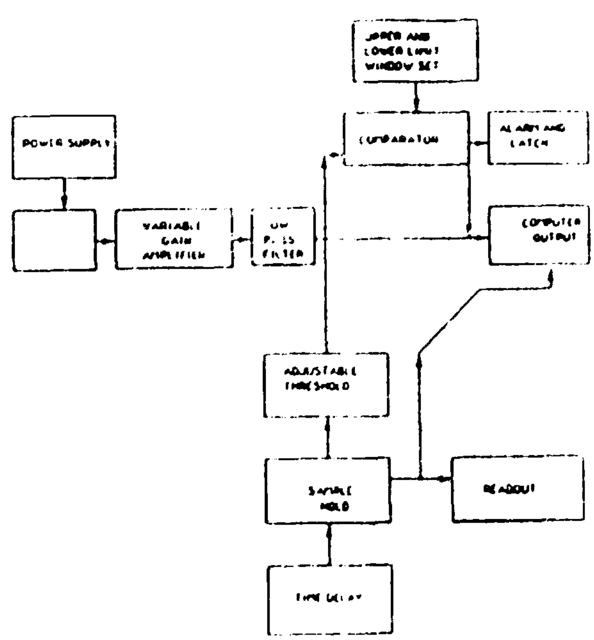


Fig. 2 Schematic diagram of OSEE r ... rument

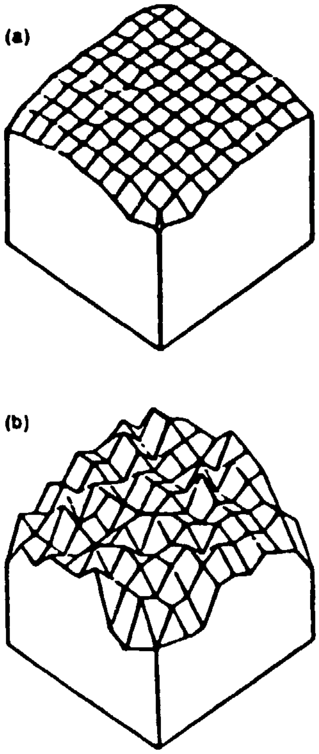


Fig. 3 OSEE scan of a silicon wafer, showing (a) clean, and (b) contaminated.

Table 1 Optically stimulated electron emission (OSEE) from wafers with different cleaning process

Wafer batch	Wafer number	OSEE
Group A	5	0 48-0 53
	8	0 49-0 53
Group B	23	0.44-0 48
	49	0 42-0 48
Group C	1	0.34-0 47
	2	0 38-0 46

Table 2 OSEE from hard disk with and without lubricant

Serial number	Disk status	OSEE
1	Aluminium substrate disk	13 7- 13 2
2	Disk plated with magnetic 1 3-1 4 medium	1 3-1 4
3	Plated disk with lubricant	
	24 25 Å thickness	0 57 0 65
	34 35 Å thickness	0 32 0 36
	46 50 Å thickness	0 13 0 19

Table 3 OSEE from printed circuit boards

Serial number	Board process status	OSEE
1	Out of crate	0 35 0 80
2	After blanking	
	Clean area	0 35
	Oil stain	0 05
3	After slurry clean	1 48
4	Rinse after cupric chloride etch	
	Clean area	0 70
	Stained area	0 13

Surface analysis

The Model 650 Scanning Auger Microscope (SAM) offers high spatial resolution and exceptional energy resolution of the Auger spectrum for rapid and precise materials problem-solving. Offering a powerful data acquisition system, the 650 features an HP-Apollo 32-bit workstation. New generation PHI windowing software includes PHI-Autocom for repetitive analysis without operator assistance and the optional PHI-Matlab for advanced data reduction and numeric analysis. The 650 SAM is especially ideal for analysis of rough surfaces. (Perkin-Elmer, Physical Electronics Div., Eden Prairie, Minnesota, USA.) (Source: Semiconductor International, June 1990)

* * * * *

Surface inspection system

The Unilux 850 is available for the inspection of highly reflective material surfaces such as steel, aluminium, paper, textiles, plastics, etc. The Model 850 makes possible the inspection of surfaces moving at up to 6,000 ft/min (1,800 m/min) in clean, misty, or dusty environments. Manufacturing operations include slitting, leveling, annealing, pickling, galvanizing, and recoiling. The Unilux light flashes 100,000 times/s, revealing defects such as random or repetitive manufacturing blemishes, including bruises, bulges, chatter marks, dimples, roll pickup, scale, and scratches. The Unilux 850 features an adjustable flash rate, a light-emitting diode display, and flood and/or spot lamps that can work in tandem. Options include a gridwork and colour filters that improve defect contrast and reduce glare. (Unilux, Inc., Hackensack, New Jersey, USA.) (Source: Materials Evaluations, 48, July 1990)

* * * * *

Surface temperature control

The Tempmatic 12000 multiwavelength noncontact infrared (IR) thermometer measures surface temperature of aluminium, brass, copper, galvanized coatings, and other surfaces that have unusual emissivity characteristics. The thermometer has applications in rolling mills, extrusion processing, forging, continuous casting, and semiconductor coatings. The Tempmatic 12000 features a temperature range of 350°-2,200°F (175°-1,200°C), an accuracy of 0.75 per cent and a repeatability of 0.25 per cent, and a water-/dust-tight sensor with visual reflex aiming. The 4-20 mA output can accommodate data loggers and computers. Options include a water-cooling system and a variety of mounting flanges and fixtures. (Williamson Corp., Concord, Massachusetts, USA.) (Source: Materials Evaluations, 48, July 1990)

* * * * *

MeV ion beam surface analyser

National electrostatics' MA1000 MeV materials analyzer provides nondestructive elemental analysis of surfaces to depths in excess of 5,000 Å. Versatile, compact system (4.2 m x 1.5 m) can perform a wide range of MeV ion-beam-based analysis techniques including RBS, PIXE, channeling, target recoil analysis, and resonant and reaction techniques with energy variable helium ion and proton beams to above 3 MeV. The instrument is fully computer interfaced for unattended data collection. (Source: MRS Bulletin, July 1991)

* * * * *

Data system for surface analysis

Advanced, comprehensive data system for surface analysis from Perkin-Elmer features a menu-driven software package which works with the 32-bit HP-Apollo® UNIX® workstation. Windowing aids tasks such as data massage, automated analysis, data reduction, and word processing. (Source: MRS Bulletin, July 1991)

* * * * *

Surface microscopy gives nanometer-scale images

A new service provides atomic-force microscopy and scanning-tunneling microscopy (AFM and STM) for materials characterization. Similar in principle to a profilometer, a stylus less than 100 nm in diameter is used to produce a three-dimensional image in detail as small as 0.2 nm. The image is said to be clear enough that surface heights can be measured directly from the readout. The analysis can be performed on any solid material with a rigid surface (film coatings, ceramics, biomaterials, metals, semiconductors and polymers, for example), and can be obtained on a per sample, daily or contract basis. (Advanced Surface Microscopy, Inc., Indianapolis, Indiana, USA.) (Source: Chemical Engineering, June 1991)

* * * * *

Technique improves surface area measurements of thin films

Improving on a decades-old method, scientists at Sandia National Laboratories have patented a highly accurate method to measure the surface area of minute samples of porous, thin films. The technique has implications for the microelectronics, gas separation, optics, and solar cell industries, which use thin films extensively. It can also be used to determine the poresize distribution of thin films, an aid in the design of highly specific chemical sensors, more effective catalysts, and gas separation membranes.

The technique combines a surface acoustic wave (SAW) device with the BET method - a surface area measurement technique named for its developers, Brunauer, Emmett, and Teller. The BET method, however, cannot discern small weight changes in materials with low total surface area, like most thin films.

Increased sensitivity comes from the solid-state SAW sensor, which uses transducers lithographically patterned on a piezoelectric substrate to launch and detect acoustic waves. These waves interact with solids, liquids, and gases on the SAW device's surface, providing information about the material's characteristics.

The BET technique is based on the premise that a porous material will adsorb nitrogen gas in measurable quantities. The surface area of the sample is calculated using the amount of absorbed nitrogen and the surface area of nitrogen molecules. Traditionally the adsorbed nitrogen was measured by weight change directly. The SAW device measures the speed of acoustic waves travelling along the surface. As nitrogen is absorbed, the mass increases and this slows the acoustic waves. This frequency change is used to determine the amount of nitrogen present.

The SAW device can measure a mass change as small as 20 picograms, while a standard BET system can only measure mass changes on the order of 1 million picograms. The SAW method can also be used to more accurately determine the range and distribution of pore sizes of thin film material. (Source: MRS Bulletin, March 1991)

* * * * *

Powder Coating Gun

Statfield has introduced an electrostatic Powder Coating Gun using "cascade in gun barrel" technology. Its special innovative features are: "foldback characteristic" of HV generator (which facilitates easy and uniform coating even in most intricate areas with safety) and a special shaping air mechanism for pattern adjustment (for easy and faster coating). The other features include hyper corona charging, direct control on powder output and velocity, tiltable container in three-piece assembly, additional small container for sample coating or small batch production. (Statfield Equipments Pvt. Ltd., A-54/55 'H' Block, MIDC, Pimpri, Pune 411 018, India/.) (Source: Popular Plastics, January 1991)

* * * * *

Coating thickness measurement

The Electromatic Equipment Co., Cedarhurst, New York, offers the Check-line® DAC-88-S1 and DAC-88-S2 coating-thickness gauges for measuring the thickness of paint, plating, anodizing, oxides, films, and clads on all metal surfaces. The pocket-sized, battery-operated gauges feature memory for up to 6,000 data points and can automatically calculate and recall for display the number of data points, mean, standard deviation, and maximum and minimum values. The data can be transferred to a printer, personal computer, or data logger. (Source: Materials Evaluation, July 199')

* * * * *

Thickness measurement of plating and coating

CMI International, Elk Grove Village, Illinois, has made available the XRX series X-ray fluorescence plating- and coating-thickness measurement system. The table-top system features computer and software packages that reduce inspection time of plated parts while improving accuracy. The system is capable of providing stable thickness readings over an extended period of time without calibration. The system features a slotted measurement chamber for inspection of multiple parts without opening the door, programmable motorized Z-axis that automatically adjusts to the correct height, software-selectable motorized collimators, pull-down menus, fail-safe shutter, light-emitting-diode indicators for X-ray and shutter power, door interlocks, a long-life Kevex 50 kV 1 mA tungsten target X-ray tube, a 16-bit microprocessor, high-resolution monitor with colour graphics display, 256 multichannel analyser, automatic drift correction for X-ray tube, and printer. The system has a three-year warranty on parts and labour. (Source: Materials Evaluation, July 1991)

* * * * *

4. TRENDS

Surface modification

Surface modification has experienced rapid growth in the past two decades as a result of the development of new processes, widespread application in the micro-electronics industry, and economical advantages.

Surface-modification techniques generally consist of surface treatments, where the composition or mechanical properties of the existing surface are altered; or the deposition of thin films or coatings, where a different material is deposited to create a new surface. Surface treatments include mechanical processes, such as shotpeening, which work-harden the surface; thermal treatments, such as laser- or electron-beam heating, which harden the surface by quenching constituents in solid solution; diffusion treatments, such as carburizing and nitriding, which modify the surface composition; chemical treatments, such as etching or oxidation, which either remove material or change the composition by chemical reactions; and ion implantation, where the surface composition is modified by accelerating ions to high energies and implanting them into the near-surface layers. Deposition techniques include traditional electrodeposition and chemical conversion coating methods, as well as newer techniques such as thermal spraying, where a plasma or electric arc is used to melt a powder or wire source, and droplets of molten material are sprayed onto the surface to produce a coating; physical vapour deposition, in which a vapour flux is created by a physical process such as evaporation, sputtering, or laser ablation; and chemical vapour deposition, where a reaction of the vapour phase species with the sample surface produces a coating.

Major incentives for developing surface modification technologies are reduced cost, improved performance, or producing unique material properties. Cost reduction may be obtained by using surface modification in lieu of substitution of a more expensive alloy for a bulk component, or by eliminating processing or fabrication steps, or processes requiring hazardous waste disposal. Improved performance and/or unique properties may be obtained by changing the surface microstructure or composition by a surface treatment or deposition of a thin film of different material. Each surface modification technique has advantages and limitations, which must be evaluated for a specific application.

Ion implantation is a process in which ions are created in a source, accelerated at voltages of several keV or MeV, and implanted into a surface. The process offers the capability to alloy surface layers completely independent of conventional metallurgical constraints such as solubility limit and diffusion rate, making low-temperature alloying feasible. It also permits surface treatment without the need to refinish the surface and does not introduce a weak interface as with coatings. The principal limitation is the shallow depth of the treatment; typically from 0.1 to 0.5 μm depending on the mass of the ion and the accelerating voltage. The type of ion available depends on the source. Gaseous species, such as nitrogen are readily available at high currents, while metal ions are more difficult to obtain and are limited to those that form volatile compounds (i.e., halides). The process requires a high vacuum and manipulation of parts with complex shapes so that all surfaces are exposed to the beam.

Naval Research Laboratory and Spire Corp. demonstrated in a Navy Manufacturing Technology programme that the technology could be scaled up to an industrial production level by cost-effective treating aircraft gas-turbine ball and roller bearings. Other research is being conducted at Oak Ridge National Laboratory in the United States, Harwell Laboratories in the United Kingdom, Toyota and Riken in Japan, and in Germany and Italy. New developments, which promise to reduce the cost and increase the flexibility of the process, include the development of a cathodic-arc metal-ion source at University of California - Berkeley and plasma-source ion implantation at the University of Wisconsin. In the latter process, ions are created in a plasma surrounding the part and the substrate is periodically biased from 10 to 100 kV to accelerate ions to the surface. All surfaces facing the plasma are implanted so manipulation of the part is not required.

Bombarding a growing thin film with energetic particles produces beneficial effects including improved film adhesion, densification of films deposited at low substrate temperatures, disruption of columnar grain growth, modification of film stress, and modification of film texture (orientation). Hybrid processes include biased sputtering, activated reactive evaporation, ion plating, cathodic-arc deposition, and ion beam-assisted deposition (IBAD). These processes combine a physical depostion source of vapour atoms with a source to produce energetic ions (and energetic neutrals), which bombard the growing film, and frequently include a source of reactive gas. IBAD provides greater control of process variables by using independent sources for ions (1-keV Kaufman) and vapour atoms (evaporative or sputtering). A low-energy Kaufman source reduces system cost and provides higher ion current density and less radiation damage (if operated at 100 eV or lower).

High-quality thin films of both pure materials and a wide variety of compounds have been deposited using IBAD. Research of the process is ongoing at Naval Research Laboratory, IBM - Yorktown Heights and San José, CSIRO - Australia, University of Arizona, University of New Mexico, University of Heidelberg, Argonne National Laboratory, and Sumitomo Electric, Nissin Electric, and Hitachi in Japan.

The process is particularly valuable for producing optical thin films where the absence of porosity is essential to prevent a shift in refractive index. Sumitomo Electric, Nissin Electric and Hitachi have patented IBAD systems including a continuous-feed system used to deposit TiN film on metal foil. IBAD potentially can have a major impact on surface modification in the next decade for high quality thin films (1 to 10 μm).

Chemical vapour deposition (CVD), used to produce a number of commercial coatings, is suitable for high-volume production at low cost after process conditions are determined. High process temperature and coating adhesion are common concerns. Plasma-assisted CVD adds excited atoms that increase reactivity, and the application of a bias to the substrate improves adhesion due to charged particle bombardment.

Plasma-assisted CVD is used to deposit diamond films on non-diamond substrates. Diamond films can be deposited from a mixture of methane and hydrogen, a discovery that spurred research to find a high-deposition-rate method. A dc discharge, and RF induced plasma, or a microwave-induced plasma also are used to produce atomic hydrogen. Deposition rates of 300 to 500 μm/hr have been reported by Japanese investigators at Fujitsu Laboratories using a dc-plasma jet.

The low friction, high hardness, high wear and erosion resistance, high thermal conductivity, and chemical inertness of diamond make it an attractive coating material for ceramic cutting tools and lenses. Research groups involved with plasma-assisted CVD include National Institute for Research in Inorganic Materials (NIRIM), Sumitomo Electric, Fujitsu Laboratories in Japan, and Pennsylvania State University, General Electric Research Laboratories, and Phillips Research Laboratories in the United States. The SDI (Strategic Defense Initiative) programme office is supporting diamond research at several US laboratories and universities with an emphasis on developing high-deposition-rate techniques for microelectronic applications.

The use of a laser-beam offers a number of advantages for surface modification. It can be used either in air or a reaction chamber, and surface heating is very rapid. Laser surface treating includes shock hardening of the surface, surface melting, local heating to cause thermal decomposition of a reactive atmosphere, rupturing bonds in a gaseous atmosphere, and laser evaporation to produce thin films. Naval Research Laboratory researchers have used laser surface melting to mix a layer of alloying elements (deposited by sputtering) into the surface region to improve the corrosion resistance of steels. A related technique involves blowing particles into a surface melted by the laser to produce a dispersion-hardened layer having excellent wear resistance. However, a disadvantage is that ripples are formed on the surface and the surface must be machined if a smooth surface is required. A similar application involves melting a normally rough and porous plasma-sprayed coating surface to seal it.

One of the newest applications is the use of a pulsed laser to "flash evaporate" complex materials and deposit a thin film; new high-temperature ceramic superconductors, for example. An excimer-laser pulse quickly vaporizes material constituents having widely varying vapour pressures and complex crystal structures so the bulk composition is retained in the deposited film. The process has produced some of the highest quality films currently available. Developed at Bellcore (Bell Communications Research Corp.), the technique is being used by other laboratories including SUNY - Buffalo, IBM - Yorktown Heights, North Carolina State University, University of Texas - Dallas, and Naval Research Laboratory, to reproduce these results. The power and flexibility of the pulsed laser technique is expected to be used widely in surface modification applications in the coming decade.

Surface modification techniques

Surface treatments	Mechanical (shot peening)
	Thermal (surface hardening-laser, electron beam)
	Diffusion (carburizing, nitriding)
	Chemical (etching, oxidation)
	Ion implantation
Thin films and coatings	Chemical (conversion coatings)
	Electrodeposition
	Thermal spraying (flame, plasma, arc spray)
	Physical vapour deposition (evaporation, sputtering laser ablation, ion-beam assisted deposition)
	Chemical vapour deposition (CVD, plasma-assisted CVD)

(Source: Advanced Materials and Processes, January 1990. Article written by Fred A. Smidt, Head of Surface Modification Branch, Condensed Matter and Radiation Sciences Division, Naval Research Laboratory, Washington, D.C., USA)

* * * * *

Surface modification continues

Continued developments are expected in surface modification of metals to improve wear, corrosion, and heat resistance, as well as in protective systems for composite materials and compliant coatings for ceramics. While much of the current activity is in the area of thermal spray, there is an ever-increasing selection of alternative coating processes. In the area of thermal treating, there is continuing progress in vacuum heat treating of metals and ceramics, ion nitriding of aluminium, and induction heating of steel, as well as extended use of the conventional HIP (hot isostatic pressing) process to some unique applications. New developments in joining technology include "intelligent" computer systems for automating arc welding, adhesives for electronic applications, and filler materials for brazing ceramics and welding duplex stainless steels.

Coatings

Thermal-spray technology and use growing rapidly

Thermal-spray technology has grown rapidly, and this growth is expected to have greater impact in gas-turbine applications as designers make use of unusual combinations of coatings and base metals. Turbine Metal Technology, Tujunga, California, USA, an industrial and aerospace coating firm, predicts that thermal-sprayed coatings also will be used as intermediate layers for further surface modification by different methods, and that free-standing parts will be made by what is now only a coating process.

This latter idea is echoed by experts at the State University of New York (SUNY), Stony Brook, who report that spray forming of near-net shapes of difficult-to-process materials is being done using the variety of available thermal-spraying materials. For example, inter-metallic compounds can be vacuum plasma sprayed to achieve dense, high-performance, free-standing forms, and thermal-sprayed composites are being considered in several applications. Of special interest will be composites such as alumina- or diboride-reinforced disilicides or aluminides.

Tafa Inc., Concord, New Hampshire, USA, expects more developments in thermal spray, including:

New coatings

- New higher velocity, lower temperature processes make it possible to apply thermal-sprayed carbides such as tungsten carbide without decarbonization, which results in harder, more wear-resistant, coatings.

- New cored-wire technology expands the possibility of simple spraying of ceramics, carbides, and materials other than conventional wires. This permits production of coatings that are even more wear-resistant because of rapidly solidified particles in the coatings.

- Wet-corrosion prevention by thermal-spray coating may be possible with some of the newer technologies such as higher velocity spraying with high-power plasmas, which yields higher deposit efficiencies, higher spray rates, and improved coating densities.

- Higher performance thermal-barrier coatings have been introduced in the hot sections of some new gas-turbine engines. The abradable ceramic coatings produce significantly higher performance by minimizing bypass flows in that section of the engine.

Shifts in process used

- In many instances, economics and reliability are forcing displacement of one process by another. For example, aircraft-engine repair and restoration, long dominated by plasma spraying, is experiencing inroads by the simpler wire-arc process because it ensures complete melting of spray material and minimizes substrate heating. It also reduces capital and operating costs and makes possible the spraying of thicker coatings.

New machines

- In the area of welding, a new variable polarity plasma machine has been introduced for welding up to 13 mm (0.5 in.) thick aluminium in one pass. Its unique feature is automatic reversal of the polarity during 10 per cent of the weld cycle to clean the weld surface prior to welding, which results in exceptional weld cleanness.

Improvements in process control

- More sophisticated automation and process controllers are becoming more widely accepted in thermal spraying.

- Control systems on the horizon appear to meet the requirements for closed-loop control of all process parameters and up to 400 mm (16 in.) of motion, along with open architecture for a later addition of positions such as vision, standoff, surface-temperature, and tracking capabilities. Use of robotic systems has become standard to increase coating reproducibility and to isolate the operator from the thermal-spray environment.

Tafa recently has introduced several innovations for improved thermal-spray processing, including the new Arc Jet electric gun system, which produces a concentrated spray stream having 49 per cent higher velocity than standard arc-spray guns, a unique pencil-shape contour, and very tight focus (less than half the standard spray area). Also introduced is their new 95MXC micromatrix-composite, high-chromium alloy arc-spray wire, which produces corrosion- and abrasion-resistant coatings having hardnesses approaching tungsten carbide that can operate in service environments to 930°C (1,700°F).

In addition, Tafa and its parent firm, Hobart, Troy, Ohio, USA offer a robotic thermal-spray cell that provides simpler control, enhanced coating quality, consistency, and productivity, and lower cost operation of plasma, wire-arc, HVOF, or combustion-spray processes.

Improvements also are being made in masking materials. For example, a halogen-free thermal-spray and grit-blast maskant has been developed by Tafa specifically for use on titanium. In addition, DeWal Industries Inc., Saunderstown, Rhode Island, USA, recently has launched a research and field-test programme to develop second-generation masking materials, with special emphasis on masking tapes for high-velocity oxyfuel (HVOF) processing. The challenge is to design and produce masking tapes that will resist particles impacting at pressures of 31 MPa (4,500 psi) and temperatures to 2,760°C (5,000°F), and replace the costly metal masks and elastomer moulds now in use.

According to SUNY Stony Brook, the use of process control is of great importance in thermal spraying, including statistical techniques that recognize the complex interplay among other thermal-spray parameters and provide clear approaches that will yield the best coating while using optimized parameters.

Reproducibility also is essential if thermal spray is to be a high-performance engineering technology, and General Electric Co. has worked with vendors to ensure that processes and materials yield the same quality coatings on gas-turbine parts from one spray booth to the next.

Databases now are being applied in the engineering of thermal-sprayed coatings. A new comprehensive interactive and menu-driven PC-based program is capable of leading a user from an application problem to the standard and recommended process and materials, and even to the name and address of the material supplier. Such an approach to application engineering, together with enabling the user to add to and modify the database, will lead to a significant expansion of the technology.

New alloys designed specifically for thermal spraying include nickel-base alloys developed by Wall Colmonoy Corp., Madison Heights, Michigan, USA, to replace cobalt-base alloys in demanding wear applications, such as valve facings and seats, in nuclear power-generating facilities. Nickel-base alloys eliminate the problem of becoming radioactive (as with cobalt-base alloys), and can be successfully used in all but the most demanding galling applications.

Advanced ceramic coatings also are being used to fight wear. For example, both Cummins Engine Co. Inc. (Columbus, Indiana, USA) and Caterpillar Inc. (Peoria, Illinois, USA) have conducted coating development and evaluation programmes sponsored by the Ceramic Technology for Advanced Heat Engines Project, which is funded by the Advanced Heat Engines Development Programme (U.S. Office of Transportation Systems) and managed through Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA. Improved wear performance at the pistonring/cylinder-liner interface in diesel engines would lower oil consumption (and reduce particulate emissions) and increase engine durability. However, improved duel-economy/emission tradeoffs needed in today's engines requires improvements to the combustion system that typically result in higher mechanical and thermal stresses on in-cylinder components, which places extra burden on their coatings. Also, the improved engine performance obtained from modern engines without increasing displacement results in higher cylinder temperatures.

The Cummins tests show that oil degradation has a major effect on wear rates, and that this effect is greater for metallic coatings than ceramic or cermet coatings. For example, wear rates for electroplated chromium were approximatley 15 times higher in used oil than in fresh, whereas chromium-oxide coatings were subject to only a threefold increase and WC/Co materials showed less than a twofold increase. Another important factor in evaluating the wear properties of a piston-ring coating material is the amount of wear occurring on the cylinder-liner counterface; for optimum engine durability, low wear rates are required of both ring and liners. Therefore, coatings suitable for abrasion resistance or cutting-tool applications are not necessarily good candidates for piston rings.

The corrosion protection afforded by thermal-spray coatings is used to advantage in several applications. For example, the US Navy has reduced maintenance downtime for the past 10 years by thermal spraying steel topside shipboard components with aluminium to control marine corrosion. Recently, the navy has gone a step further by evaluating coatings consisting of metal-matrix composites (MMCs) on shipboard components subject not only to corrosion, but also wear (e.g., chain blocks). MMC coatings such as Duralcan (silicon carbide-reinforced aluminium from Alcan Wire and Cable, Toronto, Ontario, Canada) are demonstrating corrosion resistance and wear resistance in these applications that are superior to available traditional coating systems. Other areas where the Duralcan coatings are being considered as replacements for aluminium coatings include US Marine Corps armament and offshore-platform components for the oil industry.

An entirely different property available with ceramic coatings is the capability of drawing up water. Nippon Steel, Akiyama Printing Machine Manufacturing Corp., and Tokyo Keseihin Co. Ltd., all of Japan, have jointly developed a ceramic roller in a continuous water-dampening system used in offset printing machines that lowers printing costs. The roller, which replaces a chromium-plated model, is plasma sprayed with a highly hydrophilic ceramic material, followed by a special surface treatment.

The coating ensures that the water adheres uniformly to the roller surface, thus allowing it to supply a uniform film of water to the printing plate.

The powders used in thermal spray also are important, and mechanofusion technology is being investigated by the Hosokawa Micron Group, Summit, New Jersey, as a way to improve powder performance. Characteristics of "good" powders include: constituent purity, small particle sizes, commensurate particle-size distributions of the constituents, uniform constituent blending, and reliable feeding (good flowability).

<u>Research and development projects continue on a wide range of other coating processes</u>

Improvements also are continuing in the many other types of coatings besides thermal spray. For example, The Thermoclad Co., Erie, Pennsylvania, USA, has developed Duravin ES series of PVC (polyvinyl chloride) formulations specifically designed for electrostatic-spray coating of such parts as welded-wire fencing, expanded metal, springs, castings, and stampings. Previously available vinyl powders were suitable only for fluidized-bed coating, and electrostatic spraying of thin films has been largely dominated by epoxy and polyester products.

Metal plating has taken a new twist with the introduction of a formulation that provides low friction together with high corrosion resistance on a wide range of ferrous and nonferrous substrates. Nimet Industries, South Bend, Indiana, USA, has developed NiCoTef coating, which consists of uniform dispersion of submicron-size particles of polytetrafluoroethylene (Du Pont Co.'s Teflon) throughout an autocatalytically applied matrix of a nickel-phosphorus alloy. The nonelectrolytic deposition process ensures uniform coating of internal surfaces and complex parts that would otherwise be difficult to protect and lubricate, while the uniform dispersion of Teflon in the coating ensures that lubricity is maintained throughout the life of the coating.

Boride coatings are known for their high hardness, low surface coefficient of friction, and corrosion resistance to certain acids such as HCl, H_2SO_4, and HF. Therefore, according to Materials Development Corp., Medford, Massachusetts, USA, they are used on equipment for compounding and handling ceramics, plastics, composites, and electronic materials. Recently, its Borofuse thermal-diffusion process has been used to coat nickel-base superalloys and metal-bonded carbides for oilfield valve components used in critical environments.

Diamond-like films produced by such processes as chemical vapour deposition (CVD) will become increasingly more popular because of their superior hardness, excellent lubricity, and strong bonding capacity. Unlike many other diamond-like coatings, Implant Science Corp.'s (Danvers, Connecticut, USA) Black Diamond is produced by a combination of plasma CVD and ion implantation. This results in a carbon coating and an intermixed near-surface region where carbon atoms become embedded in the atomic structure of the substrate, creating an extra-strong bond.

The various forms of vapour deposition are expected to expand their capabilities. For example, Abar Ipsen Industries, Feasterville, Pennsylvania, USA, reports that ion vapour deposition (IVD) of pure aluminum on high-strength aluminium-alloy parts is replacing anodizing, hard anodizing, and conversion coating treatments of such parts, which can be adversely affected by some of the alloying elements.

Scientists at the Naval Research Laboratory (NRL), Washington, D.C., report success in depositing high-quality coatings and thin films using two of the newer techniques - ion-beam-assisted deposition (IBAD) and pulsed-laser deposition (PLD). IBAD produces highly adherent, ductile films having low porosity and fine grain structure at deposition temperatures below those required for conventional CVD processes. Hardness and wear resistance of titanium-nitride films grown by IBAD can be controlled by the ratio of the ion-to-atom arrival rates.

NRL's studies of PLD have involved the fast, economical deposition of thin films of complex materials such as high-temperature superconductors and ferro-electrics, as well as diamond-like films and films of metals and dielectrics. Superconductor films deposited by PLD do not require further processing, and have consistently shown transport properties superior to films produced by other techniques.

Existing ion-plating systems for producing hard-surface wear films on parts such as cutting tools and gas-turbine blades can now be upgraded by the addition of a steered-arc source from Vacuum Inc., Boulder, Colorado, USA. Typical deposition rates for steered-arc cathodes are significantly higher than for planar magnetron cathodes. However, a variable-field unbalanced magnetron has been introduced by Vacuum, which also has a high deposition rate. Specific applications for it include diamond-like films and reactive-film deposition of oxides and nitrides.

Nippon Steel Corp., Tokyo, Japan, expects increased use of dry coatings on ferrous materials to improve corrosion resistance and/or appearance. Therefore, it is investigating the effectiveness of three dry-coating processes - ion plating, plasma CVD, and sputtering - for coating three types of cold-rolled stainless steels in a new, continuous-coating line. For the coating materials investigated to date - Al_xO_y, Cr, SiO_x, TiC, and TiN - Al_xO_y and Cr show the best corrosion resistance, while all five show excellent wear resistance.

Thermal treating

HIP makes headway in ceramics and composites

Established but still-growing markets for hot isostatic pressing (HIP) include densifying of investment-cast parts for aircraft gas-turbine engines and consolidation of powder-metallurgy tool steels for rerolling into various cutting-tool forms. Use of HIP to make net-shape ceramic parts also is on the rise, notes ABB Autoclave Systems Inc., Columbus, Ohio, USA. For example, new applications reported for HIPed silicon nitride include ball bearings, textile-industry thread guides, and diesel-engine parts. Other HIPed ceramics are used for nozzles in tile-glazing operations and for valve and seal components of offshore oil/gas production equipment.

HIP-bonding and densifying of clad composites is another relatively new growth market, points out Industrial Materials Technology Inc. (IMT), Andover, Massachusetts, USA. Typical applications include:

- Bonding wear-resistant faces on hot-mill rolls. Blends of hard particles in a tough, heat-resistant matrix have provided a tenfold increase in edger-roll life.

- Bonding wear- and corrosion-resistant coatings to the inside of the steel cylinders used in feeders for plastics injection-moulding and extrusion.

- Bonding tungsten-carbide wear surfaces to steel valve lifters for use in diesel truck engines.

- Bonding cobalt-base alloys and other materials to the inside surface of machine-gun barrels. The HIPed coatings are said to be fine grained, fully dense, and metallurgically bonded to the steel substrate.

- Bonding AISI 4340 alloy steel to the Ni-Cr alloy UNS N07718. The application: dual-alloy rotors for high-speed pumps used in gas-turbine engines. Bond strength exceeds 275 MPa (40×10^3 psi).

- Bonding Ni-Cr alloy UNS N06600 to ASTM A36 steel to make contacts for coolant pumps in nuclear power plants.

A future growth market, predicts IMT, is continuous-filament metal-matrix composite (MMCs). For example, HIP will be needed to bond the large panels, I-beams, and other composite components of the National Aero-Space Plane, and to fabricate superconducting wire cable consisting of as many as 20,000 Nb-Ti filaments in a copper matrix. In the latter application, explains IMT, HIP bonding prior to extrusion limits fibre damage and optimizes performance characteristics. McDonnell Douglas Corp., St. Louis, Missouri, USA, has already used HIP to make landing-gear cylinders of silicon carbide-reinforced Ti-15-3 (Ti-15V-3Cr-3Al-3Sn).

Integrated systems solve thermal-treating problems

The vertically integrated, multiprocess thermal-treating systems being developed by Vacuum Industries, a member company of Abar Ipsen

Industries, Nashua, New Hampshire, USA, are designed to help fabricators cut the cost of making ceramic and metal parts. With a Rotavac furnace, for example, ceramic companies can perform powder preparation and sintering/thermal processing in the same unit. A rotating retort tumbles powder at temperatures to 2,300°C (4,170°F), which helps maximize uniformity and minimize agglomeration. The furnace also features vacuum levels down to 10 Pa (0.075 torr) and positive pressures to 200 kPa (2 bar). Another example is Vacuum Industries' Injectavac system. It removes and condenses, in a single operation, the binders used in injection moulding of metals and ceramics. The subatmospheric-pressure method typically takes one third the time required by conventional multistep processes, while also providing good control of carbon levels, dimensions, and surface integrity. Applications to date include tungsten carbide, and high-speed, stainless, silicon, and medium-carbon nickel steels.

Ion-nitrided aluminium is hard and wear-resistant

The creation of hard, wear-resistant surfaces on aluminium alloys by ion nitriding is a promising new technology, reveals Sun Steel Treating Inc., South Lyon, Michigan, USA. By processing at temperatures below the critical, hardnesses in the 1,000 Vickers range can be obtained while minimizing distortion and size change. Potential applications include dies and wear parts. Sun Steel also notes progress in "hard-surface" nitriding, where a film of extrahard material is added to the ion-nitrided surface to further enhance the part's wear resistance. The method is said to combine the surface hardness of vapour-deposited titanium-nitride coatings with the ductility and case depth advantages of ion nitriding. Benefits include improved die break-in, and weight and cost reductions.

According to Abar Ipsen Industries, Feasterville, Pennsylvania, USA, natural gas may have advantages over electricity in fueling ion-nitriding furnaces. In a field test, a gas-fired ion nitrider attained a maximum temperature uniformity of nearly +2°C (+3.5°F) at 675°C (1,250°F) and a vacuum of 1.3 Pa (0.01 torr). Heat-up time also was significantly reduced, which translates into reduced energy and maintenance costs.

Two-zone vacuum furnaces speed tool-steel quenching

Quench time in vacuum heat treating of tool steels can be reduced by transferring the hot workload from the heating chamber to a special quenching zone, but still maintaining it under vacuum or a gas atmosphere, states All Trend Corp., Fort Lauderdale, Florida, USA. The company's Tool Treater single-chamber vacuum furnaces consist of an insulated heating module and a separate gas-quenching zone. In the "cold-wall" quenching zone, the contribution of radiation to total cooling is magnified, which increases total heat transfer. All Trend adds that hot-zone temperature uniformity is improved because, without a need to promote cooling, insulation can be beefed up. Tool Treater furnaces currently are offered with hearths of 150 x 305 mm (6 x 12 in.) to 610 x 915 mm (24 x 36 in.). Larger sizes - to 915 mm x 1.8 m (36 x 72 in.) are on the drawing board.

Induction heating takes on conventional processes

Dual-pulse induction hardening (DPIH) will be commercialized within two years for both automotive and aerospace applications, predict its developers, Allison Gas Turbine Div., General Motors Corp., Indianapolis, Indiana, USA, and Inductoheat Inc., Madison Heights, Michigan, USA. In the single-shot method, parts such as gears, pistons, and camshafts are contour hardened in less than a minute using a single workstation and power supply. Compared with conventional carburizing, DPIH is said to provide better mechanical properties and lower labour and energy costs. The solid-state power supply provides a frequency range (typically, 50 to 200 kHz) capable of handling the requirements of both preheat and final-heat stages. A 500 kW unit is suitable for parts up to 405 mm (16 in.) in diameter. Most DPIH systems incorporate a video thermography system that records heat patterns for comparison to a master.

The steel industry will take greater advantage of high-power induction heating during the 1990s, forecasts Ajax Magnethermic Corp., Warren, Ohio, USA. For example, induction heating will be used during direct hot rolling of thin slabs to equalize temperatures and keep edges from cooling. Induction will restore about 110°C (200°F) to the steel between caster and rolling mill, increasing productivity and quality. Progress also will be made in transverse-flux induction annealing by an Ajax-patented method that can readily accommodate different widths of steel sheet. In addition, the company expects continued growth in the use of induction for galvannealing and for heating steel prior to coating.

Pollution concerns foster change in metal cleaners

Stainless-steel producers and heat treaters are searching for environment-friendly pickling and descaling methods that minimize the use of mineral acids, particularly hydrofluoric acid. Kolene Corp., Detroit, Michigan, USA, reports that recent work indicates that proper molten oxidizing-salt preconditioning may enable the substitution of mild organic acids for final pickling. This is an extension of the preconditioning technology that has been used for years to reduce both the concentration and consumption of acid.

Another problem with treating stainless steels in molten salts is the introduction of water-soluble hexavalent chromium into the bath. Conventional treatment involves lowering solution pH to about 3 with acid, using sulphur dioxide or sulphite to reduce the hexavalent ion to trivalent chromium, and then adding caustic to raise solution pH and precipitate the chromium as a hydroxide. Kolene has developed a simplified method. Its 6-2-3 Reducing Agent can both reduce and precipitate the heavy metal without the use of either acid or caustic to alter pH levels.

In solvent cleaning of metal parts, water-base materials are being substituted for chlorinated vapour-degreasing solvents to reduce emissions of volatile organic compounds (VOCs) and reduce or eliminate hazardous waste. Among the available water-base solutions are Daraclean cleaners from Dewey & Almy Chemical Div., W.R. Grace & Co., Chicago, Illinois, USA. The self-cleaning, recyclable materials are designed to undercut the soil, release it from the part, and then reject it. Light oils float while heavy soils sink. Contaminants are removed from the bath by skimming and filtration. Typical applications are cleaning prior to painting, plating, or anodizing.

Grace also has developed recyclable, synthetic machining coolants that are said to be more environmentally sound than soluble oils. Compared with soluble oils, the Daracool synthetics are more bioresistant and have viscoelastic properties that facilitate filtration without having the lubricant stripped from the fluid. They also contain no chlorine, sulphur, or phosphorus.

HIP-quenching method cuts costs, saves time

In some applications, hot isostatically pressed (HIPed) parts are subsequently heat treated, usually in 600 kPa (90 psi) argon gas. This extra step often can be eliminated by performing both densification and heat treating in the HIP furnace, says ABB Autoclave Systems Inc., Columbus, Ohio, USA. The combination process, which is called HIP quenching, takes advantage of the HIP unit's high-pressure argon gas with its very high and uniform heat-transfer coefficient. Controlled cooling rates as fast as 500°C/min (900°F/min) are said to be possible by quenching at pressures to 200 MPa (29 x 10^3 psi). Reported advantages of HIP quenching include lower total cost, a shorter HIP cycle, and improved metallurgical properties due to more rapid and uniform cooling of the workload.

Joining

Welding: ideal subject for expert-system treatment

Current preprogrammed, automated welding systems use a set path and fixed parameters. They are not flexible, and may not be cost effective for many applications, particularly small batches. Overcoming these limitations is the goal of next-generation "intelligent" welding systems, such as those being developed at the American Welding Institute, Knoxville, Tennessee, USA. AWI is working on programs that automate the entire process, from planning the welding procedure to real-time weld monitoring and quality control.

Welding is an ideal application for computerized expert systems, says AWI, because it involves compliance with a complex and interrelated system of codes, specifications, tests, and inspections to ensure that welds will not fail in service. Today, this assurance is provided by a large number of engineers, designers, and welders. Problem-solving, expert-system software can help reduce the need for these expensive human experts.

One such system being developed by AWI is a computerized Welding Job Planner that functions as the welding engineer's assistant. Consisting of multiple, linked expert systems and databases, it can select electrodes, design joints, calculate preheats, perform structural-integrity and weld-material analyses, and develop welding procedures, among other tasks. Results are configured as a job description (welding schedule) that is passed on to the Welding Job Controller (also an expert system) for robotic welding. The job controller monitors various process parameters, such as voltage, wire feed, travel speed, gas flow, and temperature. In addition, deviations between the planned weld path and the actual seam location will be recorded and used in real time to adjust robot motion.

Farther down the road are combinations of expert systems and neural networks. The latter, points out AWI, excel at dealing with complex, poorly characterized problems where multiple sensor inputs must be evaluated concurrently - as in welding. Neural-network/sensor systems must be able to perform in the processing environment and provide data fast enough for intelligent controls to operate in real time. AWI and the Colorado School of Mines, Golden, for example, are developing a neural-network-based seam tracker that analyses visual-sensor data obtained during robotic welding. The intelligent seam tracker can visually guide a welding robot operating in an environment where the clarity of the visual image is reduced by as much as 70 per cent. Seam tracking using conventional image-processing techniques is computation-intensive, and ineffective when noise exceeds about 20 per cent.

Optimized welding of duplex stainless 2205

Alloy 2205 (UNS S31803) has a composition of 22 Cr, 3 Mo, 5 Ni, 0.15 N, bal Fe, and a duplex microstructure consisting of approximately 50 per cent austenite and 50 per cent ferrite. Applications of the stainless steel are said to be increasing due to its combination of strength, toughness, and resistance to both general corrosion and chloride stress-corrosion cracking. In welded construction, however, care must be taken to ensure that the matching weld metal and heat-affected zone (HAZ) also have a balanced austenite/ferrite ratio. Conventional consumables and welding procedures tend to produce structures that are largely ferritic.

Chromium nitrides precipitate, which accelerates chloride-pitting attack of the HAZ. The solution, reports Welding Products Div., Thyssen Specialty Steels Inc., Carol Stream, Illinois, USA, is to use a filler metal overalloyed with nickel (an austenite-forming element), and a relatively slow welding bead cooling rate (high heat input) to ensure adequate time for austenite to form. The predominantly austenitic microstructures that result have a higher solubility for nitrogen, which reduces nitride formation and enhances corrosion resistance. The higher-nickel-content filler metal developed by Thyssen for joining Alloy 2205 is called Thermanit 22/09. It has a composition of 0.02 C, 0.5 Si, 1.6 Mn, 23 Cr, 3.1 Mo, 9.3 Ni, 0.12 N, bal Fe. When proper procedures are used, deposited weld metal reportedly will contain 30 to 50 per cent ferrite.

Paste brazing extended to ceramic-ceramic joints

New brazing alloys in paste form have been developed by Fusion Inc., Willoughby, Ohio, USA, for making strong and ductile ceramic-to-ceramic and ceramic-to-metal joints. No metallization of the ceramic is required. The flux-free alloys, which consist of atomized filler-metal powder in a neutral binder, are recommended for use in vacuum or an argon atmosphere. Brazing temperature range is 780 to 870°C (1,435 to 1,600°F). Two alloys are currently offered: 72Ag-26Cu-2Ti and 50Cu-25Ti-25Zr.

Adhesives grip tightly and conduct electricity

Electrically conductive, pressure-sensitive adhesive tapes have been developed by Adhesives Research Inc., Glen Rock, Pennsylvania, USA, for static control, EMI/RFI shielding, interconnections, component packaging, grounding devices, flexible circuits, and other electronic applications. The tapes reportedly offer multidimensional (x-, y-, and z-axis) or z-direction-only conductivity, resistance as low as 500 mΩ, and excellent adhesive properties. Products in the ARclad 8000-series include double-coated conductive bonding tapes; conformable tapes consisting of copper foil or a semi-conductive closed-cell foam coated on one side with adhesive; and a flexible elastomeric film coated on one side with adhesive.

Silver-glass adhesives can be fired at 350°C

Conventional silver-glass paste adhesives for die-attach applications in hermetic ceramic packaging consist of lead-borate glass powder and silver flakes suspended in a solvent. The glass component has a glass-transition temperature of about 330°C (595°F), which necessitates firing at a peak temperature above 400°C (750°F). These adhesives fire at too high a temperature to be used with today's large, submicron-geometry, temperature-sensitive die, reports Ablestik Laboratories, Rancho Dominguez, California, USA. To solve this problem, Ablestik has developed a silver-glass paste adhesive with a glass component based on the vanadate-tellurate system. Its lower glass-transition temperature enables the adhesive to be fired on large die (0.45 mm^2, 0.0007 in.^{2}) at or below 350°C (660°F). The new adhesive (Ablebond 2105) does not require predrying and can be dispensed by standard die bonders. (Source: Advanced Materials and Processes, January 1991).

* * * * *

Market forecast for thermal spray coatings, powders, and equipment

Part I. Applications for thermal spray coatings

Applications for thermal spray and other coatings have been identified in 33 industrial sectors. Of the 33 industries, aircraft gas turbine applications account for 30-40 per cent of the total North American market. The remaining business is distributed over the other 32 industries. This analysis is summarized in the following table, which lists those industries currently showing the most thermal spray activity and identifies further those where there is potential for growth.

- The aircraft gas turbine industry is the most lucrative market for thermal spraying because of the widespread use of coatings from the fan to the turbine section. Some new engines have close to 5,500 parts that are thermal spray coated. Growth to the year 2000 is projected at 7-8 per cent per year on the strength of expanding applications, particularly for ceramic coatings for thermal barrier coatings (TBCs) and for clearance control, and on the basis of continuing strong demand for engines into the next decade. General Electric (GE) will remain the number one aircraft turbofan engine manufacturer, and Pratt & Whitney (P&W) will remain number two relative to dollar value. GE also will rank number one, with P&W in second place, in the number of turbofan, turbojet, and turbopropfan engines built.

- Industrial/stationary gas turbine builders will use current aircraft gas turbine experience and adapt thermal spray coatings for repair and original equipment manufacturers (OEMs) applications providing additional growth potential for current materials.

- Steam turbine manufacturers pressured to improve component life are also poised for major use of thermal spray coatings.

- The automotive gasoline engine sector is currently characterized by several OEM applications for thermal spray coatings, namely: piston rings, synchrorings, shifter forks, and oxygen sensors. The future is very bright as development activity with dielectric coatings and thermal barrier coatings suggests enormous potential for materials, equipment, and systems.

- The application of thermal spray zirconia coatings to diesel engine combustion zone components is expected to produce a market for zirconia powder approaching one million pounds/year by the year 2000. The need for nickel-alloy bonded coatings and plasma systems will also provide new business. Projections are based on the assumption that half (300,000 engines) of the yearly production rate of 600,000 engines in the year 2000 will be produced with thermal barrier coatings.

- The paper and pulp industries will expand their use of coatings for corrosion control on digesters and boilers. High velocity oxygen/fuel (HVOF) coatings are expected to perform more reliably in corrosive environments, resulting in new and broad acceptance by mill operators.

- Defence- and aerospace-related industries will continue development of plasma spray forming, taking advantage of cost-effective net- and near-net shape component fabrication, creating opportunities for vacuum plasma system (VPS) sales.

- The chemical processing industries are expected to use VPS refractory metal coatings for corrosion control, thereby creating demand for VPS systems and powders. Thermal spray polymer coatings for corrosion control of large structures and tanks looks promising, opening up business opportunities for equipment, powder, and contract shop services.

- Medical and dental companies producing prosthetic devices are expected to increase their use of porous titania coatings and hydroxyapatite coatings to promote tissue growth. Demand for commercially pure titanium powder and VPS systems will increase as a result of this activity.

- Transportation industries manufacturing automobile and bus and truck components, excluding diesel and gasoline engines, are exploring new thermal spray applications. Five applications have been identified: abradable/clearance control coatings for turbochargers; nonferrous coatings for moulding and finishing sheet metal contours; corrosion control coatings for external surfaces; dielectric coatings, such as plasma sprayed alumina, which is under development because of its high resistivity and cost-effective deposition; and thermal spray coatings as replacements for bearing inserts, pump seals, and plungers.

- Oil and gas exploration and related industries, while slow through most of the 1980s, is once again stirring and expected to create new demands. Applications targeted for growth include wear-resistant coatings applied by the HVOF process, plasma spray coatings for corrosion control, and polymer coatings for chemical resistance.

- Electric and electronic industries, including business equipment, are targeted for major growth on the strength of three applications: plasma sprayed alumina for dielectric coatings; solid oxide fuel cells, preferably spray formed yttria-stabilized zirconia components, which could spark a huge demand for zirconia powder; and tribological coatings for magnetic recording heads.

Part II, covering market profiles and forecasts for the thermal spray industry, thermal spray powders, and equipment plus business opportunities appear under the section "Marketing" on page 92. [Contributed by the Gorham Advanced Materials Institute, P.O. Box 250, Gorham, ME 04038, USA. Phone: (207) 892-5445. Fax: (207) 892-221.] (Source: Materials and Processing Report, April 1991)

* * * * *

Surface specialists unite

A new Institute of Surface Science & Technology (ISST) has developed from the Surface Analysis Group at Loughborough University of Technology. In the last ten years the group has undertaken industrial work and contract research as part of the university's own commercial company, Loughborough Consultants.

ISST has a comprehensive collection of surface analysis equipment, valued at over £2 million and funded through income from projects carried out for industry. Areas of expertise range from advanced semiconductors, high-performance metals, polymers, adhesion, adsorption, glasses and paints to building materials. (Source: Engineering, October 1990)

* * * * *

Thermal spray coating activity by industry 1/

Industry	Current activity	Growth potential to year 2000
Aircraft gas turbine	1	1
Industrial gas turbine	4	2
Steam turbine	4	3
Diesel engines	3	2
Automotive engines	5	1
Transportation	4	2
Chemical processing	4	2
Oil and gas exploration	3	3
Paper and pulp	3	3
Electric utility	2	3
Textiles	3	5
Electric/electronic	4	2
Medical/dental	4	5
Iron and steelmaking	3	5
Business equipment	4	2
Defence and aerospace	4	3

Note: Scale based on 1 equal to highest growth and 5 equal to modest growth.

1/ For comparison purposes, current activity of 5 or growth potential of 5 is higher than any of the remaining industries not listed here.

* * * * *

5. MARKETING

Paper II. Thermal spray market profile and forecast

The main elements of the existing thermal spray market consist of consumables, such as powder, wire, and rod; thermal spray guns and accessories; thermal spray systems; vacuum plasma systems; ancillary supplies; and contract coating services.

Gorham's estimated North American 1990 market is between $610-675 million. The most lucrative market segment is in coating contract services. These account for some 55-60 per cent of the total market, followed by powder supply, which is estimated at 20-22 per cent of the market. The total thermal spray market is projected to reach $1.8-2.0 billion (in 1990 dollars) by the end of the decade on the strength of a growing and expanding powder business, a strong demand for standard equipment systems and vacuum plasma systems, and a growing demand by original equipment manufacturers (OEM) for contract coating services.

Thermal spray powders market profile and forecast

The estimated present and future powder consumption is given in table 1 below. Tungsten carbide powders are available in two types: neat (unblended) cobalt-cemented tungsten carbide powder and a blend of cobalt-cemented tungsten carbide plus 30-50 per cent fluxing alloy. The former is specified for aircraft gas turbine use and will grow along with gas turbine engine manufacture. Further growth is expected as applications expand into industrial gas turbines and for steel industry rolls. Tungsten carbide blends are used primarily in the oil and gas industries; growth is projected on the basis of new oil exploration activity.

The major market for chrome-carbide powder is in the aircraft gas turbine industries. Expansion into industrial and steam turbines combined with continued use in aircraft gas turbines accounts for the projected consumption.

TABLE 1. ESTIMATED CURRENT AND FUTURE POWDER CONSUMPTION BY TYPE (Lbs/Year x 1000)

	Powder Consumption	
Powder Type	Current	Year 2000
Cobalt Cemented Tungsten Carbide[1]	600-650	1000-1100
Chrome Carbide	65-75	175-200
Stabilized Zirconia	525-600	2300-2500
High Purity Alumina	175-200	675-700
Alumina/Titania	150-175	375-400
Chromia[2]	200-225	350-375
Other Superalloys	125-150	No Projections
MCRALY's	325-375	600-625
Molybdenum Blends[3]	275-300	575-615
Special Composites (Compressor Abradable Powders)	400-460	800-850
Fluxing Alloys[4]	475-500	Moderate to No Growth
Non-Ferrous Alloys	240-250	Moderate Growth
Iron, Nickel, and Cobalt Alloys	775-825	2000-2200

[1] Includes approximately 50 000 lbs self fluxing powder as blend
[2] Does not include internal consumption by Union Carbide Coating Services
[3] Includes average 20% by weight fluxing alloy powder
[4] Does not include projections for powder used in blends noted in 1 and 3

Yttria- and magnesia-stabilized zirconia powders are projected for high growth through the 1990s on the strength of the following assumptions: continued growth in aircraft engine manufacture; the adoption of ceramic coatings by most aircraft turbine engine builders for high temperature clearance control; the thermal barrier coating with zirconia of industrial gas turbine, burner cans, and components; the production of diesel engines with plasma sprayed thermal barrier coatings on components exposed to combustion. Forecasts for the year 2000 could double if the automotive industry adopts thermal barrier coatings and if solid oxide fuel cells are manufactured with plasma sprayed zirconia.

High purity (99.8%+) alumina powder is likely to experience strong growth on the strength of demand for plasma sprayed dielectric coatings on electronic components across many industries. On the other hand, alumina/titania powders, used for wear resistance, are projected at modest growth. Highest growth is expected for high purity chromia coatings on printing rolls. However, Environmental Protection Agency restrictions on hexavelent chrome emissions could affect the use of sprayed chromia powders.

Moderate growth is projected for the MCRALY alloys (M = nickel or cobalt, chromium, aluminium, yttrium) on the basis that present gas turbine applications for corrosion-resistant coatings and for bonded thermal barrier coatings will continue. Special composite powders such as nickel/graphite and silicon-aluminium/polyester are used as gas turbine compressor abradable coatings. Growth is expected to exceed 7 per cent per year for the polyester and polyimide blends. Nickel/graphite is expected to decline, with clad bentonite coatings gaining acceptance. The use of abradable coatings for automotive turbochargers could significantly increase the demand for polyester/polyimide/metal blends.

Of the nonferrous powders, commercially pure titanium shows strong growth potential. Copper-nichel-indium will grow to meet the demand for gas turbine antifretting applications. The remaining nonferrous metals in powder form show little growth.

Nickel and iron alloys and composites used in a broad spectrum of industries for general repair and restoration are projected at 3-9 per cent per year growth in the next decade. Nickel and cobalt alloys meeting gas turbine specifications are projected at 7-8 per cent growth per year. Major growth seems likely for nickel alloy powders combined with high velocity oxygen fuel (HVOF) spraying for boiler and digester wall corrosion-resistant coatings.

Thermal spray equipment market profile and forecast

Thermal spray guns and systems are grouped into one of the following categories for purposes of this analysis and forecast:

Vacuum plasma spray systems
All other thermal spray systems

Thermal spray guns and accessories
Ancillary supplies

Vacuum plasma spray (VPS) sales have averaged about $8-10 million per year for the past five to seven years. Strong growth is predicted on the market acceptance of VPS-formed near-net shape components as a viable manufacturing process, in addition to the continued use of VPS MCRALY coatings for commercial and aircraft gas turbine corrosion applications.

All other systems sales, including plasma, electric arc, and HVOF processes are expected to grow at 15 per cent or more per year to the year 2000 on the strength of several factors: current end-users are 15-20 per cent automated and could reach 85 per cent automated by the end of the decade.

The market for thermal spray guns and accessories will experience several shifts in the next decade. Wire combustion guns sales are expected to decline in favour of electric arc guns, and the sales of HVOF guns and processes will expand as coatings replace some established D-gun niches and some established plasma applications in the gas turbine and other industries. Plasma, electric arc, and HVOF processes will form the basis of the future thermal spray business.

Including these shifts forecasts show little change in unit gun sales per year for the next five years. Many new guns will be marketed as part of a system rather than as stand alone sales, and sales of ancillary supplies will reflect the growth of the thermal spray industry at large.

Business opportunities in the thermal spray industry

Business opportunities are found in the following emerging technologies:

- Single wire electric arc
- Thermal spray forming of near-net shape components
- Titanium and nickel aluminide powder
- Polymer powders and coatings
- Centre feed plasma torches

Business opportunities also exist for suppliers of nickel alloy powders for high temperature corrosion resistance, zinc-nickel alloy powders for prevention of iron and steel corrosion, low-cost stabilized zirconia powders, and certain composites for abradable coatings. Equipment suppliers will see an increasing demand for vacuum plasma and standard plasma systems. Contributed by the Gorham Advanced Materials Institute, P.O. Box 250, Gorham, Maine 04038, USA, Tel.: (207) 892-5445, Fax: (207) 892-2210. (Source: Materials and Processing Report, May 1991)

* * * * *

Thermal-spray coating study launched by GAMI

A multiclient study of the global technology base and North American market prospects in thermal-spray coatings is due to be launched this month by Gorham Advanced Materials Institute, Gorham, Maine. According to GAMI, the current North American market is estimated at $600 million to $700 million, with annual growth over the next decade pegged at 6 to 8 per cent. Growth is being fueled by both an expansion of use in existing applications and a proliferation of new applications in traditional and emerging markets.

The final report of the seven-month study will be published in two parts: a global assessment of thermal-spray coating processes, powder and wire consumables, equipment, and competitive technologies; and the North American market profile and forecast for 1990 to 2000. (Source: Advanced Materials and Processes, March 1990)

* * * * *

Spectrum CVD announces selective tungsten process

Spectrum CVD, Phoenix, Arizona, USA, has announced what it claims is the industry's first commercially available, production-worthy selective tungsten process for CVD of high quality tungsten onto interconnects in submicron integrated circuits. Spectrum reports that the selective process is ideally suited for critical applications such as via fills, silicon contact fills and cladding of aluminium interconnects. In addition, it can save up to 75 per cent of the process costs of competitive systems. (Source: Semiconductor International, June 1990)

* * * * *

European powder coatings market to surge by 1992

Sales of thermoset powder coatings in Europe will climb sharply as new technology allows them to spread beyond merely coating metal. European consumption of powder coatings in 1987 will reach 84,670 tons, worth $379 million, and projects that by 1992, the European market will reach 128,850 tons, worth $612 million. The firm says technological advances are opening potentially vast markets in wood, glass, plastics and composites, but cautions that the powder coatings industry faces substantial market entry, as well as mergers and buy-outs.

Epoxy-polyester mixtures accounted for 41,550 tons in 1987, almost half Europe's powder coatings volume, and will reach 67,390 tons in 1992. Yet the firm sees fastest growth in the polyester-TGIC group, including carboxylated polyester resins and triglicidyl-isocyanurate. It is forecasted that consumption of these will rise from 13,190 tons in 1987 to 23,580 tons in 1992. During the same period, epoxy powder coatings should reach 24,200 tons, and polyurethane and other coatings should rise to 13,670 tons.

Sharp growth in the UK from 12,550 tons in 1987 to 21,960 tons in 1992. French volume should rise from 10,420 tons in 1987 to 19,880 tons in 1992. Italy and Germany have the largest markets, 21,820 and 20,910 tons respectively. Both should grow slowly and reach only 29,670 and 29,000 tons respectively. (Extracted from Chemical Marketing Reporter, 30 January 1989)

* * * * *

Microscopic glassy film provides high gas barrier to film and bottle surfaces

Packagers have long sought a high-gas-barrier, transparent, uncomplicated plastics material that is recyclable and economical. Technology for coating plastics with glassy silicon dioxide promises just that - clear, moisture- and oxygen-resistant monolayer films and blow-moulded bottles that can be hot-filled, microwaved, retorted, and easily reclaimed.

Four companies are involved in applying silicon dioxide (SiO_2; also known as silica) to plastics:

- Eastapac Co., a Kingsport, Tennessee, USA-based joint venture between Airco Coating Technology and Eastman Chemical Co., has a plasma-enhanced chemical vapour deposition (PECVD) process specially designed to coat polyethylene terephthalate (PET) bottles.

- Flex Products, a Santa Rosa, California, USA, venture of ICI Americas and Optical Coatings Laboratories, uses electron-beam deposition technology to coat PET and oriented polypropylene packaging firms.

- Toppan Printing Co., Tokyo, uses vacuum deposition to produce glass-coated biaxially oriented PET film.

- Toyo Ink, Tokyo, Japan, also uses vacuum deposition to produce SiO_2 coated films.

Price, coating stability are essential elements

Cost is an important determinant in the success of SiO_2 coatings. Producers will have to market their products at prices below 10 cents/6,500 cm², compared with the current range of 36 cents to 80 cents. One key to decreasing prices is increasing line speeds. A typical state-of-the-art metallizing line runs at 460 to 550 m/min, while pilot SiO_2 coating lines run only from 25 to 90 m/min.

Another key to successful commercialization is protecting the SiO_2 coating. Some SiO_2-coated films lose up to half of their barrier in handling, because the coating is so fragile.

Despite these problems, silica coating offers a positive response to one of the major issues facing the packaging market: coping with environmental attacks and solid-waste problems. SiO_2-coated films and bottles can be recycled in existing PET reclaim programs; because SiO_2 content is minuscule, pure-PET recycling streams are not contaminated.

SiO_2-coated films will find most use in retort pouches and lidding for shelf-stable, microwaveable meals. SiO_2-coated bottles and containers can replace glass in some applications, providing economical shipping and less breakage.

Ultra-thin coating provides better barrier properties

Eastapac uses its plasma-enhanced deposition process to apply very thin layers of glass (below 2,000 angstroms, or less than 0.2 micron) onto PET bottles. Coatings are tradenamed QLF, an acronym for quartz-like film. Eastapac's process employs organosilicons as a non-toxic liquid process monomer, rather than silane gas, which ignites spontaneously. Because it is a cold-temperature process, it is non-destructive to plastics. Unlike sputtering, which is line of sight, PECVD is multidirectional, an advantage in coating three-dimensional objects.

The process begins with the evacuation of a coating chamber. A three-component gas mixture (organosilicon monomer, oxygen, and helium) is fed into the system. The primary raw material, organosilicon, is vaporized, metered, and combined with the other process gases as it is bled into the coating chamber. Once the required pressure level and gas mixture are attained, the plasma is ignited with power coupling devices. The ignited plasma generates a chemical reaction that initiates a polymerlike growth of quartz on the bottle.

According to Eastapac, the technology allows companies to produce containers in compliance with food-packaging regulations. It adds that enhanced barrier properties of QLF-treated PET extend packaging shelf life, which is of particular interest to oxygen-sensitive food and beverage products such as ketchup, beer, fruit juices, and baby formulas.

Another opportunity exists for PECVD in PVC extrusion blow moulding. Because PVC has been especially subject to environmentalist attack, some extrusion-blow users of the material have considered switching to PET stretch blow moulding, which produces an inherent barrier through orientation of the PET molecules. However, equipment investment cost is a deterrent, and PET loses some of its barrier properties in extrusion blow moulding. QLF coating obviates the need for machine investment by enabling achievement of desired PET barrier properties on bottles from existing extrusion-blow equipment.

Oxygen barrier testing was performed on three types of QLF-coated and uncoated PET containers - a 32 oz. widemouth jar, a 32 oz. ketchup bottle, and a 16 oz. beverage bottle. QLF coatings were about 1,000 angstroms thick. In the tests, coated bottles demonstrated barrier protection up to 10 times that of uncoated containers, Eastapac claims. Water vapour transmission rates were improved up to three times.

One of the key suppliers of coating equipment, Leybold, which has its headquarters in Hanau, Germany, has further developed technology to produce packaging films coated with silicon oxides for greater protection. These oxides have still higher barrier properties than SiO_2 but are just as clear. Leybold supplies equipment with electron beam evaporators as coating sources.

Similar performance is claimed for electron-beam and vacuum-deposition methods of applying SiO_2 to film. For its Transpak films, Flex Products uses the electron beam method, in which a focused stream of high-energy electrons heats material contained in a crucible. The process is similar to aluminium deposition, but it allows for the higher melting temperatures and pressures required by the glassy coating material.

Clear Transpak films are claimed to be invisible to microwave energy and effective barriers to moisture and oxygen. Targeted applications include microwaveable food packaging, overwraps, medical packaging, and such surgical-care items as IV and colostomy bags.

Toppan Printing and Toyo Ink, worked together to develop a vacuum deposition technology that produces glass-coated biaxially oriented PET film. The firms have since separated and offer similar films under different names. The process heats and vaporizes SiO_2 onto the base material under vacuum; it is said to achieve thin, uniform coatings without defects. (Extracted from Modern Plastics International, June 1991)

* * * * *

6. PUBLICATIONS

Coating inspection

The National Association of Corrosion Engineers (NACE), Houston, Texas, has published the NACE Coating Inspector's Logbook (No. 51279) for recording complete and detailed information for individual coating projects. Written by NACE coating inspector Arthur Marshall, the book (152 pages, hardbound) is to be used as a permanent record of an individual coating project and as a complement to the NACE coating inspection daily report sheet.

The book has four sections. The general project data section includes site safety information, pre-inspection reporting forms, client and site information forms, and a quality control checklist. The project records and reports section includes forms for production records, materials, and equipment records; abrasive sieve test reporting, and warranty inspection. The inspector's daily log provides space for daily comments by the inspector. The reference data section includes reference materials for quick technical support. Tables on surface preparation methods and standards, abrasive/profile comparisons, formulas, temperature conversion tables, dew point temperatures in Fahrenheit degrees, and 24 pages for notes are included.

* * * * *

Materials characterization

Materials Research Society (MRS), Pittsburgh, Pennsylvania, USA, has published Defects in Materials, vol. 209 in the MRS Symposium Proceedings Series (ISBN: 1-55899-101-8). The book (hardbound or microfiche, 921 pages), ed. P.D. Bristowe et al., contains 142 papers covering defects in metals, theory and simulation of defects, point and line defects, defects in semiconductors, interfaces and surfaces, and defects in oxide superconductors. Contributors describe investigations on point, line, and planar defects in metals, alloys, polymers, ceramics, amorphous metals, semiconductors, superconductors, composites, and intercalated fibres. Most of the research in the book is experimental, but a significant part focuses on theory and simulation.

* * * * *

Surface modification technologies - an engineer's guide

Edited by T.S. Sudarshan, 1989, 509 pages, illustrated. Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016 or Hutgasse 4, Postfach 812, CH-4001 Basel. ISBN: 0-8247-8008-4.

This guide:

- Provides many examples of practical applications - furnishing readers with helpful guidelines for resolving on-the-job problems.
- Outlines principles associated with individual processes plus physical properties associated with these surfaces - examining the different areas to which these techniques can be applied.
- Details the work of eight leading experts - supplying an in-depth assessment of surface modification technologies from the viewpoints of those experienced and currently active in the field.
- Uses easy-to-understand language - facilitating communication among the numerous scientists and engineers involved in surface technology, including those working with micro-electronics and communications, power plants, transportation and heavy duty machinery, and materials for applications in medicine.

Contents: Composite Coatings, Indira Rajagopal; Chemical Vapour Deposition, Deepak G. Bhat; Ion Beam-Based Techniques for Surface Modification, Hilary Solnick-Legg and Keith O. Legg; Ion Beam Sputtering Techniques, John Keem; Plasma Techniques, Sidney Dressler; Surface Alloying Using Lasers, P.A. Molian; Electron Beam Coating, Siegfried Schiller, Ullrich Heisig and Peter Frach; Boriding and Diffusion Metalizing, Ruth Chatterjee-Fischer.

* * * * *

Surface stability

Edited by T.N. Rhys-Jones. ISBN 0 901462 61 6, September 1989. Order Code 448 294 p. 210 x 148 mm. The Institute of Metals, 1 Carlton House Terrace, London SW1Y 5DB. Tel.: 071 839 4071, Telex 8814813, Fax.: 071-839-2078 or The Institute of Metals, North American Publications Center, Old Post Road, Brookfield, Vermont 05036, USA. Tel.: (802) 276 3162, Telex: 759615 Brookfield UD, Fax.: (802) 276 3837.

This volume presents a practical overview of current methods of characterizing high-temperature materials. The problems encountered by materials used in the gas turbine section of the modern aero engine and the range of materials used in land power generation equipment are discussed. Methods of surface protection and corrosion control are outlined and the importance of the need for extensive materials evaluation before service use are highlighted with particular reference to the selection of suitable test methods and the elucidation of degradation mechanisms. The relative merits of various test techniques used to evaluate the oxidation, corrosion, erosion, and wear characteristics of high temperature materials, and the techniques available for the chemical and structural analysis of materials and their degradation products, with reference to the behaviour of high temperature materials are also described.

* * * * *

Material concepts in surface reactivity and catalysis

Academic Press, 1250 Sixth Ave., San Diego, California 92101, USA. 255 pages, 1990, ISBN: 0-12-759940-1.

Henry Wise and Jacques Oudar present the advances of the last 25 years on the complex processes occurring on solid surfaces during catalysis, corrosion, adhesion, field deposition, and related phenomena. The physical and chemical properties of the surface in a reacting system are the main topics of this book. The material includes some of the basic principles of surface science and is useful to the student in materials science, solid-state chemistry, and catalysis as well as to the specialist engaged in research.

* * * * *

Chemically modified surfaces in science and industry

Donald E. Leyden and Ward T. Collins.
Proceedings of the Chemically Modified Surfaces Symposium held in Fort Collins, Colorado, USA. June 1987. 686 pages.
Gordon and Breach, 1988.

The proceedings of the Chemically Modified Surfaces Symposium are organized into four technical chapters: biomaterials, catalysis, surface characterization and surface modification in electronics. Two additional chapters present a wide variety of papers from the general and poster sessions of the symposium.

* * * * *

Engineered materials for advanced friction and wear applications

Edited by F.A. Smidt and P.J. Blau,
ASM International. 262 pages. 1988.

Description of wear characteristics of coatings, surface modifications and alloys.

* * * * *

Surface modification technology explored in three-volume series

This comprehensive series, edited by T.S. Sudarsham and D.G. Bhat, provides detailed information on the many diverse technologies used for surface modification.

Surface modification technologies.

Phoenix, Arizona. 1988.
327 pages, illustrated, index, hardcover.

This first volume is a comprehensive update and review of techniques being developed and applied in this field today. The procedures examined range from composite coatings by electrochemical techniques to more advanced techniques such as ion implantation, electron beams, lasers, plasma, physical and chemical vapour deposition processes.

Surface modification technologies II.

Chicago, Illinois. 1988.
Approx. 356 pages, illustrated, index, hardcover.

This edition expands on the information presented earlier and introduces several new technologies. Attention is also given to procedures for the characterization of coatings and surfaces. Specific topics include: conventional and plasma-assisted chemical vapour deposition, several ion and electron beam deposition techniques, laser surface modification techniques and electrochemical techniques for depositing composite coatings.

Surface modification technologies III

Neuchatel, Switzerland. 1989.
Approx. 1,000 pages, illustrated, hardcover - 1 volume.

The latest in surface modification techniques are explained in this third volume of the series. Topics of discussion include: diamond coatings, industrial electroplating, coatings for space applications, electrospark alloying, metallizing and electron beam applications.

For the above three books, please contact:

TMS, Attn.: Book Order Department,
420 Commonwealth Drive, Warrendale,
Pennsylvania 15086, USA. Tel.:
(412) 776 9000.

In Europe, contact: STM Distribution Ltd.,
Enterprise House, Ashford Road, Ashford,
Middlesex, TW15 1XB, England. Tel.:
(0784) 241636.

In Japan, contact: Neutrino, Inc.,
Takahashi Building, 1-44-3 Fuda, Chofu-Shi,
Tokyo 182, Japan. Tel.: 0424 84 5550.

In Australia, New Zealand, Papua New Guinea,
contact: D.A. Book Pty., P.O. Box 163,
Mitchum, Victoria 3132, Australia. Tel.:
(03) 873 4411.

* * * * *

Deposition technologies for films and coatings - developments and applications

By Rointan F. Bunshah, et al.

This book presents a unique collection of knowledge on deposition technologies. It breaks new ground in the extensive coverage for those processes used in high technology, covering the entire spectrum from thin films to bulk coatings. The contents deal with various technologies for the deposition of films and coating, and the resulting microstructure, properties and applications. Written by leading researchers in the field, this book will be useful and needed by scientists, engineers and managers working in industries associated with coatings for optical, electrical, mechanical and decorative applications.

* * * * *

Handbook of plasma processing technology - fundamentals, etching, deposition, and surface interactions

Edited by S.M. Rossnagel and J.J. Cuomo, both of IBM Thomas J. Watson Research Centre, and W.D. Westwood, Bell-Northern Research.

This book is a comprehensive overview of the technology of plasma-based processing, written by an outstanding group of 29 contributors. Plasma processing currently provides the most practical way to carry out many of the process steps involved in integrated circuitry. The advantages provided by plasmas, plasma fundamentals, and a broad range of plasma processes, relevant to the deposition and etching of thin films for micro-electronics and other fields, are described in this handbook.

* * * * *

Mechanisms of reaction of organometallic compounds with surfaces

Edited by D.J. Cole-Hamilton, University of St. Andrews, Scotland, UK and J.O. Williams, University of Manchester Institute of Science and Technology, UK.

This unique text brings together the current data available on the mechanisms of industrially important organometallic compound surface reactions. Particular emphasis is placed upon the mechanisms of metallization, metalorganic vapour phase epitaxy (MOVPE) by thermal and photochemical routes, metalorganic molecular beam epitaxy, and metalorganic magnetron sputtering. Chapter topics include: photo-induced organometallic processes in semiconductor surface technology, reactions of Group V metal hydrides with surfaces; monitoring chemical reactions in metalorganic chemical vapour deposition (MOCVD); anisotropic growth of GaAs in MOVPE; gas source molecular beam epitaxy; the mechanisms of the photochemical growth of cadmium mercury telluride.

* * * * *

Chemical vapor deposition for microelectronics - principles, technology and applications

By Arthur Sherman, Varian Associates Inc.

This text present an extensive, comprehensive study of chemical vapour deposition (CVD). Understanding CVD requires knowledge of fluid mechanics, plasma physics, chemical thermodynamics and kinetics, as well as homogeneous and heterogeneous chemical reactions. This text presents these aspects of CVD in an integrated fashion, and also reviews films for use in integrated circuit technology. Because of the inordinate complexity of CVD, most studies of the subject have been empirical.

* * * * *

Proceedings of XV International Conference in Organic Coatings Science and technology

Technomic Publishing AG, Missionsstrasse 44, CH-4055 Basel, Switzerland.

Now in its fifteenth year, the International Conference in Organic Coatings Science and Technology has become well established as a major forum for the presentation of the latest coatings technology.

Advances in Organic Coatings Science Technology - Volume 13 contains the complete illustrated texts of 36 new reports presented at the July 1989 international conference.

The authors of the reports represent the leading international coatings companies and research organizations including AKZO, E.I. du Pont de Nemours & Co., Bayer AG, Sandoz Ltd., ICI, Kansai Paint Co., American Cyanamid Co., Hitachi Chemical Co. Ltd., DSM Resins B.V., Nippon Paint Co. Ltd., Dow Chemical Co. and BASF.

Richly illustrated by over 400 figures and tables, the reports include information on recent developments in automotive coatings, advances in silicon and fluoropolymer coatings, test methods for accelerated ageing and durability, evaluation of water-based coatings, coatings for corrosion protection, and novel coatings based on a variety of polymeric systems.

Volume 13 will provide those involved in coartings R&D with a valuable new compilation of information.

* * * * *

PVD/CVD coatings

New brochure highlights chemical vapour deposition (CVD) and physical vapour deposition (PVD) coating capabilities and equipment from Multi-Arc Scientific Coatings Div., Andal Corp., Rockaway, New Jersey, USA. The company specializes in CVD and PVD titanium nitride (TiN) coatings.

* * * * *

Engineering adhesives

Dymax Corp., 51 Greenwoods Road, Torrington, Connecticut 06790, USA.

General catalogue reviews company's engineering adhesives and light curing systems for a wide variety of end-use applications. Material selection charts list adhesives, sealants, coating materials and potting formulations. Text explores curing with pre-applied activators, exposure to long-wave ultraviolet light for on-demand bonding, and accessories such as UV curing lamps and systems.

* * * * *

Coating selector guide

Master Bond Inc., 154 Hobart St., Hackensack, New Jersey 07601, USA.

Four-page application/selector guide gives data on high temperature resistant adhesives/ sealants and coatings. Silicones, one- and two-component epoxies, ceramics, and hydrocarbon systems are listed with information on viscosities, cure schedules, gel times, operating temperatures, strength, and performance characteristics. Applications are noted for all grades, including specialty insulating or conductive types.

* * * * *

Coating powders for electronics

ICI Fiberite Moulding Materials, Concord Pike & Murphy Road, Wilmington, Delaware 19897, USA.

Series 7000 and 7500 electronic grade coating powders are said to exceed existing performance needs for thermal shock, heat stability, and moisture resistance in passive component applications. This eight-page brochure discusses both series in terms of performance features, test results, physical properties, chemistry, and handling. Many applications are noted. Standard and special colours, cured and electric values, laser-markable characteristics, and compatibility with coating equipment also are discussed.

* * * * *

Advances in surface and thin film diffraction

Editors: Ting C. Huang, Philip I. Cohen, David J. Eaglesham.
Materials Research Society,
9800 McKnight Road, Pittsburgh,
Pennsylvania 15237, USA. 1991, hardcover or microfiche, 48 papers, 369 pages. ISBN: 1-55899-100-X. Order Code: 208B.

Highlights recent advances in X-ray, electron, and atom diffraction techniques as well as the vitality of studies of surfaces, absorption and phase transformations, epitaxial, superlattices and strained layers, and thin films and buried interfaces. Topics: electron diffraction studies of surfaces; surface ordering and phase transition; diffraction studies of epitaxy; sensitivity of diffraction to lattice parameter; advances in technique.

* * * * *

Plasma-spray powders

Stellite Coatings Div., Deloro Stellite Inc., a subsidiary of Thermodyne Industries Inc., St. Louis, Missouri, USA, offers a four-page brochure covering the plasma-spray process, applications, a list of powder chemical compositions, and a chart that cross-references Stellite grades with competitive grades.

* * * * *

Wear-resistant coating

Four-page brochure from Wear Management Services Inc., Alquippa, Pennsylvania, USA, describes characteristics and applications of Tribolite, a patented surface-engineering material designed to resist wear, scoring, galling, and seizing. Procedures used in the application of the material by thermal spraying and by spatula are covered.

* * * * *

Additives for water-based coatings

Editor D.R. Karsa.
Cambridge: Royal Society of Chemistry, 1990.
Pp v plus 283. ISBN 0 85186 607 7.

* * * * *

Advanced surface coatings

Innovation 128, 24 rue du Quatre Septembre, 75002 Paris, France. 156 pages. 1989.

This report provides a comprehensive review of thermal spraying, chemical vapour deposition, physical vapour deposition, the Toyota diffusion process, and ion implantation. For each technique, the report details the technology, compares the principal advantages and disadvantages with those of other coating techniques, and illustrates major applications. Technical and commercial limitations, such as problems relating to process control and quality assurance are examined.

* * * * *

Physical Chemistry of Surfaces

Fifth edition by Arthur W. Adamson.
John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10158, USA. 1990.
777 pages.

* * * * *

Laser- and particle-beam chemical processes on surfaces: symposium held 29 November - 2 December 1988, Boston, Massachusetts, USA

Edited by A. Wayne Johnson, Gary L. Loper and T.W. Sigmon. Pittsburgh: Materials Res. 1989, pages 649. Materials Research Society Symposium Proceedings; Vol. 129. 620'.44 TA418 89-27866. ISSN: 0272-9172; ISBN: 1-55899-002-X

Contents, abridged: some recent results of fundamental studies of beam-induced surface processes. Thermal and photolytic decomposition of adsorbed cadmium and tellurium alkyls. Photochemical vapour deposition of aluminium thin films. Laser-indused chemical vapour deposition of high purity aluminium. Selected area growth of GaAs by laser induced pyrolysis of adsorbed Ga-alkyls. Laser patterning of II-VI epitaxial thin films. Low temperature deposition of hard, amorphous diamond-like films by laser evaporation. UV enhancement of surface catalytic polymerization of ethylene. Laser-induced atomic chlorine etching of silicon. Laster induced chemical etching of composite structure of ferrite and sendust. Laser-induced reactive evaporation and condensation. Mass and energy analysis of ionic fragments from photo-ablation of polyimide. High current density electron beam induced desorption. Indices.

Note: Eighty-eight papers presented at a symposium "devoted to a discussion of recent advances in the use of photon, electron, and ion beams to induce or enhance chemical reactions on surfaces". Beam-induced materials processing and applications provide a focus. References included. For research-level collections.

* * * * *

"Particles on surfaces" Vol. 1

Editor K.L. Mittal.
New York/London, Plenum Press. 1984.
ISBN 0 306 43030 4.

This volume contains the proceedings of the Symposium on "Particles on surfaces: detection, adhesion, and removal" held under the auspices of the Fine Particle Society in San Francisco, California, 28 July - 2 August 1986.

The study of particles on surfaces is extremely important in many areas (ranging from micro-electronics to optics to biomedical). The particulate contamination on surfaces is undesirable from functional, yield, and reliability points of view. This symposium was organised with the following objectives in mind: to bring together active practitioners in this field, to provide a forum for discussion of the latest research and development activities in this area, to provide opportunity for cross-pollination of ideas, and to highlight topics which needed intensified effort.

This volume contains a total of 28 papers divided into four sections as follows: general papers; particle-substrate interaction and particle adhesion; particle detection, analysis, and characterization; and particle removal.

* * * * *

Metallic and ceramic coatings: production, high temperature properties and applications

M.G. Hocking, V. Vasantasree and P.S. Sidkey. John Wiley & Sons, Inc., 605 Third Avenue, New York, New York 10158, USA. 1989 xv plus 670 pages. ISBN: 0-582-03305-5.

* * * * *

Advancing surface mount technology: an IFS executive briefing

Edited by Stephen McClelland. NY: Springer-Verlag, 1988. 218 pages. 621 3815'1 TK7874. ISBN: 0-387-50090-1.

Contents: Surface mount technology design. Surface mount technology manufacture. Testing, rework, quality and reliability. Surface mount technology - the challenge to management.

Note: Surface mount technology (SMT) is a means of attaching electronic components to printed circuit boards. SMT allows for greater miniaturization and lower cost manufacturing, and has been heavily utilized in Japan. This work is an overview of the current state of the technology and issues relating to its implementation. SMT encompasses not only technological processes but also management and design processes, and utilization of computer-aided engineering. Chapters by many authors provide an international perspective on SMT technology and management. For electronics and manufacturing collections.

* * * * *

Surface mount technology: principles and practice

Ray P. Prasad. NY: Van Nos Reinhold, 1989. 610 pages. 621.381'74 TK7868 88-25885. ISBN: 0-442-20527-9.

Contents, abridged: Implementing surface mount technology. Surface mount components. Substrates for surface mounting. Surface mount land pattern design. Adhesive and its application. Metallurgy of soldering and solderability. Soldering of surface mounted components. Quality control, repair, and testing. Index.

Note: Recent advances in miniaturization of elctronic products are largely a result of surface mount technology (SMT). The text presents basic principles and practice of SMT, concentrating on equipment features and selection criteria. Organized into three sections, presents an over-view of SMT and implementation strategies, design considerations, and manufacturing procedures. Appendices include information on SMT standards and a glossary of terms. For electronic engineering and manufacturing collections.

* * * * *

Surface mount technology: materials, processes, and equipment

Carmen Capillo. NY: McGraw, 1990. 347 pages. 621.381'531 TK7868 89-12699. ISBN: 0-07-009781-X.

Contents: Surface mount components. Surface mount design. Assembly. Soldering and cleaning. Testing SMAs. Index.

Note: Surface mount technology (SMT) allows for the highest electronic densities and performance levels, and has evolved from initial usage in the military and aero-space industries to all industries where electronics play a role. Describes the variety of challenges inherent in SMT, as well as the technologies developed to counter them. Will be important reading for all involved in electronic engineering, from design through quality control.

* * * * *

Surface alloying by ion, electron, and laser beams

Edited by L.E Rehn, S.T. Picraux, and H. Wiedersich. ASM International, Metals Park, Ohio 44073, USA. Tel.: (216) 338-5151. Fax.: (216) 338-4634.

Focuses on the surface alloying of metals by these directed energy sources and the accompanying microstructural and property changes induced by exposure to them. The book is based on presentations by 17 internationally-recognized experts in their fields at a 1985 ASM materials science seminar on this subject. The first chapter is an introduction and overview of the subject followed by three chapters that discuss how the input energy is dissipated, namely as heat and via atomic displacements, plus recent advances in understanding the recovery process, specifically resolidification and defect annealing. Microstructural changes that occur subsequent to recovery are covered in the next three chapters followed by three chapters that discuss the effects of these changes on materials properties. The final three chapters focus on the industrial applications of these surface alloying techniques, including the surface alloying of large and complex shapes. The editors suggest this book would be of value to researchers wishing to gain an overview of a new field, as a general reference for those already working in this area, and as a textbook for a gradua e lev l materials science course.

* * * * *

Paint and surface coatings: theory and practice

Editor R. Lambourne. Chichester: Ellis Horwood 1987. Pages 696. ISBN: 085312-692-5.

* * * * *

Corrosion-resistant coatings technology

Ichiro Suzuki.
NY: Dekker, 1989. 266 pages.
620.1'1223 TA418.74 89-33780
ISBN: 0-8247-8150-0.

Contents: Principles of corrosion protection by coatings. Cathodic control protection by sacrificial metal coatings. Anodic control protection by noble metal coatings. EMF control protection by noble metal coatings. Mixed control protection by conversion coatings. EMF control protection by organic coatings. Index.

Note: Emphasis is on the protective qualities of coatings for many environments. In the past 20 years technology for corrosion-resistant coatings has advanced; present text draws upon much of the work already done in corrosive science. Environments in which water or moisture plays a part are dealt with in particular. For students, engineers, and others interested in corrosion protection.

* * * * *

Handbook of thin film deposition processes and techniques

Editor K.K. Schuegraf.
Park Ridge (USA), 1988. 413 pages,
24.5 x 16 cm, bound, English.

This book was written by 23 experts on coating technologies. It therefore represents a sort of manual which first gives a general survey and then deals with various main groups in 12 chapters.

* * * * *

Thermal spray: advances in coating technology: conference proceedings

Edited by David L. Houck.
Metals Park: ASM, 1988. 426 pages.
620 TS655 87-073419. ISBN: 0-87170-320-3.

Contents, abridged: Materials processing and characterization. Equipment and process. Wear. Coating characterization and testing. Applications. Panel on finishing of coatings. Corrosion. Ceramic coatings.

Note: The proceedings of the first National Thermal Spray Conference organized by the Thermal Spray Division of ASM International. Reviewed prior to publication, papers address the variety of applications, materials and techniques in the field of thermal spray. Discusses applications ranging from aerospace turbine engine components to farm machinery, materials from metals to ceramics; and processes from arc, flame, and plasma spraying in air to hypervelocity spraying and robotic control. Material accessible to neophytes and experienced thermal sprayers.

* * * * *

Surface mount technology: principles and practice

Ray P. Prasad. xxii plus 610 pages.
Van Nostrand Reinhold, 115 Fifth Avenue,
New York, New York 10003, USA. 1989.

* * * * *

Solids and surfaces: a chemist's view of bonding in extended structures

Roald Hoffman. x plus 142 pages.
VCH Publishers, Distribution Center,
303 N.W. 12th Avenue, Deerfield Beach,
Florida 33442-1705, USA. 1989.

* * * * *

Solvay conferences on surface science: invited lectures and discussions

Editor: F.W. de Wette.
xii plus 501 pages.
Springer-Verlag, New York, 175 Fifth Avenue,
New York, New York 10010, USA. 1988.

* * * * *

Protective coating advantages

General Magnaplate Corp., 1331 Route 1,
Linden, New Jersey 07036, USA.

The use of a protective coating that prevents most molten metals from adhering to its surface is explored in Brochure 26. Discussion also notes other advantages such as preventing adhesion of all common soldering materials to soldering equipment and serving as a barrier for weld-splash adherence. Surface requirements, coating physical properties, performance at temperatures over 1,500°F, and thicknesses under 0.0003 in. are described.

* * * * *

Catalysis at Surfaces

By Ian M. Campbell.
Chapman & Hall, 29 West 35th Street,
New York, New York 10001. 1988. 250 pages.

* * * * *

7. PAST EVENTS AND FUTURE MEETINGS

1991

12-15 March Adelaide, Australia	International Conference on Surface Engineering: Practice and Prospects (Techsearch, 183 Melbourne St., North Adelaide SA 5006, Australia. Fax: (08) 267-4031)
22-24 May Amsterdam, the Netherlands	First ASM Heat Treatment and Surface Engineering Conference and Exhibition in Europe (ASM Europe, rue de l'Orme, 1040 Brussels, Belgium)
24-28 June Seattle, Washington USA	Surface and Colloid Science Course, College of Engineering, University of Washington, GG-13, 4725 30th Avenue N.E., Seattle, WA, USA
2-6 September Nice, France	Diamond Films '91: 2nd European Conference on Diamond, Diamondlike and Related Coatings (COMST, Ave. de la Gare 52, P.O. Box 415, 1001 Lausanne 1, Switzerland Fax: 41-21-234-972)
9-12 September Stockholm, Sweden	Surface Science - 12th European Conference (University of Uppsala, Dept. of Physics, P.O. Box 530, S-75121 Uppsala, Sweden)
11-13 September Paris, France	Synthesis, Processing and Modelling of Advanced Materials (ASM European Office, rue de l'Orme, B-1040 Brussels, Belgium Fax: 32/2-734-67-02)
23-26 September Fontana, Wisconsin, USA	Heat-Resistant Materials, ASM International, Materials Park Ohio 44073-0002, USA
23-26 September Cambridge, UK	Third National Association of Corrosion Engineers (NACE) Symposium, NACE Europe, P.O. Box 251, Guildford, Surrey UK
26 September Manchester, UK	Environmental Cracking and Localized Corrosion of Duplex Stainless Steels (Corrosion Group of the Materials Engeering Division of the Institute of Metals, 1 Carlton House Terrace, London SW1Y 5DB, UK Fax: 071-839-3576)
2-4 October Stuttgart, Germany	Reliability of Advanced Materials: Design & Failure Analysis (ASM Europe Council/Verein Deutscher Ingenieure) ASM International, Materials Park, Ohio, USA Fax: 216/338-4634
14-18 October Budapest, Hungary	4th European Conference on Applications of Surface and Interface Analysis (Academy of Science, Institute of Nuclear Research, Pf. 51, H-4001 Debrecen, Hungary. Fax: 36-52-16181)
5-8 November Kauai, Hawaii	Third National Association of Corrosion Engineers (NACE) Symposium NACE Europe, P.O. Box 251, Guildford, Surrey, UK
14-15 November York, UK	Second International Conference on the Behaviour of Materials in Machining (The Institute of Metals 1 Carlton House Terrace, London SW1Y 5DB. Fax: 071-839-357[illegible]
25-27 November Berlin, Germany	6th International Congress for Surface Technology, SURTEC '91, (Deutsche Forschungsgesellschaft f[illegible] Oberflächenbehandlung, Aderstrasse 94, 4000 Düsseldorf 1, Germany. Fax: 0211-37-04-59)
3-4 December Lille, France	CONIMAT '91 - 3rd International Business Convention concerning New Materials (Adhesion & Associés CONIMAT 91, 9 rue de l'Ancienne Mairie, F-92100 Boulogne, France. Fax: (33) 146038626)

1992

5 February London, UK	Meeting. Advanced Coating Technologies (Department of Materials Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, UK)
12-18 February Moscow, USSR	Metallurgija Event will focus on metallurgical and foundry engineering, industria[illegible] furnaces and thermal production techniques. (NOWEA International GmbH, Postfach 32 02 03, 4000-Düsseldorf 30, Germany Fax: 0211/4560-740)
14-16 February Las Vegas, Nevada, USA	Surfaces '92, (Sponsored by Wester[illegible] Floor Covering Association) Fax: (714) 978-6066)
24-25 February London UK	The continuous casting mould and the prevention of surface defects. Sponsored and organized by the Iro[illegible] making and Steelmaking Committee o[illegible] the Ironmaking and Steelmaking Division of the Institute of Metal[illegible] (The Institute of Metals, 1 Carlto[illegible] House Terrace, London SW1Y 5DB. Tel.: 071-839 4071 (direct line 071-976 1332); Fax: 071-830 3576; Telex: 8814813)
9 March Florida USA	Course on surface science. The University of Florida Center for Surface Science and Engineering will present a short course entitled "Surface Science and Technological Applications". It will cover principles and wide-ranging applications of surface science fo[illegible] scientists, engineers, and R&D sta[illegible] from industry. Complete details should be requested from D. O. Sha[illegible] Center for Surface Science and Engineering, University of Florida Gainesville, FLA 32611-2022; Tel.: 904 392-0877; Fax: 904 392-[illegible]
30 March - 3 April Monterey, California, USA	10th International Conference on Plasma-Surface Interactions in Controlled Fusion Devices (Sandia National Laboratories, Livermore, California 94551-0969. Fax: (415) 294-3231)

31 March - 1 April Orlando, Florida, USA	Research Symposium on Interfaces (Areas of interest include composites, adhesive bonds, coatings, and liquid-to-solid interfaces) Texas Research Institute Austin, 415 Crystal Creek Dr., Austin, Texas 78746 USA Fax: (512) 263-3530.
29 April London, UK	Introduction to Technology Transfer and its Application in the Field of Corrosion (Materials Engineering Corrosion Group of the Institute of Metals, 1 Carlton House Terrace, London SW1Y 5DB, UK. Fax: 071/839-3576)
7-16 May Buenos Aires, Argentina	International Exhibition of Machine Tools (EMAQH) (Argentinian Association of Manufacturers of Machine Tools, Accessories and Related Products; the Argentine Chamber of Machine Tools; Argentine Chamber of Manufacturers of Measurement Tools and Instruments.) Held every two years, the exhibition is open to both Latin American and foreign companies. (For more information: Commercial Office, Argentine Embassy, 233 North Michigan Ave., Suite 1408, Chicago, Illinois 60601; Fax: 312-565-4105.)
13-20 May Kiev, USSR	Poroschkovaja Metallurgija Event will feature equipment and processes for powder metallurgy and ceramics. (NOWEA International GmbH, Postfach 32 02 03, 4000-Düsseldorf 30, Germany. Fax: 0211/4560-740)
28 May - 4 June Alma Ata, USSR	Tsvetmet - Nonferrous metals will be the focus of this show (NOWEA International GmbH, Postfach 32 02 03, 4000-Düsseldorf 30, Germany. Fax: 0211/4560-740)
1-4 June Espoo, Finland	12th Scandinavian Corrosion Congress and EUROCORR '92 (Mr. P. J. Tunturi, FINNCORR Fax: 358-0624462)
7-11 June Seattle, Washington, USA	International Chemical Recovery Conference (Canadian Pulp and Paper Association, 1155 rue Metcalfe, Montreal, Quebec, Canada H3B 4T6 Fax: (514) 866-3035)
10-12 June Ann Arbor, Michigan, USA	14th Symposium on Applied Surface Analysis (General Motors Research Laboratories, 30500 Mound Road, Box 9055, Warren, Michigan 48090-9055. Fax: (313) 986-0136)
10-17 June USSR	Zaschita ot Korrozii Anti-corrosive treatments (NOWEA International GmbH, Postfach 32-02-03, 4000-Düsseldorf 30, Germany. Fax: 0211/4560-740)
18-25 June Moscow, USSR	Aluminium - Will provide information on the manufacture and applications of aluminium and semi-finished aluminium products. (NOWEA International GmbH, Postfach 32-02-03, 4000-Düsseldorf 30, Germany. Fax: 0211/4560-740)
7-9 October St. Louis, Montana, USA	Symposium on Metal Surface Technology for Adhesive Bonding (Sponsored by ASTM, 1916 Race Street, Philadelphia, Pennsylvania 19103-1187, USA)
12-16 October The Hague, the Netherlands	The Twelfth International Vacuum Congress and the Eighth International Conference on Solid Surfaces (Contact W. F. van der Weg, Department of Physics, University of Utrecht, P.O. Box 80.000, 3508 TA Utrecht, the Netherlands. Tel.: +31-30-533269; Fax: +31-30-543165)
9-12 November Osaka, Japan	8th International Congress on Heat Treatment of Materials (Research Institute for Applied Science, 49 Tanaka Ohi-cho, Sakyo-ku, Kyoto 606, Japan)
17-20 November Kyoto, Japan	Heat and Surface 1992. 8th International Congress on Heat Treatment of Materials. Sponsored by the International Federation for Heat Treatment and Surface Engineering (IFHT) and hosted by the Japan Society for Heat Treatment and the Research Institute for Applied Sciences on behalf of IFHT. (For further information, please contact: Congress Secretariat of Heat and Surface '92, Research Institute for Applied Science, 49 Tanaka Ohi-cho, Sakyo-ku, Kyoto 606, Japan (Tel.: +81 75 702 0043; Fax: +81 75 701-1217))
9-19 December Bangalore, India	East West Convention on Surface Engineering. 1. Surface engineering by material removal 2. Surface engineering by material addition 3. Surface characterization, and instrumentation 4. Surface engineering by modification 5. Semantics, design and realization of textures (Dr. Indira Rajagopal, INCOSURF-92, ECSI, Indian Institute of Science, Bangalore 560 012, India. FAX: 91-812-34 16 83)

Previous issues

Issue No. 1	Steel
Issue No. 2	New Ceramics
Issue No. 3	Fibre Optics
Issue No. 4	Powder Metallurgy

Issue No. 5 Composites
Issue No. 6 Plastics
Issue No. 7 Aluminium Alloys
Issue No. 8 Materials Testing and Quality Control
Issue No. 9 Solar Cells Materials
Issue No. 10 Space-related Materials
Issue No. 11 High-temperature Superconductive Materials
Issue No. 12 Materials for Cutting Tools
Issue No. 13 Materials for Packaging, Storage and Transportation
Issue No. 14 Industrial Sensors
Issue No. 15 Non-destructive Testing
Issue No. 16 Materials Developments in Selected Countries
Issue No. 17 Metal-matrix Composites
Issue No. 18 Plastics Recycling
Issue No. 19/20 Advanced Materials Technology: CAD/CAM Application
Issue No. 21 New Materials Technology and CIM
Issue No. 22 Powder Metallurgy
Issue No. 23 High-temperature Ceramics