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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

Advances in Materials Technology: MONITOR

Distributed free to a targeted audience in developing countries

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Dear Reader,

This is number 29 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 MODERN FERRITE TECHNOLOGIES AND PRODUCTS and consists of two main articles written for UNIDO by Dr. W. F. Kladnig from the University Linz, Austria and Dipl. Ing. M. Zenger from Siemens Matsushita Components, Germany.

We invite our readers also 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 as we cannot send all the requested copies of back issues as many of them are out of print. Will you kindly inform us whether you are still interested in receiving the Monitor and notify us when there is a change of address.

Technology Development and Promotion Division

CONTENTS

1. MODERN FERRITE TECHNOLOGIES AND PRODUCTS

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Abstract

A review is given of the most important aspects of ferrite manufacturing with a concentration on several soft ferrites. Some information also relates to hard ferrites. The article describes the state-of-the-art in the field, the recent technological developments and ferrite applications, as well as future trends. A collection of publications on the subject is included.

1. Introduction and some definitions

Ferrites are soft or hard (permanent) magnetic oxide ceramics, usually showing a polycrystalline microstructure. Only a small production level of monocrystalline ferrites is used in the production of video heads. As in the case of magnetic metals, their special properties are deducible from the spontaneous parallel or non-parallel alignment of adjacent atoms in magnetic domains. The word "ceramic" relates to both technology and mechanical properties, because the classical method of powder preparation starts with the mixture of raw materials. After the process of forming cores a thermal treatment, the sintering procedure, is carried out in kilns at high temperatures, usually between 1,200° C and 1,400° C, depending on the ferrite type.

Ferrites show high hardness, therefore grinding or any mechanical finishing must be done by the use of diamond or carbide.

Ferrites are oxides and their chemistry provides semiconductor properties as low electric conductivity, enabling the reduction or avoidance of eddy current effects. Compared to metallic soft magnetic materials the main advantage of magnetic ferrites is that they can be used at much higher frequencies, e.g. MnZn-ferrites generally up to 2 MHz, for some applications also higher, and NiZn-ferrites up to 1,000 MHz. Another important advantage of ferrites is that they can be fashioned into a wide variety of shapes, while metal core shapes are limited by the lamination facilities.

2. Most commonly commercially-used ferrites

As mentioned above, there are two main families of ferrites differing in coercivity; soft ferrites with low coercivity, and hard (permanent) ferrites with high coercivity.

2.1 Hard ferrites

The best combination of properties for hard ferrites is given by a hexagonal (magneto-plumbite) structure, which provides a preferred axis for the magnetic crystalline energy. This structure can be achieved by the formula $MO6Fe_2O_3$, where M can be Ba, Sr or Pb. By these elements high energy products (BH)-max materials can be realized, i.e. high Br or high Hc materials adapted to the corresponding requirements.

2.2 Soft ferrites

Best soft ferrite properties can be achieved by a spinel crystal structure because of the many equivalent crystal directions. The magnetization process needs only low energy, especially at a low flux density. To form spinel ferrites a number of bivalent elements can be combined with hematite Fe_2O_3. Several combinations and compositions are possible and in use in generating many specific magnetic characteristics. Of most interest are manganese-zinc-ferrites, magnesium-zinc-ferrites and nickel-zinc-ferrites, providing high saturation magnetization and a large variety of many other well adjusted magnetic properties of an Ac-characteristic concerning permeability, dependence of permeability on frequency, time and temperature, as well as the loss characteristic, Curie-temperature, DC-resistivity, etc. as described in the suppliers' literature (ref. Literature II, Data books).

3. Production volume

The annual production of ferrites may be estimated by the consumption of iron oxides, provided for ferrites. For 1990, the developed countries' production of hard ferrites was about 190,000 mt without polymer-bonded magnets and 150,000 mt soft ferrites. An important part of the industry is located in Japan, the other in the United States of America and Europe. In spite of the high consumption of hard ferrites, the total turnover is almost the same, about 1.6 10^9 DM respectively (ref. Literature IV, 3 and 4).

4. Processing of soft ferrites

The manufacturing sequence of soft ferrites can be roughly divided into powder and core production.

(a) Powder and granular production

Choice of raw materials
Weighing and blending (dry or wet)
Calcining (pre-firing), including preparation

Milling
Granulation

(b) Core production

Forming (pressing, extruding, injection moulding)
Sintering (including removal of binders), and
Finishing (e.g. surface grinding, air gap grinding).

Powder production consists of many more steps than core production, which is predominately forming and sintering. It is a long experience that the final core properties of which are reached by forming and sintering and is heavily dependent on the quality of powder manufacturing. Similarly, the quality of the powders is closely related to the properties of the starting raw materials. Therefore the influence of the raw materials needs to be considered as the most important basic condition with respect to the final performance of all the magnetic and mechanical properties of the core products.

4.1 Choice of raw materials

Because usually 70 per cent of the weight of the soft ferrites consists of iron oxide, both the cost factor and quality of the iron oxides used are predominantly important, even though the other constituents are often more expensive, e.g. manganese oxides by the factor of 2 to 4, zinc oxides roughly by a factor of 2 depending on the actual market situation.

The main source of medium and high quality soft ferrites is iron oxide produced by spray roasting of steel mill pickle liquor, partly including a purification step beforehand. High quality soft ferrites are manganese-zinc-ferrites of high initial permeability, of low losses and low power losses, the latter combined with high saturation magnetization at high operation temperatures for both.

Spray roasted iron oxides produced today can be roughly classified into three grades by their SiO_2 weight per cent, their Cl weight per cent, their residual summarized content of non-volatile impurities (Σ) except manganese-oxide, SiO_2 and CaO and last but not least, by some physical parameters. The most important one describes the particle parameter by the BET value (SSA refers to specific surface area in m^2/g; (BET indicates the well known usual method of measuring SSA. BET is the abbreviation for BRUNNER EMMET and TELLER).

Classification of spray roasted iron oxides

	Weight:				
Grade	ppm	SiO_2	Cl	Σ	SSA m_2/g
1		100	1000	400	4-5
2		250	1500	3000	3-5
3		400	1500	3000	3-4

Because SiO_2 can cause cannibal grain growth and is needed on the other hand for the definition of the grain boundary chemistry, SiO_2 should be specified by toleranced values. It is well known that CaO provides high resistive layers within the grain boundaries brought on by the existence of a special content of SiO_2. The quantity required depends on the microstructure desired, with decreasing grain size as the need for SiO_2 increases. CaO is more easy to contribute homogeneously by addition than SiO_2. Therefore special Fe_2O_3 grades are in demand that have a little higher SiO_2-content at a low content of summarized impurities.

By the fact that high purity manganese oxide and zinc oxide raw materials have been available for some time, soft ferrites can now be realized, wherein the total impurity content (inside the sintered ferrite body) is low or very low compared to the summarized content of the usual ingredients or additives such as Ca, Si, Ti, Nb, Co, Ta, Ga, V. Obviously, the effects of these elements are much more pronounced in this case.

The table below gives some information on the reported effects of the remaining impurities.

The content of iron oxide grade 3 impurities is given by conventional steel quality production including the spray-roast technique.

Grade 2 is qualified by a lower SiO_2 content.

Grade 1 includes additional purification before spray roasting. Since the introduction of this technique, very low levels of remaining impurities could be achieved.

By using this purer type of iron oxide the ferrite industry world wide could realize highly improved ferrites, especially with manganese-zinc-ferrites of high permeability and low losses.

Beneath the chemical properties of the raw materials, the physical parameters such as particle size and distribution, bulk density, specific surface area (SSA) must also be considered. Overall, a main requirement for the raw materials is that all properties must remain constant, lot for lot of the deliveries specified by very narrow toleranced variations.

For example, the particle properties, shape and size and other morphological parameters influence blending, presintering and even sintering. Although much expertise exists, only a few fundamental studies had been carried out on this subject, because the mentioned physical parameters depend on the raw material production process only and cannot be varied systematically by the ferrite ceramic engineers.

In practice, the SSA values preferred for manganese-zinc-ferrites are between 3 and 5 m^2/g for iron oxides, between and 5 and 10 for zinc oxides and between 10 and 20 for manganese oxides.

Type of impurity	Contents in ppm in iron oxide grade		Observed effects
	1	2+3	
Na_2O	10	500	Suppression of grain growth
B	3	3	Generating glass phases
Pb	10	50	
P_2O_5	10	400	
Cr_2O_3	30	300	If dissolved in spinel lattice will influence crystal effects
Al_2O_3	80	800	
CoO	40	30	
CuO	50	70	
NiO	50	70	
MgO	50	100	
SnO_2	10	20	
TiO_2	30	30	
K_2O	30	50	
$\sum$	400	3000	

4.2 Weighing and blending

Since today weighing is mostly done by automatically operated devices, the oxides should have the proper properties for transportation, e.g. flowability. The powder should not contain too small particles in order to avoid agglomeration and gluing effects with the transportation devices.

The mixing method applied, e.g. wet or dry, depends on the raw materials used and/or the subsequent processing steps. To achieve a high homogeneity in general, wet mixing is preferred. As a drying process is subsequently necessary, this method is more energy consuming and expensive. Therefore many ferrite producers are opting for dry mixing. As the succeeding presintering and final milling will improve homogeneity, it is not so important to ensure high homogeneity during the mixing stage.

Of course, if ferrite powder is to be manufactured without presintering, the mixing step includes milling and the homogeneity achieved at that phase determines the final results.

The mill types used vary from ball mills to rod mills and to modern attritor mills. The mixing may be integrated in a system suited for intermediate preparation of pellets or similar products suitable for subsequent calcination.

4.3 Presintering (calcining)

There are some reasons for the application of a thermal treatment to the well mixed powder. It is essential to adapt the reactivity - together with the subsequent milling step - to the shrinkage rate, which is fixed by the relation between the press die geometry and the final, specified dimensions of the cores. The reactivity of a mixed powder may vary due to different raw materials and lots.

Second, presintering causes chemical and interdiffusion reactions, also generating partly ferrite spinel formations. Although by the subsequent cooling in air some reoxidation occurs, some authors believe that presintering increases homogeneity in both chemical and crystalline structure.

Last, but not least, presintering enables the removal of Cl and S, which is important to avoid the corrosive effects on equipment, and degradation of some properties of the final sintered ferrites. Preferably, rotary kilns should be used for prefiring. With respect to the specified powder characteristics, the parameters: temperature, throughput and atmosphere, should be strictly controlled.

As the cooling down rate also has an influence on the chemistry and morphology, a high grade of reducibility can be achieved by a controlled cooling down procedure, which can be carried out, for example, in a separate rotary tube.

As mentioned above, the way the powder is prepared for presintering depends on the presinter-kiln type and the connected transportation system.

For rotary kiln application the powders are usually pelletized. Obviously the size of the pellets should be controlled, in addition to the above-mentioned parameters. If powder is directly fed into a rotary kiln, transportation must be supported by proper devices inside the kiln itself. The resulting powders are controlled by various methods: detection of the amount of spinel formation, and the oxygen content, further measurement of the reduced BET value, etc. These data are usually evaluated as being only arbitrary.

4.4 Milling

Milling must be carried out to establish the final specified SSA values as described in 3.2, i.e. to increase homogeneity to a high level; to add ingredients if necessary; and to correct the composition with respect to the specification. The final particle distribution should be narrow (as specified), abrasive from the balls, with the mill walls remaining as low as possible to avoid the incursion of iron and other elements.

In the case, the starting material consists of pellets, the ball size should not be much smaller than the pellet size, especially if the hardness of the latter is high. To mill down to the desired final powder particle size, sometimes a second and a third milling step must follow. If the presintered powder consists of only small particles, one milling step may be enough to meet the requirements. From the economic aspect presintering and milling of not preformed powder seems to be the best resolution.

With respect to the high grade of homogeneity generally desired, it should be kept in mind that the performance of the wet milling is affected by the solid content of the slurry and the resulting grade of viscosity. During milling the viscosity increases slightly and the milling effect somewhat decreases. Therefore the viscosity should also be controlled.

4.5 Granulation

Granulation means bringing the powder to a state ready for the pressing of cores. After milling, the solid concentration of the slurry is decreased by the addition of water in order to enable spray drying - the most popular granulation technique.

In order to ensure a good pressability at low pressure and to also ensure the necessary strength of the pressed cores for handling operations, a number of organic binders are added. Basically polyvinyl alcohol is used as a binder, with polyethylene glycol as a plasticizer, zinc stearate as a lubricant, etc.

Types and concentrations of these organic aids depend on core shape and size, and are limited by the need to remove all the binders in as short a time as possible before sintering.

The particles generated by spray drying have spherical shapes and are therefore well suited for filling the press dies quickly and homogeneously. The best result is achieved by a granular comprised of spheres only. To regulate the consistency of the granules the following spray parameters should be specified and controlled: size of the spray nozzles, the pressure during operation; the throughput, by regulating the pressure; temperature distribution inside the reactor; the viscosity of the slurry, which should be permanently stirred.

4.6 Forming core shapes

Today fully automatically operating die-presses are often used. To ensure a high homogeneity of the green density a moderate pressure force should be applied.

The parameters to be specified at first depend on the desired final (sintered) density in connection with all electromagnetic and mechanical properties of the material to be produced. Second, with respect to the final core dimensions and the (given) die dimensions (approximately equivalent to the green dimension) the green density to be met is fixed.

Subsequently, the prepared powder has to fulfil the requirements to reach this green density by an acceptable pressure force. Usually the variations of the green density are between 2.5 and 3.1 g/cm^3, and the accepted force should not exceed approximately 20 N/cm^2. If the green density is too low, the final density will also be too low and vice-versa. If the pressure force is too high, inhomogeneity will cause geometrical deviations, etc.

There are some other forming processes, e.g. extruding or injection moulding. Higher binder contents and also other types of binders are used for these techniques.

4.7 Sintering

Generally sintering should be carried out at as low a temperature as possible, firstly to ensure a high grade of microstructural homogeneity, secondly to avoid cannibal grain growth, and thirdly to save energy costs. Therefore, any method is welcome that reduces the soak temperature and excludes any undesired effects. Modern kilns may combine facilities to burn out the added organic binders and integrate the sinter process directly in order to save handling, time and cost.

In order to keep the sintering time as short as possible, an exact knowledge of both the burning out procedure and solid state reactions during sintering is necessary.

As the content of O_2 in the atmosphere influences the formation of manganese-zinc spinels, the firing cycle must be related to graphs, which describe the oxygen-temperature-equilibrium of the ferrite and its Fe^{++} content at each stage.

It is also important to adapt the oxygen partial pressure during cooling, especially at the higher temperature stage, as almost all properties (mainly permeability and loss characteristics) are influenced.

Modern kilns are run by means of computers that are equipped with a wide variety of programs dealing with the vast number of parameters to be controlled that occur with core types, sizes and materials in an up-to-date ferrite plant.

Modern elevator batch kilns provide such highly skilled facilities. Another interesting aspect of this kiln type is its low heat capacity. Heating up and cooling rates can be drastically reduced when compared to conventional batch kilns. Also, this kiln type enables a quick change of batch and is therefore more suitable for small core lots, for which push kilns are not economical, due to the long time needed for adaptions. The economical meaning of push kilns refers to the sintering of a large number of the same core type out of the same material and powder lot. Sintering of magnesium-zinc-ferrites and nickel-zinc-ferrites can only be carried out in air and at lower temperatures.

4.8 Some finishing operations

Most core types consist of two parts which have to be paired when assembling the final inductive component. This happens for instance with the different and numerous types of Pot-cores and E-cores.

The mating surfaces of these cores must be flat grinded in order to avoid undesired residual air gaps, where by means of a "A_1 zero" concept the maximum inductance value based on the initial permeability of the used material is required. The grinding process is very critical, especially with high permeability cores, because of the strong effect of each small residual air gap. For example, in a core produced from a high permeability material of 10,000, the separation of only 1 micron causes a reduction of the permeability down to approximately 7,000. Therefore, for the highest permeability cores instead grinding or additionally polishing has to be carried out.

Some further finishing operations are with ring cores, removing of edges and insulation, if needed. Cores to be prepared for inductance adjusting by an adjusting element must be equipped with sleeves to catch the screw of the elements.

5. Processing of hard ferrites

As mentioned in section 2 of this paper, the important criterion for hard magnetic materials is the maximum energy product (BH) max. The remanence depends on chemistry density and orientation, the coercive force on microstructure. To stabilize the magnetic domain structure after magnetization, the grain should be so small that only one domain will exist inside, because demagnetization only occurs easily by wall motion.

There are two typical processing sequences, depending on whether oriented or isotropic magnetics are to be manufactured. The latter is, in principle, the same as in soft ferrites, the first differs by application of a magnetic field during pressing.

5.1 Choice of raw materials

Because Barium carbonate and Strontium carbonate both are not expensive and because cheaper grades of iron oxides can be used, as with soft ferrites, the raw material price for 1 kg powder mix is usually between 0.90 and 1.10 DM. The calcining is carried out at temperatures higher than 1,200° C, generally between 1,270° C to 1,370° C for a full ferrite synthesis. Double milling (dry and wet) must generate particles lower than 1 µm with respect to the fact that the pressed bodies at final sintering conditions (in air only) should reach as high a density as possible combined with a low grain size of about 1 µm.

The highest B_r values can be achieved by total orientation of the particles by application of a magnetic field already during pressing, by a density similar to the X-ray density achieved at sintering and by full conversion of the material to the hexagonal crystal structure.

In spite of that low grade iron oxides can be used, the highest magnetic performance also needs e.g. a stabilization of their impurities. Al_2O_3 and Cr_2O_3 are lower than B_r and should therefore be lower than 0.1 per cent, SiO_2 which can be used to increase density, but should not exceed 0.4 per cent in order to verify the control of grain growth. Contrary to soft ferrites, the production of hard ferrites in modern plants is almost fully automated. It is reported that their process yields approach 99 per cent.

6. Alternative technologies

Alternative techniques with soft ferrite production mainly concern raw material and powder processing. Only co-spray-roasting should be mentioned here, because this procedure has been introduced by two big ferrite manufacturers at the industrial plant scale.

By means of co-spray-roasting equipment a ferrite producer becomes independent of the facilities of the respective raw material suppliers, because an iron-manganese-oxide mix can be produced by own controlled specification. Preferable metals may be dissolved in aqueous HCL. In this state purification can be carried out.

The mixture will be co-spray-roasted like iron chloride at steel mills. The advantages of such a procedure may be increased homogeneity, therefore improved magnetic properties and elimination of prefiring, thereby achieving economic progress.

Optimized processing renders a product of high specified reactivity, while expensive milling can be subsequently reduced to a de-agglomeration process, which includes the addition of zinc oxide.

Another possibility of co-spray-roasting is to start from nitrates. In this case zinc is included (as well as all desired additives), since the operating temperature can be lower than that at which zinc evaporation occurs. Nitro-hydrochloric acid has to be regenerated here. By use of this technique the purification method needs to be varied.

Alternative presintering can be carried out by a newly developed vertical kiln (ref. VI, 9, M. Ruthner). Due to a short time temperature treatment spinel reaction should occur without sintering effects. The feed material has to be prepared in an exactly narrow toleranced and small pellet size to ensure homogeneity of reaction. Suitable raw materials must be provided.

Vertical presintering seems to be of considerable interest for hard ferrite powder preparation, where low particle sizes are desired, as described in 4.2.

7. Soft ferrite products

Several classifications for soft ferrite products can be used: briefly, for industrial or consumer application; for two-part or one-part cores, for the two-part cores in E- and U-core types and in P- and RM-core types. Last but not least, classification can also be made with the material.

Previously the requirements in the industry, e.g. for the multiplex telecommunications system, were much more pretentious than for the consumer market. Meanwhile the trend towards miniaturization and automatization in the consumer area has given rise to the need for higher quality materials and more sophisticated core types. Concerning the material grade, there is no usual typical separation with relation to the core types. It seems, therefore, that the most useful classification is: (1) materials in connection with applications and (2) with core types. All data books by leading ferrite producers present this system as a general guide.

The core types are listed in detail, each type being described by toleranced dimensions, the available air gaps and the material grades used.

The most important aspects of material and core types are:

(a) Materials and cores for filter coils need low losses, precise inductance values and a high time and temperature dependence stability. The frequency range up to 100 MHz will be provided by five or six different materials, at the highest frequencies by NiZn-ferrites. There are hardly any activities in new material development. Gapped pot-core types are used for closed circuits, for open, tube-, cylindrical- and screw-cores;

(b) Materials and cores for broad band transformers need high permeabilities to achieve high inductance values. New developments concern the combination of low losses at low and a little increased flux densities, from 1 mT up to maximum 10 mT. Ungapped pot-core types are usually for this application. To ensure high inductance the cores are sintered to a low porosity and the pole faces are polished;

(c) Materials and cores for power transformers belong to the fastest growing field of soft ferrite application.

In particular, the application of SMPS (Switched Mode Power Supplies) has stimulated the development of new material grades and core types with respect to applied higher frequencies and also to the need for miniaturization. During the last years the introduction of frequencies up to 500 kHz required some new materials. As with filter materials at higher frequencies the permeability must be decreased to limit resonance phenomena. Because of a typical high temperature operation, the minimum high flux density losses must be placed at the corresponding high temperature, which is usually between 60 and 100° C. The magnetization does not drastically drop at this condition in order to provide the necessary high amplitude permeability. At any rate, the power application is an operation under loss or saturation limited conditions, if optimized. As with filter materials in the area apart from approximately 2 MHz the NiZn ferrites are superior to the MnZn ferrites because of their higher resistivity. At the application of Mn-Zn ferrites the control of losses needs the use of very pure raw materials (as with high permeability broad band transformer materials) as a first condition to achieve both a suitable homogeneous microstructure and the best effect of loss reducing additives. Grade 1 iron oxides have to be used as described in chapter 4.1.

To minimize eddy current losses in the range and above 500 kHz the mean grain size diameter of a homogeneous grain structure should at the same time be reduced less than 5 microns. Application of high frequencies is done to increase the throughput power, but more often to reduce the transformer size. Since in many cases the industry requires flatter constructions, new core types had to be introduced. A new creation to cover this demand is, for example, the EFD (economic flat design) core (ref. VI, 7, W. Holubarsch et al.).

This core combines geometrical and handling advantages with respect to the accessories suitable for automatic assembling. The general trend towards miniaturization and automatization generates core types with very small legs and floors. Therefore higher requirements of strength properties are being sought and the manufacturers of such products must not only consider the magnetic, but also the mechanical characteristics of the cores after sintering.

Another way to meet customer requirements is to offer a total assembly of the inductive components, as in the case of SMD-inductors or transformers. The best condition is to have very flexible production facilities in order to be in a position to meet the demand for custom-built products as much as possible.

Apart from the three larger groups of soft ferrite materials discussed, a number of others exist that were developed and optimized for several specific applications, and which often have their origins in the three above-mentioned grades.

These applications concern, for example, from the more important ones: EMI-suppression functions, inductive proximity switches, tuning coils, impeder cores and deflection cores. EMI means electro magnetic interference and the task of an EMI-filter is to separate unwanted signals from the specified signal pass in the concerned frequency range. Therefore an EMI-filter material needs to combine a high impedance with a high permeability in the operating frequency range, and the most commonly used core types are ring and U-cores. Existing ferrite materials are able to cover a frequency range up to 1 GHz, for the higher frequency obviously Ni-Zn ferrites are used.

As an example of the need for a new material, the application of deflection yokes should be mentioned. Because the introduction of the high definition television (HDTV) technology means an increase of line-density and therefore a higher sweep frequency, the resistivity of the yoke material must be increased correspondingly. In spite of some less advantageous properties, MgZn-ferrite instead of MnZn-ferrite is preferred due to its high resistivity of 10^7 - 10^8 cm.

8. Products: hard ferrites, material grades and products

As mentioned in section 2, several material grades are used, depending on their application; either high B_r, high H_c or high BH products are preferred. The table below from Goldman gives typical values (ref I, 5, p. 222).

Ba-ferrites are going on to be substituted more and more by Sr-ferrites (although these are more expensive), because Ba generates environmental problems and Sr provides an approximately 25 per cent higher resistance to demagnetizing fields.

Material of higher H_c can be realized by additives including Al_2O_3 or Cr_2O_3. Therefore Al_2O_3 and Cr_2O_3 need to be controlled in the basic raw materials. Higher grade hard ferrites include the use of better controlled raw material properties, similar to soft ferrites. It is important that iron oxide is fully oxidized to Fe_2O_3. If not, pre-treatment is necessary for oxidation.

Compared to soft ferrite cores, the hard ferrite products have relatively simple shapes. Concerning application, 45 per cent of hard ferrite magnets are used in permanent magnet motors, 30 per cent in loudspeakers and the rest in many other applications. During the last ten years, the typical product began to shift from the simple to produce loudspeaker magnets to a growing content of complex arc segments as the applications for magnetic motors grew.

Most of these products are magnetically oriented. Meanwhile, 30 per cent of all hard magnetic products are polymer bonded magnets; partly isotropic, partly oriented. A very informative survey about this is given (ref. IV, 3, R. E. Schwanke), which describes the different forming and particle orientation processes and their effects on the typical magnetic properties. The procedures of calendering and extrusion and the combination of both and of the injection moulding are considered.

Table 9.1

Properties of commercial ferrite permanent magnet materials

Grade	B_r(gauss)	H_c(oe)	H_{ci}(oe)	$(BH)_{max}$ (MGO)a/
Isotropic	2,700	2,300	3,250	1.05
High B_r	3,850	2,000	2,020	3.5
High H_{ci}	3,700	3,550	4,950	3.2
Premium High $(BH)_{max}$	4,400	2,850	2,880	4.5
Alnico 5	12,800	640		5.5

a/ MGO = Mega gauss-oersteds = gauss oersteds x 10^6

Bonded ferrites are used in many applications as refrigerator gaskets, magnetic motors, magnetic pickups for electronic ignition, latch magnets, reed relays and so on. Polymer bonded magnetic shapes are manufactured in a large variety.

9. Future trends

(a) Soft ferrites

Generally, the demand for higher quality ferrites showing smaller manufacturing tolerances will continue. Many companies introduced the "Zero defective" programme and modern TQM methods to approach them. The background for this is that the consumer needs products of higher reliability with all the properties specified, enabling him to save costs on input checks and to trust the producer's quality-ensuring system. As a way of coupling the producer's facilities and the consumer interest for a general quality system in the meantime, in 1987 the ISO 9000 standard series was introduced and found wide acceptance.

The future product trend has to be considered in respect of the fact that the power electronic ferrite market is growing fast. It now covers almost 50 per cent of the total market followed by the high permeability market of approximately 30 per cent. Only 10 per cent or less of the market remains with the earlier dominating telecommunication multiplex channel filter application.

A review was recently given by the author on the topic of the main developments in the field of soft-magnetic ferrites (ref. VI, chapter 9). In the area of power application there is a continuous pressure to reduce the size of electronic equipment in general; miniaturization of SMPSs is also demanded. Because the transformer size can be reduced by increasing the switching frequency, the family of low loss power ferrites is permanently growing. The application up to 1 MHz covered by MnZn-ferrites can be expected to be introduced everywhere. Higher frequency application over 2 MHz needs the shift to NiZn ferrites because of their higher DC-resistivity and lower initial permeabilities.

In the field of high permeability ferrites, the decrease of low induction level losses is called for to enable a brighter frequency application for numerous applications. For the improvement of both ferrite families, one of the main conditions is a better control of the chemical and physical properties of the raw materials.

Due to the progress in the field of high quality iron oxides, new ferrite materials could be developed. Two trends can be observed: ferrite producers are controlling their own raw material source, e.g. by the mentioned co-spray-roasting; or raw material producers are starting their own activity to produce ferrites. Economic aspects are, of course, contributing to these trends. A special item is the replacement of MnZn ferrites for television deflection yokes by MgZn ferrites, caused by the higher demand for DC resistivity in HDTV technology, as mentioned before. Overall automatization in the powder and core manufacturing area, also with soft ferrites, must proceed to meet consumer expectancy for lower prices, especially by the entertainment consumer industry.

(b) Hard ferrites

The growth of the hard ferrite market in the past was heavily influenced by the exorbitant increase of the Co-price, from 4 to 80 Dm/kg, causing the replacement of Alnico magnets by ferrites materials.

Due to environmental problems connected with barium the production of Sr-ferrites became more important, in spite of the somewhat higher Sr-price.

Experts predict a major increase of hard ferrite application in cars and trucks, e.g. for permanent magnetic starter motors, electronic mufflers, magnetic gaskets, for further PM motor types, etc. Also, the replacement of low efficiency AC motors to highly efficient and versatile permanent magnet motors will generate more demand for ferrites. Most of the efforts concerning hard magnet materials will be focused on further improvements of the quality of Sr-ferrites. As mentioned above, a greater part will be directed to the installation of much more exact specifications for the raw materials, especially for iron oxides.

To finish the discussion about ferrite trends, a quotation by Goldman is appropriate: "The ferrite supplier has always been able to provide the materials and shapes that were needed by the designer. Because of the wide variation in chemistry, microstructure and shapes that are available in ferrites, I feel that we have just scratched the surface of the potential in the technology of ferrites." Goldman sees a bright future for this technology.

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Appendix III

IRON OXIDES 91
San Diego

A conference organized by Falmouth Associates Inc.

1. Gordon Webb, W., Effects of iron oxide in hard ferrite production.

2. Hart, W. G., Market characteristics and future outlook for hard ferrites.

3. Schwanke, R. E., Iron oxides for ferrite permanent magnets.

4. Ruthner, M. J., Main issues affecting world supply of iron oxides: market survey.

5. Karner, W., New developments in the spray-roasting process for pickle liquor regeneration.

6. Tonaka, S., Ferrite developments and the corresponding improvements of iron oxides as raw materials in Japan.

7. Goldman, A., Advanced raw materials for soft ferrite production.

8. Knight, J., The effect of iron oxide properties on soft ferrites.

Appendix IV

SOFT FERRITES '91
San Diego

A conference organized by Falmouth Associates Inc.

1. Ruthner, M. J., Long-term availability of iron oxide starting materials for soft ferrite production.

2. Watanabe, T. Introduction of soft ferrite business in Japan.

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4. Olsen, A., Jr., Design trends in ferrite-core transformers.

5. Strasser, R., The soft ferrite market in Europe - new developments.

Appendix V

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2. A REVIEW ON SELECTED CERAMIC OXIDE POWDER TECHNOLOGIES

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Abstract

A survey is given which includes some of the most important representatives of ceramic oxide powders and their present status of technology until the most modern technologies to make ultrapure and composite ceramic powders. Special attention is paid to the Ruthner spray-roasting technology.

A. Classical technologies

1. Making alumina (Al_2O_3) by the Bayer route

The Bayer process, due to the German patents 43977 (1887) and 65604 (1892), bases on the sodium hydroxyde extraction of Al_2O_3 from the bauxite ore under pressure of 40 bar and at $T = 250° C$.

The process route can be formulated with:

$Al(OH)_3 + NaOH \dashrightarrow Na^+Al(OH)_4^-$
(autoclave process)

$Al(OH)_4^- + seeds \dashrightarrow Al(OH)_3 + OH^-$
(Al_2O_3)

Ninety-five per cent of the world alumina is derived by this route. It's end product is: $Al(OH)_3$, bayerite. During dehydration a number of transition modifications are passed through, bayerite->boehmite->delta->theta->alpha-(Al_2O_3. Leading producers are Kaiser, Alcoa, Reynolds, GTE- Sylvania, Corning, Coors (USA), VAW, Martinswerk, Giulini (Ger). Crucial are contents in Fe, but especially in Na_2O which interferes in Al_2O_3's insulating action in IC's. The Bayer product is typically 99.5 per cent in pureness. Impurities are Na_O, Fe_2O_3, SiO_2, CaO 100-200 ppm, TiO_2, V_2O_5 20-50 ppm. The powder contains agglomerates of prime crystals 0.2 μm in size, which are 50 to 100 μm of dense structure.

Lowest Ceralox grades of Alcoa offer Na_2O contents such low as 0.01 per cent, but the usual range is in between 0.2-0.4 per cent Na_2O. For best sintering abilities powders are marketed as fine ground powder with an average of d_{50} as low as 1 μm. Grinding is done in Al_2O_3 lined ball mills or in gap mills and by jet milling. Such fine alpha-Al_2O_3 (corund phase) powder particles have a surface area of 20 m^2/g.

Contrarily has gamma-Al_2O_3 as much as the tenfold surface area of 100-250 m^2/g. Its major use of around 50000 tpa is as catalyst carrier. Careful calzining makes a broad range of catalyst carriers available for heterogeneous catalysis ranging from 10 to 250 m^2/g. Greatest producer of Al_2O_3-catalyst carriers is the Norton Company, United States of America.

Production of non-metallurgical grades amount to 25,000,000 tpa which split into, e.g.:

Refractories	400,000 t
Abrasives	150,000
Spark plugs and electr. insulators	250,000
Catalysts (calzined grades)	100,000
High grade aluminas for electronics	5,000

High grade >97 per cent Al_2O_3, up to >99 per cent is most widely being used in several applications for engineering, refractorial, grinding materials, spark plugs, cutting tools, high temperature bearers, rollers, tubes, high tension insulators, catalyst support. Its overall consumption can be estimated to be more than 200,000 tons p.a.

Ultrapure ceramics are required in electronics in ICs, garnets (lasers) such as YAGs: $Y_3Al_5O_{12}$, made f.e. by Allied Corp., or for supports, such as ceramic wafers or electroceramics, such as translucent ceramics and in bio-ceramics.

Alumina used for sodium vapour arc lamp tubes have not to exceed 10 ppm Fe contents because of that elements significant absorption of Na-emission line. Ultrapure powders containing trace amounts in the range of 10-100 ppb (parts per billion) are being produced by Pechiney (Fr) and E.I.du Pont de Nemours and Co. (USA). The production is done mostly by the alum process, i.e. thermal decomposition of $Al_2(SO_4)_3$. The process is being performed by Baikowski Chemie in France, and Baikowski Int. Corp., North Carolina, USA. Other processes to make high purity aluminas are:

Nitrate decomposition (Shikoku Chem. Corp, Japan)

Hydrolysis of Al-alcoholates (Vista Chemicals, USA)

Purities being offered are 99.98 per cent - 99.99 per cent.

Also sol-gel methods are used (Sumitomo).

Alumina grades on the market are:

activated alumina, Alpha trihydrate
calcined types, calcined alphy trihydrate

tabular (2000 calcined)

fused grades 2200 grad.

Medical applications of Al_2O_3:

Alumina is the most important bioceramic material. Bone grows in tight apposition to this material, but cannot penetrate the dense ceramic. Since the material is brittle it cannot sustain the range of physiological forces so well as metallics. Its best application is in load bearing use. Analytical requirements for biomedical use is a minimum of 99.5 per cent and a max grain size of 7 μm. Typical are compressive strength of 4000-5000 MPa and bend strength of 400-550 MPa.

In Japan experiments were run to introduce sapphire as a bioceramic, which nowadays is used as translucent ceramic f.e. in dental surgery.

The alumina support:

Alumina for supports is obtained by precipitation of Al^{3+} solutions. The first precipitate, a gel-like substance, undergoes aging and calzining at 600° C. The end-product gamma-alumina is received after passing through several intermediates, such as bayerite $Al(OH)_3$, boehmite Al(OOH), O, delta, kappa forms and intermediates: $Al_2O_3.nH_2O$ ($n<1$), which are amorphous. Above 1100° C alpha-Al_2O_3 is formed. Finally fired alumina consists of closed oxygen packings in hexagonal and cubic symmetry. Alumina is considered as an amphoteric (equally acidic and basic) catalyst support, due to its surface oxy and hydroxy groups (Bronsted basic and acidic sites).

2. Titanium dioxide pigments

Titanium dioxide ores which mostly go to be processed to make TiO_2 pigments are ilmenite $Fe_2O_3.TiO_2$, natural rutile or TiO_2 slags. There are two basic processes competing on the world market - the sulphate and the chloride process. The sulphate route uses H_2SO_4 (sulphuric acid) for digesting the ore and to make $Ti(SO_4)_2$ wastes which usually are contaminated by iron sulphate. The chlorine process uses chlorine gas which converts the ore by the additional use of carbon into volatile $TiCl_4$ and other (non volatile) chlorides (mostly ferric chloride). Purified $TiCl_4$ is oxidized into TiO_2 by a special burning technique in pure oxygen to form TiO_2 and chlorine gas which is being returned into the process route. Chlorine process pigment plants usually require feeds with high TiO_2-content (85-96 per cent), such as high grade slags or natural rutile.

The leaching process, usually with H_2SO_4 employs ilmenite ores which are poorer in Ti content or titaniferous slags. Although slags are high in TiO_2 (72-85 per cent) they usually contain alkaline and alkaline earth elements which have to be eliminated in special process routes (DuPont process). Total production nowadays amounts 2.5 mio tpa, of which 60 per cent are due to the sulphate route. Sixty per cent of total world market is used up by paint manufacturing. The market growth was extraordinary and world production has nearly doubled since the beginnings of the 80s.

Besides these major routes there exist also a series of different leaching processes where HCl is used instead of H_2SO_4. The ore (ilmenite) is being digested under pressure using 30 per cent HCl. Waste acids are being recycled by the thermal decomposition route (the "Ruthner" process) which is being detailed later on. Most important TiO_2 producers of pigments grades (rutile, anatase) are Du Pont, Kronos Titan, SMC, Sachtleben, ICI (Tioxide), Kraft, Bayer, CVRD (Brasil), IRE (India).

3. Synthetic iron oxide pigments

The majority of the industrially most important red pigments are based on synthetic iron oxides. There are a number of process routes such as the Penniman, the Abiline, the Rasquin or the English process, which are all traditional. World leader in synthetic pigment production is the Bayer AG. Others are Pfizer, Ferro, ICI. The mostly wanted yellower colours are based on precipitation and controlled thermal decomposition of ferrous sulphate (copper reds), which are a by-product also from the TiO_2-sulphate route. Small grain particles of 0.1-0.9 μm produce yellower shades, whereas bigger ones produce darker colours which tend towards blue. Black oxides are derived from the aniline liquors or from sulphate liquors by precipitation under a certain pH and air ratio, which is blown into the stirred solution. Black pigments can be transferred into red tones during oxidation at elevated temperatures. Brown pigments are produced usually by blending or controlled reduction of black oxides.

Synthetic Fe_2O_3 pigment market amounts around 50,000 tpa. Growing demands of synthetic pigments is being achieved with the so-called spray-roasted iron oxides of the Ruthner, Perox, Woodhall-Duckham or Chemirite route. Since these powders exhibit a different physical structure, a further conditioning is essential, especially by high intensive grinding. (The Ruthner process will be covered further on).

Magnetic pigments

Magnetic pigments basically belong to the mineral magnetite (Fe_3O_4) of high magnetic strength, which are of synthetic origin for production of special paints, magnetic toners and recording media. They are produced by precipitation from aqueous ferrous solutions by ammonia or sodium hydroxide. Magnetic particles formed after careful drying and calzining are spherelike magnetite platelets of certain geometric form. They must exceed high saturation magnetization of up to 10,000 Oersted (10Ex104A/m). Apart from platelet structures also needle structures of gamma-iron oxide are mostly used. Modern developments tend towards coprecipitation of iron oxide together with mostly cobaltoxides, but also together with oxides of Zn, Cu, Mn, Ni. Magnetic pigments are also applied in resins, such as epoxies, thermoplastic resins, polyurethanes as wave absorbing materials, i.e. in radar shieldings.

4. Zirconia: the promising future

Zirconia's most abundant ore from where it gets processed is zirconium silicate, also called zircon, mostly to be met together with TiO_2 ores such as ilmenite or rutile, or as often to be found in Brasil, being accompanied by rare earth elements, such as monazite. World's consumption of this silicate form ($ZrSiO_4$) amounts to around 1 million tons per year, of which most is being used in refractories and abrasives. The richest sources are to be found in Australia, followed by South Africa, Russia, USA and Brasil. Natural ZrO_2, named Baddeleyite, in very pure occurrings is being found in Brasil and South Africa.

ZrO_2 usually is made thus from the silicate sands by carbo-chlorination, or by digesting at elevated temperatures with sodalime or NaOH. Australia and UK also employ plasma dissociation into ZrO_2. The pure compound being synthesized is in the monoclinic form, a white powder.

ZrO_2 can also be made by a spray roasting process starting from $ZrOCl_2$, using the Ruthner technology. A similar way has been developed in Japan by Toyo Soda, using a spray roasting route, which allows the in-situ blending with other elements, like yttria, to form partially or fully stabilized systems. A further route to make zironiumdioxide powder is being done by the so-called sol-gel route, which is being handled in that paper in a separate chapter. A first industrial plant using this technology has been established by Mitsubishi, Japan.

Modern ceramic science welcomed zirconia as the most promising element to be able to achieve a certain level of plasticity after careful blending with other elements like yttria, ceria, magnesium and calcium, something which until then has been unknown to a ceramist.

Since ZrO_2 undergoes a reversible crystallo-graphic change, of which the tetragonal towards the monoclinic one is being used in the so-called transformation toughening (t--> m). Since a similar change is being known within the austenitic to martensitic transformation in steel, this change is also named martensitic change, whereby the tetragonal particles exhibit a 5-6 per cent higher volume and thus are able to perform a stress induced toughening effect. The ZrO_2-tetragonal particles which precipitate along intergranular faces and within certain patterns were part of very intensive investigations. High resolution transmission electron microscopy (TEM) allowed an insight into these patterns of tetragonal, monoclinic and cubic (high temperature form of ZrO_2) forms especially due to different alloying with Ca, Mg, Y, Ce in molar ranges of 2-12 per cent. A very large number of publications has been written on that topic of which the most important will be named under the literature section.

Zirconium dioxide, monoclinic or tetragonal offers excellent material enhancement to alumina ceramics, to form ceramic composites, called ZTA (zirconia toughened alumina), with enhanced bend strength of up to 700 MPa (compared to the regular 250-350 MPa of pure Al_2O_3).

B. Special technologies

Classical technologies which mostly start from certain natural occurrings like ores or salts to make ceramic powders by chemical procedures of leaching, digestion, melting, chlorination, as previously described, lead to different chemical compouds of the elements such as hydroxides, oxides, or salts. These may form a new source of starting material for further technological treatments in order to get pure or blended oxided powders. These processes may be combined under thermal decomposition processes, to be discussed in that chapter. These are:

- The Ruthner pyrohydrolysis process (in some instances also called Aman's process);
- EDS processes (evaporative decomposition of solution);
- Flame pyrolysis processes;
- Microwave decomposition of solution (MDS) processes.

1. The Ruthner spray roasting process

The Ruthner process is a way of thermal decomposition of solutions, like purified brines or spent pickle liquors. The process was originally introduced into practical industrial application in the late fifties. Its original goal was to recycle hydrochloric solutions of

Fe(II) to regain HCl for pickling purposes. With the successful introduction of ferrite ceramics the demand of synthesized Fe_2O_3 rose drastically in the late sixties and especially in the seventies, which made spray roasted iron oxide an important contribution to chemically precipitated types. In the same time which enabled the Ruthner company of Vienna to build nearly 200 of such plants world wide, its technology was also applied to convert other chloride solutions, like those of Mg, Co, Ni, Al as well as mixtures of them into the respective oxides.

The original idea of J. Aman in Israel to convert the carnallitic brines of the Dead Sea to make MgO as a raw material for refractories, finally was then realized by Ruthner Engineering in collaboration with American Magnesite Company (nowadays Radex of Austria). The process which was established in Rehovot, Israel, was able to successfully produce 25,000-30,000 tpa of the most pure MgO powder. In the following a series of similar plants were erected in Austria, former Czechoslovakia, former Yugoslavia, Eastern Germany, with a concerted output of over 100,000 tpa.

The process requires four essential operations: firstly to make the chloridic, or nitratic solution, then to purify such a solution, to have the solution spray roasted and finally to have a post-treatment of the oxide powder done. There are no strict rules of how to make up the brines, the units will have to be tailor-made in any case. Examples are, ilmenite leachings to have iron oxide processed and TiO_2 made, bauxite leachings to separate them from iron oxide, leachings of nickel matte or nickel rich serpentines to make NiO, leachings of magnesite ores, or concentrates (ashes) to have MgO processed. In many applications chloride solutions are received from pickling processes, first of all from steel (mild or high alloyed) ones using HCl or HF/HNO_3, aluminium foil pickling with HCl to produce Al_2O_3 of purest grade, titanium and zirconia pickling using HF/HNO_3. Here the approach is to regain the acid(s) and the oxide(s) from the solution.

A third application is to have metal oxide(s) produced by dissolving metal scrap in hydrochloric acid (eventually HF and HNO_3) and to recycle the acid permanently to the leaching units, whilst producing the oxide(s). Examples given are the production of manganese-ferrite powder by Spang (USA) and TDK (Japan) using the Ruthner technology.

Other process possibilities, starting from metals by acidic dissolution, have been developed but were not yet realized industrially. Examples are the route to make nickel hydrogenation catalysts, TiO_2 (anatase) prime material for SCR (selected catalytic reduction NO_x-gases in stacks) and the process to make aluminatitanate (Al_2TiO_5, tialite).

By running the spray-roasting process with nitrate solutions, ternary ferrite systems can be made, which have been successfully tested as a prime material for high-u soft ferrites.

The conversion through pyrohydrolysis is done in a brick lined cylindrical reactor, which in the greatest plants built has a height of up to 40 ft. The solution is being sprayed into the reactor by means of nozzles and is thermally converted by means of gas or oil driven burners, which are circumferentially arranged at the lower level of the reactor. In some cases, whilst spray roasting very volatile substances, the pyrolysis is run co-current, i.e. with the burners being arranged at the upper level of the system. The acids produced are being reabsorbed by means of packed towers. The emerging gases are being washed and purified by means of scrubbers, water sprayed vents and eventually by means of De-NO_x catalytic systems, in order to fulfill even the stringent environmental requirements (figure 1).

Powders received from this process have specific surface areas starting from 2.0 m^2/g up to 50 m^2/g and bulk densities of 0.3 to 0.9 g/cm^3, depending on process conditions and the salt system used. Specific energy requirements which strongly depend on the plant size range from 700 to 1,200 kcal/1 solution, or 4,000 to 7,000 kcal/kg oxide. The process therefore is rather energy consuming and requires cheap sources of prime energy (natural gas).

Most important is the production of iron oxide (hematite) by this process, which is being performed in all industrialized nations. Some 160 plants are on-stream using the genuine Ruthner technology, with an overall output of around 500,000 tpa of Fe_2O.

Spray roasted iron oxide usually finds its way to the ferrite industry, to make hard and soft ferrites, of the general formula Me(II) 0.6 Fe_2O_3 and Me(II)O.Fe_2O_3, respectively, which together amounts to more than 400,000 tpa world wide, with very high growth rates of 8-10 per cent in demand. The leaders of it are in Asia, most of all Japan and Korea. But also China keeps up with two new regeneration lines to produce around 20,000 tpa hematite of very high pureness and low silica content. SiO_2 which is even added during the production of hard ferrites, is most disadvantageous for soft ferrite applications. In most cases nowadays a proper iron oxide for that purpose must have a SiO_2 level beyond 100 ppm (0.01 per cent). To meet these requirements Andritz-Ruthner has developed several technologies to purify pickling liquors from SiO_2, such as a chemical precipitation method which works by adsorption of SiO_2 on flocculated $Fe(OH)_3$ or by applying cross-flow microfiltration.

Iron oxide is also used in the pigment industry mostly for colouring concrete, tiles and bricks which is of growing importance for the construction industry. Spray roasted iron oxide after proper milling and blending is more and more being used also for that purposes.

Apart from the iron oxide production by the Ruthner spray-roasting process, a further process has been developed by co-spray-roasting solutions to make f.e. manganese-ferrite. It consists of two different leaching units, where steel scrap and ferro-manganese or electrolyte manganese are being leached in hydrochloric acid and the final solution of a certain Fe-Mn ratio is then being spray roasted at elevated temperatures. The powder, after proper post treatment in a rotary kiln is being practically ready for the ferrite production. There are a few plants working in Japan and in the USA, which are based on this process. The final soft ferritic material is considered to be of better quality than conventionally made ones by mixing-blending-grinding technologies.

2. Other spray roasting processes

Lurgi had developed a HCl regeneration process already in the thirties which is based on a fluidized bed decomposition. Its outcome however is not a fine powder but pellets of some mm in diameter which are very hard to ground up and therefore mostly are returned to the steel-making process.

A modern approach which actually is a combination of both, the Ruthner and the Lurgi process, has been developed in Japan by the Chemirite Co., Tokyo. It basically consists of a fluidized bed reactor which is run at very high temperatures and therefore produces a high amount of iron oxide dust which is being recovered by means of a huge electrostic filter. Chemirite's powder is of very small particle size and of light colour.

Dornier of Germany has developed a spray-roasting process which they call RSV (Reaktions-Sprüh-Verfahren) process. It basically consists of the same process units as the Ruthner process, the difference being the heating device, which is an indirect electric wall heating of the reactor. Its equipment is designed for only small throughputs. The process is able to make very pure powders for electronic purposes, as well as for catalysts and engineering ceramics.

3. Other similar processes

EDS stands for evaporative decomposition of solution. It has been developed at the Pennsylvania State University and basically consists in spraying a solution into a tube mounted in a horizontally heated furnace and to get a very fine oxide powder after proper decomposition. The process is of no industrial use but serves as a research instrument mostly to make small amounts of mixed oxide powders for different physical applications.

Flame pyrolysis is a way to make very fine powders which industrially is being used by Degussa to make oxides like SiO_2 (Aerosil), as well as TiO_2, ZrO_2, which are used for fillers because of their very high surface areas. The way to make them is to directly spray a solution of their corresponding chlorinated compounds into a flame where they are burned and thus oxidized.

Microwave decomposition of solution is a novel approach to have an aqueous or organic solution thermally decomposed to form oxides. The advantage is the dielectric heating of the material itself which avoids any contamination and enables to regain even organic solvents by proper absorption devices, which would decompose if conventional heating procedures were applied. Such a process has been developed at Andritz-Ruthner and is being called MDS (microwave decomposition of solution).

There is great interest nowadays also to have ceramics directly sintered by means of microwaves, like in Los Alamos National Laboratory and in Oak Ridge National Laboratory, USA. The technique is being called microwave ignition and controlled combustion synthesis (MICROCOM). The magetron being developed for these purposes work at the commercialized frequency of 2.45 GHz but are applied for some thousands of watts power input.

C. Submicron powder processings

1. Sol-Gel technology

Sol-gel methods belong to a special way of ceramic chemical processing and was developed in the early eighties in the USA, at the University of Florida. The process route starts from organic compounds (metal-organics) which are hydrolyzed under very careful conditions. The particles are in the nanometer-size range and of a nearly perfect spherical shape. The process was firstly developed to make nuclear ceramics, such as urania, thoria and plutonia.

The procedure is in the consequence: Starting solution-->sol-->gel-->oxide. The secrete lies in the sol, which is comprised of a colloidal mixture of nanometer particles. The art is to have the sol stabilized and finally to remove the solvent by careful drying or freeze drying. Sol-gel processes are used also for coating of metallic or ceramic substrates. The powders are of a very narrow size distribution and of very high purity. Studies which were undergone of controlled hydrolysis of metal oxides were TiO_2, ZrO_2, Al_2O_3, Al_2O_3-ZrO_2, SiO_2, mullites, ThO_2, HfO_2, UO_2.

Compactation of such very fine particulates requires high forces but yield ceramics of very uniform grain sizes. Of industrial importance is the production of bariumtitanate starting from Ba-acetate and titanium-tetra-isopropoxide.

2. Different methods to produce ultrafine powders

Instead of precipitation those methods comprise of gas phase decomposition, like plasma synthesis and laser decomposition methods. At the Technical University of

Berlin the plasma synthesis is investigated to produce silicon-nitride-powders (Si_3N_4), starting from $SiCl_4$ and NH_3. Also ultrafine nitrated powders like TiN and AlN were made by plasma synthesis at temperatures of more than 10,000 K with high frequency induction plasma.

3. Experimental processes of special interest

Those are processes where f.e. amorphous powders by chemical sol-gel methods are made (organic glasses). They are applied for optical coatings, f.e. ZrO_2-SiO_2 on substrates. Other methods include hydro-thermal processes of chemical reactions under pressure and at elevated temperatures in autoclaves. Most important is the synthesis of zeolites which have gained enormous industrial importance in heterogenous catalysis. Pure quartz crystals are grown by hydrothermal methods, which are used world wide in watches and ultrasonic devices. Other investigations focus on new crystallographic methods to produce pure crystals like $K_2O.6TiO_2$, $FeTiO_3$, niobates, ferrites, etc. The hydrothermal method is of essential interest to make single crystals of substances.

D. Market survey on fine ceramics

There are several market reports available on ceramics, such as from BCC (Business Communications Co., Norwalk, CT), Predicasts, Gorham Advanced Materials Institute, Wheeler Associates, Industry Analysis Division, Department of Commerce, to name some of the most important institutions.

Around 60 per cent of the total market is dominated by electronic ceramics with a market value of 1700 million US$ (1985), of the whole 3 billion dollar world-total ceramic market (1985). The strong growth as predicted for the automotive market, with a predicted 22 per cent annual growth virtually did not happen. There is no one car producer in the world who uses f.e. ceramic turbo chargers in mass production. Actually the automotive sector was the biggest hope for the ceramic industry. However there is another very high potential growth using ceramics in the chemical industry because of their excellent corrosion resistance. Nowadays pumps, bearers, dies and linings are being used in a 100 million dollar market. World-wide bioceramics market, another market of great importance amounts to some 5 million dollars.

The ceramic powder market values nowadays around 500 million dollars for the whole world, of which Japan takes part to a 50 per cent. Of it the oxide powder market of course contribute the biggest part with around 70 per cent or 350 million dollars. In 1985 only within the USA the total oxide powder market amounted to some 500,000 tons, with 150,000 tons being SiO_2, 300,000 tons steatite and 20,000 tons ferrites and 60,000 tons being Al_2O_3. World market nowadays might be 3-4 times of that total number, i.e. 1,500,000 to 2,000,000 tons.

Advanced ceramics are being promoted by the United States by the Advanced Ceramics Association (USACA) which is held by around 40 US companies. Only US consumption in electronic ceramic parts, such as electronic packings, ceramic capacitors, ferrites piezolectrics, sensors and thick film pastes, are reported to amount to some 2 billion dollars in 1987

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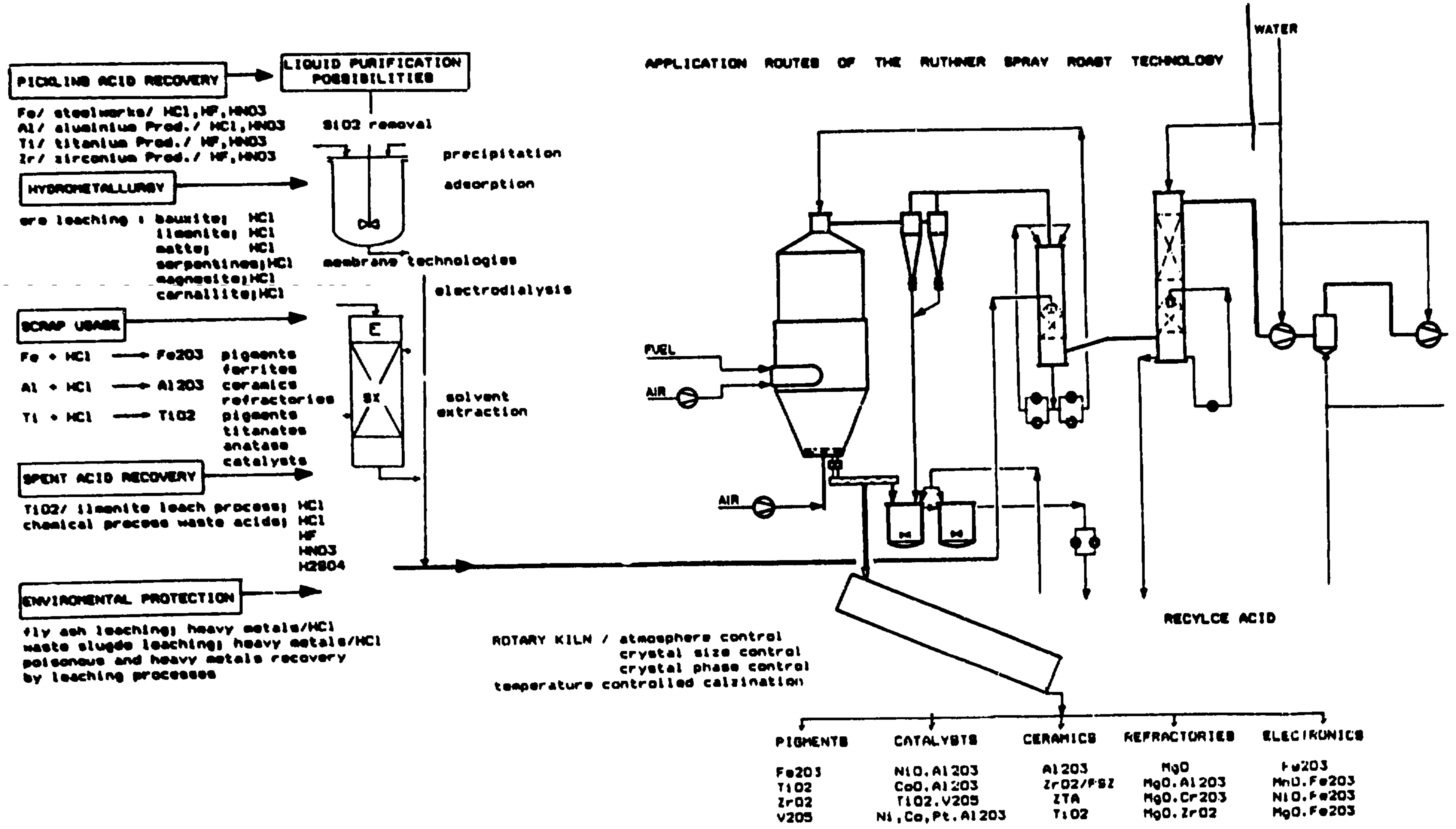
APPLICATION ROUTES OF THE RUTHNER SPRAY ROAST TECHNOLOGY



3. THE RUTHNER PROCESS

Description of the process

The production of pure metal oxides requires four essential operations including leaching of the raw material with hydrochloric acid, purification of the metal chloride solution, pyrohydrolysis, and post-treatment of the oxide. The metal chloride solution is produced in a leaching unit. In the simplest case this leaching unit may be the pickling line or, as in the case of magnesium oxide, a separate leaching unit for magnesium-containing raw materials. Generally this unit can be tailored to the individual raw material used. Metal chloride solutions may also be obtained in the form of by-products from upstream processing stages. Such by-products include cobalt chloride and iron chloride from solvent extractions during the production of nickel metal. Leaching solutions of ilmenite processing during the production of synthetic rutile is another source for iron oxide as by-product.

Depending on the application, the still-unpurified chloride solutions can subsequently be purified by precipitation or co-precipitation of impurities, by solvent extraction, by ion exchange, or by crystallization. When purified by means of solvent extraction or ion exchange, the metal chloride solutions normally will be sufficiently concentrated for further treatment in the hydropyrolysis reactor.

The pure-metal chloride solutions are then fed into the pyrohydrolysis unit. Utilizing the hot gases from the reactor, the solution is further evaporated in a so-called preconcentrator and then transferred into the pyrohydrolysis unit. In the absorption column, the wastewater from the previous purification steps is used to regenerate hydrochloric acid out of the acid gases formed during the pyrohydrolysis process. This acid is then used again in making chloride solutions. Fresh hydrochloric acid has to be used only to replace those amounts of hydrochloric acid which cannot be recuperated because of the formation of chlorides not susceptible to pyrohydrolysis, such as calcium chloride or the alkali chlorides.

The spray-roasting process is named after its essential element, the spray-roasting reactor. In the upper portion of the reactor the chloride solution is sprayed through ceramic spray nozzles at a pressure of 3 to 5 bars (3×10^5 to 5×10^5 Pa). Basically, the reactor consists of a cylindrical tower lined with refractory ceramic material and several burners circumferentially arranged on the exterior. These burners, which are oil or gas fired, supply hot gases to the inside of the reactor, thus producing a rotary flow, the rate of which is determined by the diameter of the reactor.

The droplets produced by the nozzles are moved along by this flow, and intimately mixed with the reactor atmosphere. As the droplets fall, water and hydrochloric acid evaporate so that a crust of chloride crystals will form on the droplet surface. During evaporation of the residual solution on the inside, additional crystals will settle on this crust. When the vapour escapes, the crust is frequently broken up or perforated. As previously mentioned, the chloride particles formed in this way react with water vapour and possibly oxygen to form metal oxide and hydrochloric acid gas, with the original agglomerates remaining largely intact. For this reason the oxide shows the characteristic structure of a hollow sphere.

Since the evaporation process at high temperatures is very fast, it may happen that the chloride crust is completely fragmented. In this case, and with processing solutions of low metal chloride concentrations, the end product will be a very fine oxide powder. Depending on type and production conditions, the oxide powders will have bulk densities between 0.2 and 0.8 kg/L, and specific surfaces between 2 and 30 m^2/g (BET). The primary crystals have a diameter of approximately 0.2 to 0.4 µm, whereas the diameters of the agglomerates usually range from 100 to 200 µm.

The oxides are continuously withdrawn from the lower conical or truncated cone-shaped part of the reactor by means of a rotary valve and a variety of conveyors. The roast gases are then removed from the reactor head and, depending on the type of plant, pass through one or two cyclones or an electric filter for dust precipitation. In the downstream preconcentrator the roast gases are cooled to approximately 120° C in direct contact with the solution. In modern plants this process takes place in a Venturi scrubber.

The hydrochloric acid gas is subsequently washed out of the cooled roast gases in an - mostly adiabatic - absorption column, and leaves the column in the form of azeotropic hydrochloric acid (20 wt%). The roast gases, which contain only very small amounts of hydrochloric acid (in addition to water vapour and inert gases such as nitrogen, oxygen and carbon dioxide) are then removed by downstream fans at the column head.

To remove the last traces of hydrochloric acid from the roast gases, water is fed into the fans. Together with additional wastewater, this water is used to absorb hydrochloric acid in the column. A slight negative pressure is maintained in the pyrohydrolysis reactor as well as in all other downstream parts of the plant, by means of the exhaust fans, so that even in the event of nozzle replacement, noxious gases or oxide dust are prevented from escaping into the atmosphere.

For some applications the spray-roasted oxide requires a post-treatment. In the production of magnesium oxide, for instance, magnesium oxide is treated with deionized water to wash out any undecomposible calcium chloride or alkali chlorides that are extracted together with the oxide. At the same time, magnesium oxide is converted into magnesium hydroxide. After calcination, briquetting and sintering, sintered magnesium oxide of more than 99 per cent purity is obtained.

During production of manganese ferrites and high-purity ferric oxides, the spray-roasted oxide is transferred to a downstream rotary kiln for controlled heat treatment in a controlled atmosphere. This is necessary to achieve specific material properties. Other types of oxide post-treatment include the reduction of ferric oxides to iron powder, and the partical reduction of mixed oxides.

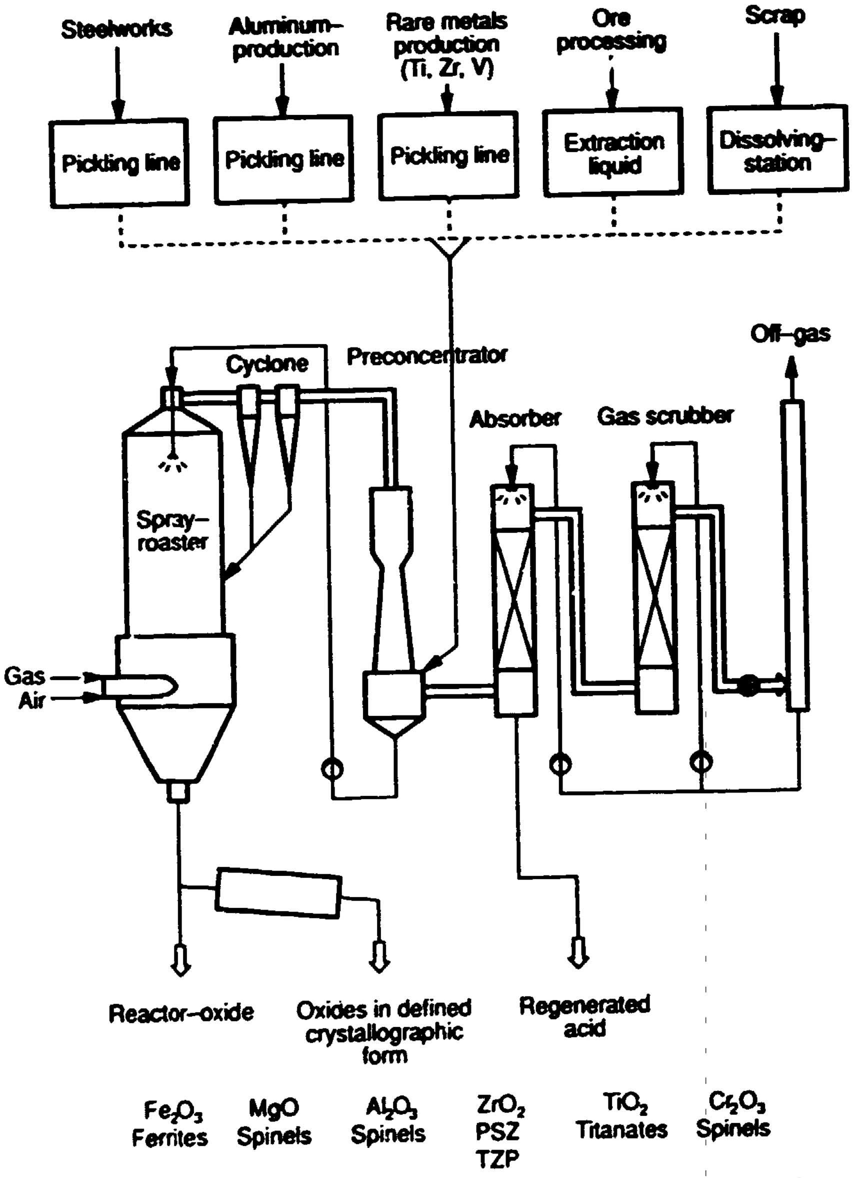
Products for the ferrite industry

Because of the enormous developments in the electronics industry, the demand for raw materials for the production of both magnetic materials and data media has dramatically increased. In principle, the ferric oxide produced in hydrochloric acid regeneration plants would lend itself to such applications, were it not for its silica content. According to the specifications of the ferrite manufacturers, this content should not exceed 0.02 wt%, even though the silica content is higher mostly because of the higher silicon content of the pickled steel. Ferric oxides with a silica content of less than 0.01 wt% (100 ppm) can thus be sold at prices three to five times higher than those of conventional qualities. To produce spray-roasted ferric oxides with a low silica content, Maschinenfabrik Andritz-Ruthner Division has developed a process for the separation of silica from waste pickle acids. The process is based on the principle that, under appropriate conditions, silica in colloidal solution can be adsorbed to iron(III) hydroxide.

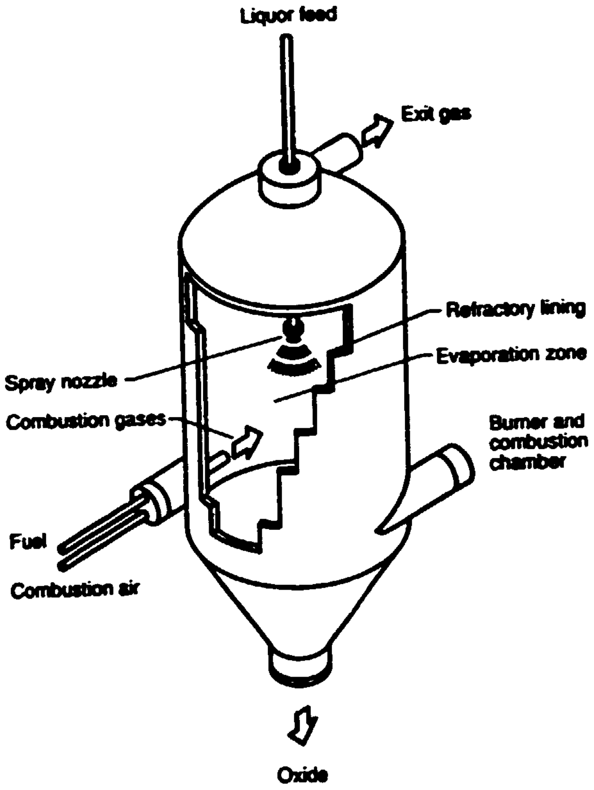
Most ferrites, including manganese ferrites, are traditionally produced by mechanical mixing of the required components using a blade mixer or a mill, and subsequent spray-drying of the aqueous suspension. After adding a binder the powder is compressed into the desired shapes. Finally, the compacts are sintered in a controlled atmosphere in a tunnel furnace, where proper ferrite formation takes place.

Experience has shown that the high-frequency properties of manganese ferrites produced by pyrolysis of a mixed ferric/manganese chloride solution are superior to those of ferrites produced by traditional methods. Since the product obtained is a solution, absolutely homogeneous oxide mixtures can be achieved, which is not possible even with the best mechanical-mixing method. As in the case of ferric oxide, the silica content has to be kept at a mimimum.

Pyrolysis of nickel ferrite is also possible by using mixed iron chloride/nickel chloride solutions. This process yields a nickel ferrite powder with excellent magnetic properties, which is being used to an increasing extent for electronics. Also, in the case of pyrolysis, product properties have been considerably improved compared with conventionally produced ferrites. By varying the decomposition temperature in the reactor, the specific surface of the product may be varied over a range of 3 to 20 m^2/g: the higher the temperature, the smaller the specific surface of the material. By combining the two chloride solutions, products with any desired nickel(II) oxide/iron(III) oxide ratio can be achieved.



Schematic drawing of the closed hydrochloric acid circuit used for the production of pure metal oxides according to the Ruthner pyrohydrolysis process.



Schematic drawing of the principle of the hydropyrolysis or spray-roasting process.

Common Pyrohydrolysis Reactions
$2FeCl_2 + 2H_2O + \frac{1}{2}O_2 \rightarrow Fe_2O_3 + 4HCl$
$MgCl_2 + H_2O \rightarrow MgO + 2HCl$
$2FeCl_3 + 3H_2O \rightarrow Fe_2O_3 + 6HCl$
$2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 6HCl$
$3CoCl_2 + 3H_2O + \frac{1}{2}O_2 \rightarrow Co_3O_4 + 6HCl$
$CoCl_2 + H_2O \rightarrow CoO + 2HCl$
$2MnCl_2 + 2H_2O + \frac{1}{2}O_2 \rightarrow Mn_2O_3 + 4HCl$
$2FeCl_3 + MnCl_2 + 3H_2O + \frac{1}{2}O_2 \rightarrow MnFe_2O_4 + 6HCl$
$2FeCl_3 + NiCl_2 + 3H_2O + \frac{1}{2}O_2 \rightarrow NiFe_2O_4 + 6HCl$
$2AlCl_3 + NiCl_2 + 4H_2O \rightarrow NiAl_2O_4 + 8HCl$
$NiCl_2 + H_2O \rightarrow NiO + 2HCl$
$2CrCl_3 + 3H_2O \rightarrow Cr_2O_3 + 6HCl$
$2(RE)Cl_3 + 3H_2O \rightarrow (RE)_2O_3 + 6HCl$ (RE = rare earths)
$TiOCl_2 + H_2O \rightarrow TiO_2 + 2HCl$

(Excerpt from an article "Pyrohydrolysis for the production of ceramic raw materials" written and given to us by Mr. Wolfgang F. Kladnig, for Ceramic Bulletin, Vol. 69, No. 5, 1990 (© Acers))

4. CERAMICS AS MAGNETIC MATERIALS (FERRITES)

Certain classes of ceramic materials normally termed ferrites exhibit unusual magnetic properties due to the particular nature of their crystal structure. All ferrites have iron oxide (Fe_2O_3), as a major constituent. They are combined with oxides of divalent metals like zinc, manganese, nickel, barium, strontium, etc. to produce crystal structures which have magnetic properties. Depending on the nature of their behaviour, magnetic materials are termed hard or soft. Hard magnets retain their magnetism once they are magnetized (it is hard to demagnetize them). Soft magnets, on the other hand, are easily magnetized and demagnetized and hence the term soft. Barium ferrites and strontium ferrites are hard, while manganese zinc ferrites and nickel zinc ferrites are soft.

Soft ferrites have lower eddy current losses and higher resistances as compared to more traditional soft magnetic materials, such as transformer steels. This makes them useful in applications where magnetic fields have to be switched on and off very fast (say from 15,000 to 20,000 times a second).

Hard ferrites (though having inferior properties to traditional permanent magnetic materials like ALNICO and cobalt samarium magnets) are much cheaper and are therefore widely used. Barium- and strontium-based ferrites are the most used hard ferrites. Manganese zinc ferrites and nickel zinc ferrites are the most used soft ferrites. Ferrites compete with a wide range of alternative materials in all uses where applications of magnetic fields are required.

Types of ferrites

There are three main categories of ferrites. These are:

- Spinel ferrites (they are called spinel because their structure is similar to the structure of the mineral spinel). These are "soft" magnets which mean that they are used in temporary magnet applications. TV, radio and telecommunications represent the major market segments. Magnetic core memories also use these materials, but do not constitute a major market, since semiconductor memories have replaced them almost entirely;
- Hexagonal ferrites, whose atoms are arranged in a hexagonal-shaped crystal structure, are used mainly in permanent magnet applications and occupy a lion's share of the permanent magnet market. The markets are loudspeakers, low-power low-torque DC motors, toy motors, alternators, etc.;
- Garnets, the crystal structures of which resemble the structure of the precious gem garnet and whose magnetic properties are similar to the soft spinel ferrites.

The critical parameters governing the behaviour of any magnetic material are:

- The residual magnetism that the material retains when the external field is removed. This is called remanence or residual magnetism;
- The saturation flux or the maximum magnetic field that can be induced in the material by a coil carrying a current, which is wrapped around the ferrite material;
- The demagnetization field or the value of the external field applied in the negative direction, that removes the residual magnetic field.

Magnetic materials are characterized as "soft" or "hard" based upon these parameters. "Soft" magnets reach large saturation values of their induced magnetic flux at low values of the applied external field. They also require very small demagnetization fields. Hard magnets, on the other hand, require very high demagnetization fields to eliminate their induced magnetism. They also have high values for their residual or remanent magnetism.

Manufacture of ferrite materials

Ferrites are normally prepared by standard ceramic processes. The spinel ferrites and the hexagonal ferrites have many similarities in preparation and some differences. A typical sequence of operations for a spinel ferrite material is shown in figure 1 (page 31). Hard ferrite preparation follows similar sequences.

The input materials, iron and zinc and manganese or iron and zinc and nickel, can be oxides, hydroxides or carbonates. They are weighed in the proper proportion, water is added and the resultant mixture is milled in a steel mill. They are filtered and then dried. This is followed by a calcining step, in which the raw materials are heated to about 1050-1600° K, 1/ to form the ferrite compound. In the case of nickel zinc spinel ferrites, the calcining temperature is about 1300° K and the material consists of crystals, which are practically 100 per cent spinel in structure. In the case of

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1/ To convert degrees Kelvin to degrees Centigrade, subtract 273.

manganese zinc ferrites, the temperature of calcining can be adjusted to vary the spinel structure content from 50-85 per cent. The time of calcining and the temperature are crucial to achieving final properties. In-process control of the composition and crystal structure by X-ray diffraction, measurement of the surface area of the calcined powder and inductance measurement from a toroid-shaped sample, are often used to ensure that the required properties are obtained. After the calcining step, the material is milled again (with or without addition of water) and spray dried to give the fine ferrite powder, which is the basic material for producing most components. The method giving optimum results appears to be to add binders such as polyethylene glycol or polyvinyl alcohol (1-4 per cent by weight) and sufficient water, to form a slurry that is 65-70 per cent ferrite by weight. This slurry can be spray dried to produce the required powder. This powder is then made into the required parts using normal ceramic processes.

Very thin parts are normally fabricated by tape casting. For parts which are long with small diameters, extrusion or isostatic pressing can be used. To control the magnetic properties of the final component the oxygen content of the kiln has to be carefully controlled during the cooling portion of the sintering cycle. This is quite a technological challenge. Spinel ferrites are normally fired in continuous tunnel kilns at temperatures ranging from 1550-1725° K, with sintering times ranging from 20 minutes to 12 hours.

For hexagonal (hard) ferrite manufacture, the steps are very similar. However, because of their higher iron oxide content and their relatively lower selling price per kilogram ($3 per kg) of finished product compared with spinel ferrites ($5 per kg), lower grade raw materials are sometimes used. Iron oxides produced by the reclamation of acid pickling liquors, synthetic oxides produced by the Lurgi process and mineral iron oxides are often used. Though these are less expensive, they are less pure, and therefore considerable process control is required to achieve desired properties.

Rotating or oscillating tube calciners, which are 2-3 m in diameter and 20-30 m long, with throughput capacities of 500-1500 kg/hr, are used. The temperature of calcining is in the range of 1500-1650° K, at which temperature the material reacts to form the hexagonal ferrite. If calcining takes place at lower temperatures, magnetic properties are not seriously affected. However, the material is too soft and subsequent milling gives too fine a particle size, leading to difficulties in subsequent pressing and high shrinkage during sintering. If the temperature of calcining is too high, the particles that result are too hard and coarse. Although these can be pressed easily, the shrinkage is high and the magnetic properties are affected.

Hard ferrites are prepared by dry or wet pressing of the calcined powder in the presence of an external magnetic field. Dry pressing is cheap. However, because of friction between adjacent particles, the magnetic alignment is not optimum. In wet pressing, the slurry coming from the ball mill (after calcination) is pumped into a die cavity where alignment takes place with the help of a magnetic field. After alignment, the water is removed by applying a vacuum to the die cavity. A fine filter paper prevents particles from being pulled out of the die cavity. The design for wet dies is more expensive and the pressing time is longer. Sintering can take place immediately for dry pressed parts. Wet pressed parts, however, have to be dried carefully before being placed in a kiln. The pressed parts are sintered in air at 1400-1650° K to yield a dense ceramic material. After this, the grinding of the part takes place to meet required geometrical tolerances for loudspeaker rings and the arc-shaped segments used in D-C motors.

Applications

Spinel soft ferrites

The major applications of spinel ferrites (predominantly manganese zinc spinel ferrites and nickel zinc spinel ferrites) are in the following areas:

TV and radio applications: Ferrites are used as magnetic elements in yoke rings for the deflection coils for TV picture tubes and in flyback transformers in TV sets - crucial elements in the scanning by the electron beams. They are used as antenna rods in radio applications.

Recording heads: Both manganese zinc spirel ferrites and nickel zinc spinel ferrites are used in magnetic recording heads for duplicating magnetic tapes and the recording of digital information.

Most recording heads are fabricated out of nickel zinc ferrite. Metallic alloy heads are ruled out because of large eddy current losses. Manganese zinc ferrites can also be used and do offer superior properties. However, they need a complicated sintering cycle and are not as strong as nickel zinc spinel ferrites. However, improved fabrication processes, such as isostatic hot pressing, have yielded good results. Hot pressed heads of manganese zinc ferrites are used in high performance digital and video recording applications.

Switched mode power supplies: Ferrite materials have lower magnetic losses as compared to laminated transformer steels. They also have a resistance of 10 ohms/cm as compared to about 50 micro-ohms/cm for transformer steels. This permits the use of ferrite core materials as transformer elements, in high frequency power supplies. These are normally referred to as switched mode power supplies and can operate at frequencies of between 15 kilo-cycles and

30 kilocycles, with higher efficiencies. This means that the power will be switched on and off from 15,000 to 30,000 times a second. Because of these properties the size of the transformer core and the number of turns of wire can be reduced. Ferrites are also used for chokes and filters.

These represent a growing market for spinel ferrites in TV sets, telecommunications and a whole range of other professional electronics items.

Linear applications: The induced magnetic field in a soft ferrite can be made to vary linearly with the current in the coil creating the external magnetic field. This linear relationship is exploited in these applications. At low signal levels (low current in the coil around the ferrite core), ferrites act as transformers or as inductors. Manganese zinc ferrites are usually used for applications where frequencies involved are less than 2 Megacycles. Nickel zinc ferrites find use in applications between 2 and 70 Megacycles. By varying the nickel zinc ratios, a large number of materials for use as high frequency inductors, antenna rods, high power transformers and pulse transformers can be made.

Magnetic core memories: Torroidal cores made of spinel ferrite are used as magnetic core memories. Spinel core memories are used in applications where loss of power does not result in loss of information. Since the memory consists of torroidal cores strung on a wire and there are no moving parts, it is very reliable. This makes it suitable for military applications. Even though they were originally used for computer applications, they have been completely replaced by semiconductor memories.

Applications of hexagonal ferrites (hard ferrites)

The major applications of hard ferrites are as permanent magnets in a variety of Direct Current (DC) motors. The hexagonal ferrites of commercial interest are barium and strontium ferrites. The other major area where hexagonal ferrites are used is in loudspeakers, where they replace the more expensive aluminium nickel cobalt (Al Ni Co) permanent magnets. They have also been used in travelling wave tubes, telephone ringers and receivers, door closers, seals and latches in refrigerator doors and in toys. Hexagonal ferrites are used in bubble memories. However, bubble memories do not represent a major market, since other memory devices offer superior capabilities. Hard ferrites compete with Al Ni Co, cobalt-samarium and iron-neodymium boron, in permanent magnet applications. Their price makes them attractive though their magnetic properties, especially at higher temperatures, are poorer. Table A gives advantages/disadvantages of hard ferrites and competitive materials.

New iron-neodymium boron magnets, developed by both Sumitomo (Japan) and General Motors (USA), can substitute Al Ni Co and cobalt samarium magnets in the lower temperature ranges. Their prices ($15-$20 per kg) may also pose some threat to the lower cost hard ferrites in the future.

Soft ferrites: world market trends

In 1988-89, the world production of soft spinel ferrites, mainly manganese zinc spinel ferrite and nickel zinc spinel ferrite, has been estimated at 1,005,000 tons and this is expected to grow at an annual rate of around 10-12 per cent. The market value of world ferrite production in 1989 was estimated at 2 billion dollars, of which the soft ferrite market was about 1.2 billion dollars.

Soft ferrites compete mainly with low resistivity iron, low resistivity low carbon steels, iron-aluminium-silicon alloys and nickel iron alloys. Iron silicon alloys are the material most used in power and distribution transformers and large rotating machinery. World production of iron silicon alloys is probably in excess of 4 million tons. Soft ferrites are the preferred material in all high frequency applications and for recording heads. The Japanese are the world leaders in soft ferrites and three companies - TDK Electronics, Sumitomo and Fuji Electro-chemical - dominate the world market.

Table A

COMPARATIVE PERFORMANCE CAPABILITIES OF DIFFERENT PERMANENT MAGNETIC MATERIALS

Ranking	Residual [a] magnetism (Remanence)	Coercivity [b]	Volume magnetism [c]	Thermal stability [d]	Price
Good	Nd Fe B	Nd Fe B	Nd Fe B	Al Ni Co	Ferrite
	Al Ni Co	Co-Sm	Co-Sm	Co-Sm	Nd Fe B
	Co-Sm	Ferrite	Al Ni Co	Nd Fe B	Al Ni Co
Poor	Ferrite	Al Ni Co	Ferrite	Ferrite	Co-Sm

Source: New Advanced Materials, edited by Marc J. Ledoux, Springer Verlag Press 1986.

Notes:

1. Nd Fe B is neodymium iron boron magnet.
2. Al Ni Co is aluminium nickel cobalt magnet.
3. Co Sm is a cobalt samarium magnet.

a/ Residual magnetism or remanence should be as high as possible in a permanent magnet.

b/ Coercivity is a measure of the external magnetic field required to remove the permanent magnetic field of the magnet. For permanent magnets, coercivity should be as high as possible.

c/ This is a measure of the volume of material required to achieve a given field. The better the volume magnetization, the lesser the amount of material required to achieve a given magnetic field.

d/ High temperature performance dictated by this parameter.

Figure 1

STANDARD SEQUENCE FOR SOFT FERRITES

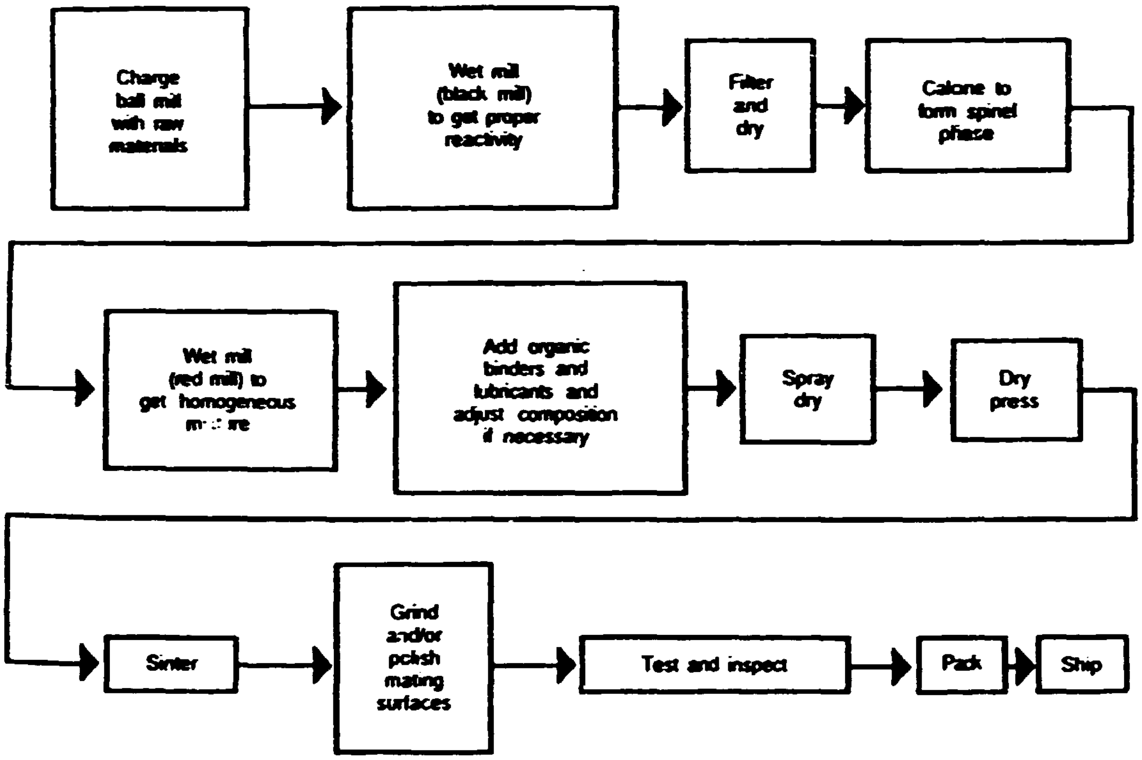
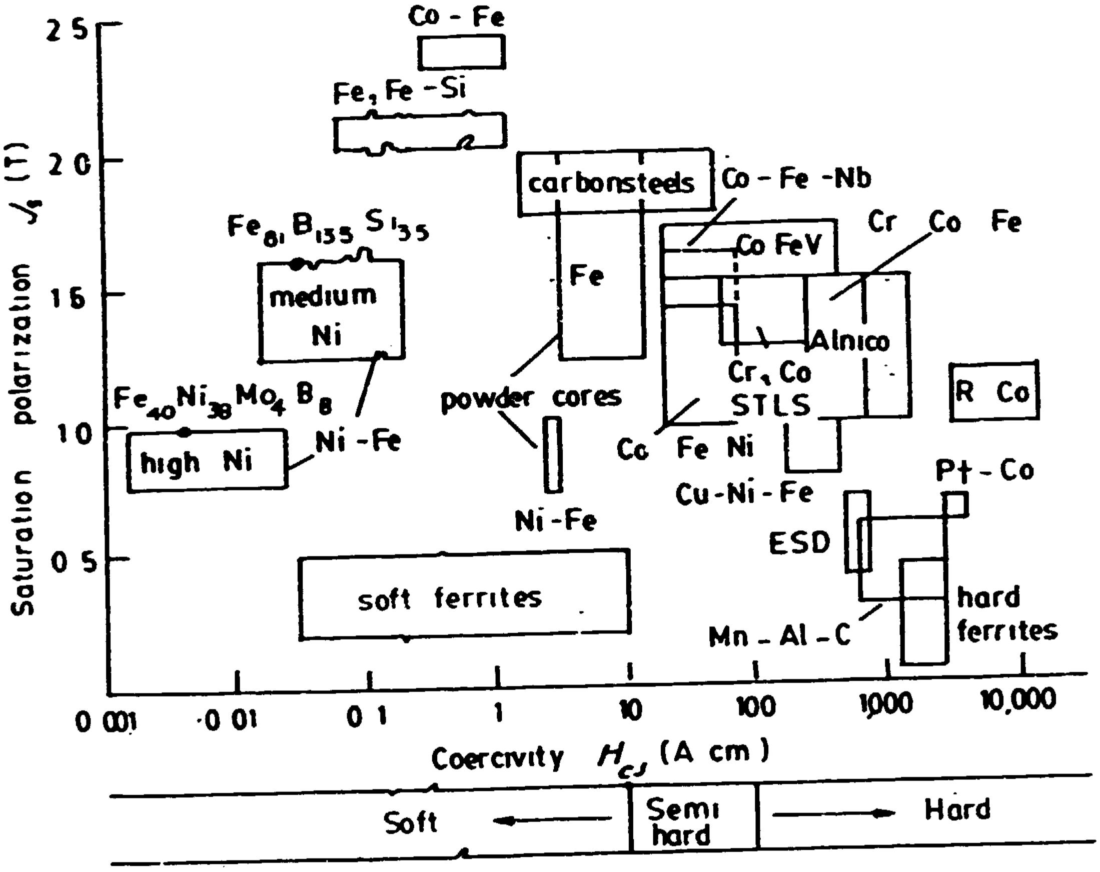


Figure 2

provides an overview of different magnetic materials including hard and soft ferrites.

AN OVERVIEW OF MAGNETIC MATERIAL



Source: Encyclopedia of materials science and engineering, by M. B. Bever.

(Extracted from High-Tech for Profit, Business Opportunities in Advanced Ceramics, produced by Technology Exchange Network, 6 Ware Road, Cleveland Town, Bangalore-560-0051, India.

5. APPLICATIONS

Ultra-fine, ultra-pure oxide powders

Increased use of ceramics as electronic and structural materials has led to increased demands for ultra-fine and ultra-pure ceramic powders, as the end product properties are critically dependent on precursor quality. Researchers at Penn State have developed a new method of producing fine and ultra-fine powders for such specialty applications as nanocomposite components, based on work begun by Faraday in the last century. The technique, called reactive electrode submerged arc (RESA) processing, uses two submerged metal or otherwise conducting electrodes that arc in a dielectric fluid that reacts with the metal. The extremely high temperature generated by the brief spark vaporizes the electrode material and the surrounding fluid, creating a reactive bubble for an instant. The reaction product of the combined vapours is quickly quenched by the surrounding dielectric fluid, yielding a colloidal sol of spherically shaped particles.

The process can be readily demonstrated with normal line voltages (~230V) across thin metal foils immersed in water or mineral oil. Using somewhat more sophisticated equipment, the researchers generated gamma-aluminium oxide, a variety of titanium oxides, zirconias and oxides of tin, tungsten, and iron, all using metal rods and such common dielectrics as water. Control of voltage, amperage, and liquid composition allows the production of fine sols of aluminium, titanium and zirconium anhydrous oxides, and even some phase control of variable valence metals such as chromium. Oxide particles ranged in size from 10 to 1,000 nm. (Amitabh Kumar and Rustum Roy, Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802, USA. Tel: (814) 8651174). (Source: New Materials World, December 1989)

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Method for fabricating large pieces of perovskite composite oxide

Researchers from Japan's NIRIM report that they have formed PLZT ceramic discs measuring 31 x 2.5 x 10 cm. PLZT is a composite oxide ceramic composted of lanthanum, zirconium and titanium. The fabrication method involves mixing the powdered components in nitric acid followed by alkali precipitation. The hydroxide powder produced is washed and fired under pressure to yield a ceramic. (National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba-Shi, Ibaraki-Ken 305, Japan. Tel.: 0298 51 3351. Fax: 0298 52 7449.) (Source: New Materials World, September 1990)

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Low cost production of barium ferrite powder

A Japanese company's fine powder research centre has developed a process for producing barium ferrite powder at about half the cost of conventional processes. Barium ferrite, used for high density recording media such as digital audio tapes and floppy disks, is conventionally produced by a hydrothermal process.

In Showa Denko's new process, iron, barium, cobalt and titanium chloride ions are co-precipitated in an alkaline solution. The resulting material is then oxidized by treatment with hydrogen peroxide, followed by neutralization with hydrochloric acid, to obtain a mixture of hydrated oxides of iron, cobalt and titanium, plus barium carbonate. This mixture is dehydrated in the presence of sodium chloride, fired at approximately 750° C, and washed to yield barium ferrite.

The magnetic powder has a particle diameter of 60 nm and a saturation magnetization rate of 70 emu/g, some ten times higher than powder produced by conventional processes. (Showa Denko KK, 2-10-12, Shiba-Daimon, Minato-Ku, Tokyo 105, Japan. Tel.: (03) 432 5111. Telex: 26232. Fax: (03) 436 2625) (Source: New Materials World, August 1990)

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Near-net ceramics

The University of Michigan (475 East Jefferson, Ann Arbor, MI 48109-1248) has developed a process whereby a dense, near-net shape ceramic with oriented microstructures has been developed. Technique gets crystallographic texture in sintered ceramics by seeding with oriented particles. Strength or conductivity frequently depend on crystallographic directions. Normal ceramic processing randomly orients individual crystallites, giving isotropic properties which are an average of the directional single crystal properties. New technology for obtaining crystallographic texture does not depend on hot pressing, which limits the shape and complexity of the densified ceramic. Crystallographic texture is developed during pressureless sintering.

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Synthesis of ceramic wire

A new synthesis method for ceramics, called the localized reaction method, has been developed by researchers at Seikei University's Faculty of Engineering. A ceramic wire 10-100 μm in diameter and several centimetres in length has been synthesized using this process, which employs a hollow thread made from polymer metal or ceramic, as a "micro-reactor".

Alkoxides are introduced into the tube and hydrolysed by water or atmospheric moisture, after which the hydrolysed product is removed from the tube, dried, and fired at between 300 and 1,200° C.

The method has been used to produce ceramics such as PZT (lead titanate zirconate), barium titanate, strontium titanate, manganese ferrite, barium titanate and manganese ferrite, and can also be adapted to produce spherical materials and regularly structured integrated ceramics. (Faculty of Engineering, Seikei University, 3-3-1 Kichijoji Kita-Machi, Musashino-Shi, Tokyo 180, Japan. Tel: (0442) 51 5181. Fax: (0442) 56 0115.) (Source: New Materials World, October 1990)

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Ceramic chip could write off discs

An Australian company has launched an erasable computer memory chip that retains data when its power source is switched off. The chip could revolutionize the design of computers and other electronic devices by doing away with the bulky magnetic disc memories that are currently used to store data permanently.

Current computers rely on a selection of memory devices. These include chips known as read-only memories or ROMs that store preprogrammed data without power but cannot be erased, and instantly erasable chips that require constant power, known as random-access memories or RAMs. To store more data and programs when the power is off, most computers use magnetic discs.

The new chip is known as a ferroelectric random-access memory of FRAM. If it proves as successful as its developer, Ramtron, claims, it could replace all other types of data storage. (Excerpt from New Scientist, 16 February 1991)

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Ceramic substrate for powder modules

A molybdenum clad ceramic powder module substrate for use in power inverters has been introduced by Mitsubishi Electric. The substrate, which can prolong the life of a powder module by a factor of ten, is designed to be resistant to thermal stress and uses a newly developed active titanium paste to bond a copper plate onto the ceramic substrate.

In an experiment at temperatures ranging from -40 to 125° C, a powder module in which this ceramic substrate was used lasted more than ten times as long as a conventional module. The heat dissipation characteristics of the substrate are said to have been improved by 10% by increasing the thickness of the copper plate.

The company plans to use the new substrate to increase both the capacity and density of its insulated gate bipolar transistor powder modules and its existing modules. (Mitsubishi Electric Corp., 2-2-3, Maranouchi, Chiyoda-Ku, Tokyo 100, Japan. Tel: (03) 218 2111. Telex: 24532. Fax: (03) 218 3686.) (Source: New Materials World, December 1990)

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Synthesis of ultra-fine powders by microwave heating

Ultra-fine powders (<0.1 µm) are produced by microwave heating of dissolved nitrates, sulphates, or chlorates to minimize energy consumption and eliminate the need for expensive capital equipment. For example, 100 g nickel nitrate and 1.5 g aluminium nitrate first are dissolved in 80 ml water and then are exposed to microwave radiation (700 W and 2.45 GHz for 35 minutes) until the water is removed. The resulting $NiO + Al_2O_3$ powder has a surface area (measured by BET gas absorption) of about 3.7 m^2/g. The surface area increases to 5.158 m^2/g when the water volume and time of heating are increased to 320 ml and 55 min, respectively. Further, for ultra-fine powders containing a metal that reduces from its oxide in hydrogen, a metal-oxide composite can be formed by heating the powder in a conventional tube furnace (600° C for 2 hours) in a hydrogen-rich atmosphere. Microwave heating also can be applied to producing superconducting ceramic powders with the composition $REBa_2Cu_3O_x$ (where RE represents rare earth elements Sm, Eu, Gd, Tb, Dy and Ho). The resulting powders are super-conducting up to 95 K. (Source: Materials and Processing Report, June 1990)

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Iron particles from organometallic compound

A new method of producing ultra-fine iron particles, which are used in magnetic recording materials and magnetic fluids, has been devised by Mitsubishi Petrochemical Co., Ltd. The new process uses iron carbonyl, an organometallic compound that is liquid at room temperature, vaporizes at about 110 248° C and decomposes at temperatures of above 250° C, as a raw material.

The company used a stainless steel flow reaction system, consisting of an evaporator, a decomposition reactor, and a unit for collecting the particles produced. Liquid iron carbonyl was vaporized, mixed with nitrogen, and then continuously fed to the reactor which was heated to 400-600° C, producing ultra-fine iron powder 100-1,000 angstroms in diameter. The reactor is surrounded by a coil which applies a magnetic field, causing the ultra-fine particles to be attracted to each other, and thereby producing needle formed ultra-fine particles which are suitable for use in magnetic recording materials.

Magnetic recording materials based on ultra-fine iron particles have higher recording densities than is possible with conventional iron oxide and cobalt ultra-fine particles, and are already used in 8 mm video recording tapes. (Mitsubishi Petrochemical Co. Ltd., 2-5-2, Marunouchi, Chiyoda-Ku, Tokyo 100, Japan. Tel: +8133283 5510. Telex: 2223172. Fax: +81 3 3283 5472.) (Source: New Materials World, December 1991)

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Preparation of high purity, homogeneous zirconia mixtures

A method to prepare homogeneous mixtures of zirconia with another metal oxide (e.g., alumina, silica, titania, yttria) with low Na_2O impurity level (<0.01 wt%) is presented. The particle size of the powder product is less than 100 Å, eliminating the need for grinding or milling. Carbonated hydrous zirconia is mixed with another metal salt [e.g., $Y_2(CO_3)_3$] in an acidic (HCl) solution to form a homogeneous mixture, which is then added to an NH_4OH solution (>5M), resulting in a precipitate of the hydroxides of the metals. The precipitate is then dried by removing the water through an azeotropic distillation. The resulting zirconium mixture is brushed through a 100-mesh sieve. The collected powder sample is calcined at 850° C for 16 hours, pressed uniaxially at 10,000 psi, and then isostatically at 27,000 psi to pellets (0.5 in. size). The pellets are heated to 1,450° C (100° C/hour), held at 1,450° C for 3 hours, and then cooled at 100° C/hour. The zirconia mixture is a solid solution and the density of the pellet is greater than 99.0 per cent of the theoretical value. (Corning Glass Works, Corning, New York, USA) (Source: Materials and Processing Report, January 1991)

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Platelet-shaped iron oxide pigments

Pigments of the formula $Al_xFe_{2-x}O$ (x = 0.02-0.50) can be heated in a reducing atmosphere to form new platelet-shaped pigments of the formula $Al_xFe_{2-x}O_{3-y}$ (x = 0.02-0.50, y = 0.3-1.0) that have a lower oxygen content and interesting colour effect. Pigments prepared according to previous patent specifications are reduced at 500° C in a flowing gas mixture (100 l/hr) of 60 parts nitrogen to 40 parts hydrogen in a rotating tubular oven. The temperature and the duration of treatment determine the degree of reduction. High-gloss pigments ranging in colour from black-yellow to black-red to pure black are obtained. The pigments can be coated further before or after reduction with a discrete layer of 20-40 wt% oxides of zinc, zirconium, titanium, chromium, silicon, tin and bismuth. These pigments possess magnetic properties and electrical conductivity. In addition, because of their attractive colour gloss, the pigments are useful as printing inks and in decorative lacquers, paints, ceramics and cosmetics. (Merck Patent Gesellschaft mit Beschränkter Haftung, Darmstadt, Germany) (Source: Materials and Processing Report, June 1990)

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Gelcasting - a new ceramic forming process

"Gelcasting", a new ceramic forming process in which a slurry of ceramic powder in a solution of organic monomers is cast in a mould. The monomer mixture is polymerized in situ to form gelled parts. The process has aqueous and nonaqueous versions. Gelcasting is generic and has been used to make both monolithic and composite ceramic parts. It produces complex-shaped, near-net-shape parts.

Applications of the gelcasting process

The development of gelcasting, a process based on concepts from traditional ceramic processing and polymer chemistry, has led to two versions of the process: aqueous gelcasting, if the solvent for the monomers is water, and nonaqueous gelcasting, if an organic solvent is used. The aqueous process has been developed more vigorously as it represents less of a departure from traditional ceramic processing methods. However, the nonaqueous process should be better suited to gelcasting ceramic powders which react with water such as aluminium nitride, tungsten carbide, or titanium nitride.

Gelcasting represents a flexible ceramic forming process which has several noteworthy features. It is a generic process which is applicable to many ceramic systems - monolithics, composites, water sensitive or not. It uses a high solids loading slurry with low viscosity. Although developed for the production of complex-shaped parts, it can be used to produce simple ceramic parts. It produces strong machinable green body which can, if desired, be green-machined to more complex shapes. It produces near-net-shape parts which require minimal final finishing. (Excerpt from Ceramic Bulletin, Vol. 70, No. 10, 1991 (© ACerS). Article was written by: Ogbemi O. Omatete, Mark A. Janney and Richard A. Strehlow, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA)

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Spray pyrolysis for fine particles

Spray pyrolysis is a process that has potential to produce powders on the submicron scale and even smaller. Although this process also can produce spherical particles, there are many parameters that must be controlled, including spray temperature, concentration and solvent of the solution, atomizing-droplet size, and amount of added water. For instance, researchers at the Institute of Technology (Tokyo) eliminated the heterogeneity of $BaTiO_3$ and $SrTiO_3$ powders by increasing the concentration of the solutions or complexing Ti^{4+} ions in the solutions with the H_2O_2. Starting solutions were prepared from $Ti(OC_3H_7)_4$ and $Ba(NO_3)_2$ or $Sr(NO_3)_2$.

By using an ultrasonic sprayer for atomization, spray pyrolysis can be improved; therefore, a number of researchers in several countries are investigating this technique. The Seoul National University (Korea) has made spherical TiO_2 particles from $TiCl_4$ aqueous solution by ultrasonic spray pyrolysis. Powders with almost the same normalized particle-size distribution can be made reproducible even when the concentration of source solution is changed. Average particle size is in the range of 0.2 to 1.4 µm. The Seoul researchers have also prepared $BaTiO_3$ fine powders with an average diameter of 0.3 to 0.9 µm at 1,000° C with this technique. Solutions containing $Ba(NO_3)_2$ and $TiCl_4$ resulted in a particle morphology consisting of small primary particles with hollows around the centre. The particle size and morphology were a function of the concentration of starting solutions from 0.0032 M up to 0.053 M.

Another Korean university is also studying ultrasonic spray pyrolysis to make several compositions. Kangweon National University (ChunCheon, Korea) has prepared fine MgO-ZrO_2 powders (0.73 µm) using an aqueous solution of $ZrOCl_2.8H_2O$ and $MgCl_2.6H_2O$ corresponding to 5 to 14 mol% MgO. The powders had a spherical morphology and a specific surface area ranging from 23.45 to 27.02 m^2/g. $PbTiO_3$ powders of similar characteristics have also been prepared at Kangweon by using a $TiO(NO_3)_2$ solution as the Ti source. The powder morphology had a tetragonal crystal structure, a mean particle size of 1 µm, and a porous surface.

The Tsinghua University (Beijing, China) is another organization interested in this process. They have made fine zirconia powders from an aqueous mixed solution of zirconium salts. The powders consisted of smooth spheres with a mean particle size of 0.5 to 1.0 µm. These powders were used to make partially stabilized zirconia (3 mol% Y_2O_3) having a bulk density about 5.9 g/cm^3, a bending strength of 102.29 kg/mm^2, and a toughness of 11.9 $MPa.m^{1/2}$.

Another variation of spray pyrolysis uses an inductively coupled plasma for atomization. Tsinghua University is also investigating this process and has made homogeneous, submicron zinc oxide powders that have a specific surface area of 50 m^2/g. Similarly, Tohoku University (Sendai, Japan) has synthesized ultrafine particles of single-component oxides, titanates, chromites, aluminates, and molybdates by introducing aqueous solutions of metal salts into an inductively coupled RF plasma above 5,000 K. Particle morphology varied with composition; oxides of rare earths and corundum were platelike; cubic fluorite and chromite-type spinel (chromites) were polyhedral; and perovskites were spherical. The mean particle sizes of the latter ranged from 15 to 35 nm.

Hydrothermal processing for improved properties

Another widely used process is based on hydrolysis and has other benefits besides improved properties. Hydrothermal synthesis has been demonstrated to be a viable process for production of barium titanate-based dielectric powders. Its advantages include use of relatively inexpensive raw material, preparation of powder with uniform, controlled particle size in the range of 0.1 to 0.5 µm, and the ability to sinter at reduced temperatures.

Sakai Chemical Industries Company (Osaka, Japan) has already developed this process on the commercial scale for making powders of titanate perovskite, Mn-Zn spinel, and acicular hematite for capacitors, ferrite cores, and magnetic recording media. Particles sizes of 0.1 µm have been achieved for perovskites and are almost of single-crystalline morphology. Higher densities are also possible at lower sintering temperatures.

Hydrothermal processing has also been used at Tokyo Institute of Technology (Yokohama, Japan) for preparing ultra-fine hydroxyapatite (HA) crystals. Crystals obtained at 200° C, 2 MPa, and 10 h had hexagonal prismatic shapes of about 25 nm x 90 nm in size. By varying the sintering conditions, a wide variety of microstructures could be obtained. For instance, crystals sintered at 900° C for 3 hours showed a three-dimensional porous structure with a homogeneous pore distribution. Using a HIPing method (1,000° C, 200 MPa of Ar for 1 hour) increased the density to 99.9 per cent with transparency. HA ceramics with tailored microstructures (dense/porous layered HA ceramics and with ZrO_2 particles or Si_3N_4 whiskers dispersion) have also been prepared with toughnesses of 3 $MPa.m^{1/2}$.

Chemical preparation methods

Such methods as sol-gel, colloidal processing, polymer pyrolysis and chemical vapour deposition (CVD) are all receiving wide attention for preparing powders. Sol-gel techniques are popular because they can lower sintering temperatures and produce homogeneous, fine particles with high sinterability and high purity. In fact, the Tokyo Institute of Technology (Tokyo) has produced Ni and Cd ferrites with a particle-size range as small as 200 to 800 Å from alkaline solutions of Fe, Ni and Cd tartrate and dextrose at 100° C.

A wide range of compositions are possible as well, including superconducting oxides. For instance, the Japanese Government Industrial Research Institute has produced 123 precursor materials from metal alkoxides which are then decomposed and crystallized in vacuum. Agglomerate size ranged from 50 to 100 nm. Kobe Steel, Ltd., in conjunction with Dobelco-kaken (both of Kobe) are also using alkoxides of Y, Ba and Cu acetates to produce these materials, which can be converted to the superconducting phase at temperatures as low as 850° C.

Thin films can also be produced via sol-gel, which is being pursued by a number of organizations including Nagoya University (Nagoya), Ecole Polytechnique Fédérale de Lausanne (Lausanne, Switzerland), Yokohama National University (Yokohama), and Fraunhofer-Institut für Silicat forschung (Würzburg, Germany). Compositions being produced are Bi-based superconductors and $(Ti,Sn)O_2$, In_2O_3-SnO_2, and $YBa_2Cu_3O_x$, perovskite ferroelectrics and oxide coatings for SiC platelets, respectively. (Excerpts from Ceramic Bulletin, Vol. 70, No. 6, 1991 (© ACerS))

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Microwave sintering of multiple alumina and composite components

From laboratory to full-scale production

Large quantities of ceramic parts can be simultaneously sintered using microwave techniques. Ceramics produced by this technique are of good quality. Densities and grain size are comparable to those which result from conventional processing.

Microwave sintering has been brought out of the realm of small-scale laboratory experiments into the range of the pilot-plant facility. On the basis of these results it is easy to envision either a full-scale continuous or batch manufacturing operation.

Power utilization information indicates that microwave sintering is competitive with conventional electric furnacing techniques. It is unlikely, however, that microwave sintering will be competitive with conventional techniques fired by natural gas, the reason having to do mostly with the inefficiency of converting fossil fuels to electricity rather than that of converting electricity to microwaves. (Excerpt from Ceramic Bulletin Vol. 70, No. 8, 1991 (ACerS). Article written by: Joel D. Katz and Roger D. Blake, Los Alamos Laboratory, Los Alamos, New Mexico 87545, USA)

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6. TRENDS

The following three tables are from the article by W. David Kingery "Looking to the Future in Ceramics", which appeared in the book "The Materials' Revolution"

Electronic and magnetic applications of high-technology ceramics

<u>Electric functions</u>	
Insulation materials (Al_2O_3, BeO, MgO)	IC circuit substrate, package, wiring substrate, resistor substrate, electronics interconnection substrate
Ferroelectric materials ($BaTiO_3$, $SrTiO_3$)	Ceramic capacitor
Piezoelectric materials (PZT)	Vibrator, oscillator, filter, etc.
	Transducer, ultrasonic humidifier, piezoelectric spark generator, etc.
Semiconductor materials ($BaTiO_3$, SiC, $ZnO-Bi_2O_3$, V_2O_5), and other transition metal oxides	NTC thermistor (temperature sensor, temperature compensation, etc.)
	PTC thermistor (heater element, switch, temperature compensation, etc.)
	CTR thermistor (heat sensor element)
	Thick-film thermistor (infrared sensor)
	Varistor (noise elimination, surge current absorber, lighting arrester, etc.)
	Sintered CDS material (solar cell)
	SiC heater (electric furnace heater, miniature heater, etc.)
Ion-conducting materials ($\beta-Al_2O_3$, ZrO_2)	Solid electrolyte for sodium battery
	ZrO_2 ceramics (oxygen sensor, PH meter fuel cells)
<u>Magnetic functions</u>	
Soft ferrite	Magnetic recording head, temperature sensor, etc.
Hard ferrite	Ferrite magnet, fractional horsepower motors, etc.

Source: Adapted from Yano Research Institute Report by G. B. Kenney and H. K. Bowen, <u>Am. Ceram. Soc. Bull. 62(5)</u>: 590-596 (1983).

Nuclear, optical, and mechanical applications of high-technology ceramics

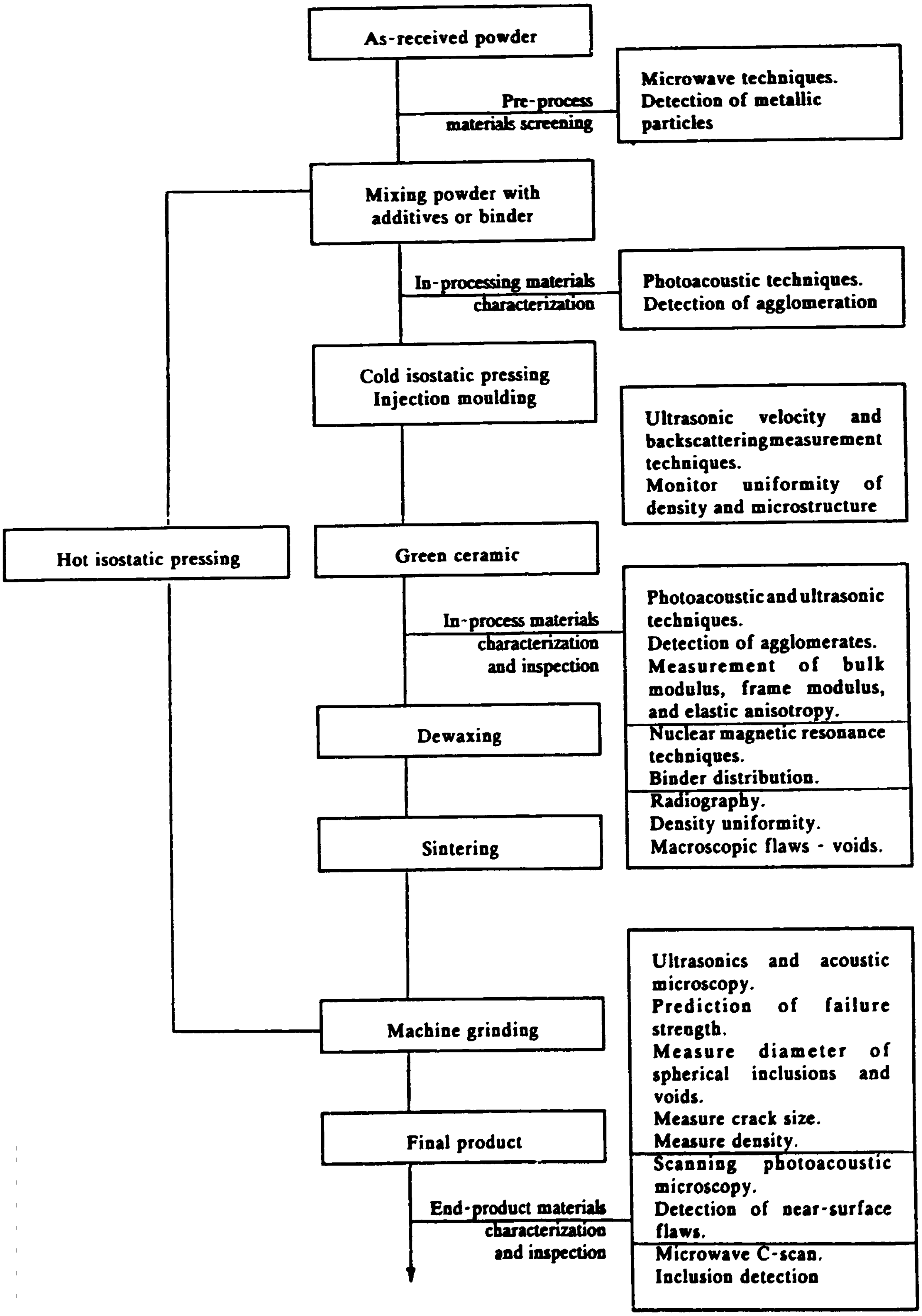
Nuclear functions	
Nuclear fuels (UO_2, UO_2-PuO_2)	
Cladding material (C, SiC, B_4C)	
Shielding material (SiC, Al_2O_3, C, B_4C)	
Optical functions	
Translucent alumina	High-pressure sodium vapour lamp
Translucent magnesium, mullite, etc.	For a lighting tube, special-purpose lamp, infrared transmission window materials
Translucent Y_2O_3-ThC_2 ceramics	Laser material
PLZT ceramics	Light memory element, video display and storage system, light modulation element, light shutter, light valve
Mechanical functions	
Cutting tools (Al_2O_3, TiC, TiN composite, SiC whiskers in Al_2O_3, others)	Ceramic tool, sintered SBN Cermet tool, artificial diamond Nitride tool
Wear-resistant materials (Al_2O_3, ZrO_2)	Mechanical seal, ceramic liner, bearings, thread guide, pressure sensors
Heat-resistant materials (SiC, Al_2O_3, Si_3N_4, composite SiC fibres in glass and recrystallized glass, composite Al_2O_3 fibres in Al, composite SiC whiskers in Si_3N_4, others)	Ceramic engine, turbine blade, heat exchangers, welding burner nozzle, high-frequency combustion crucibles

Source: Adapted from Yano Research Institute Report by G. B. Kenney and H. K. Bowen, Am. Ceram. Soc. Bull. 62(5): 590-596 (1983).

Biological and chemical applications for high-technology ceramics

<u>Biological function</u>	
Alumina ceramics implantation	Artificial tooth root, bone, and joint
Hydroxyapatite bioglass	Gas leakage alarm, automatic ventilation fan, hydrocarbon, fluorocarbon detectors, etc.
<u>Chemical functions</u>	
Gas sensor (ZnO, Fe_2O_3, SnO_2)	
Humidity sensor ($MgCr_2O_4$-TiO_2)	Cooking control element in microwave oven, etc.
Catalyst carrier (cordierite)	Catalyst carrier for emission control
Organic catalyst	Enzyme carrier, zeolites
Electrodes (titanates, sulphides, borides)	Electrowinning aluminium, photochemical processes, chlorine production

Source: Adapted from Yano Research Institute Report by G. B. Kenney and H. K. Bowen, <u>Am. Ceram. Soc. Bull. 62(5)</u>: 590-596 (1983).


As-received powder
Pre-process materials screening
Microwave techniques. Detection of metallic particles
Mixing powder with additives or binder
In-processing materials characterization
Photoacoustic techniques. Detection of agglomeration
Cold isostatic pressing
Injection moulding
Ultrasonic velocity and backscatteringmeasurement techniques. Monitor uniformity of density and microstructure
Hot isostatic pressing
Green ceramic
In-process materials characterization and inspection
Photoacousticandultrasonic techniques. Detection of agglomerates. Measurement of bulk modulus, frame modulus, and elastic anisotropy.
Nuclear magnetic resonance techniques. Binder distribution.
Radiography. Density uniformity. Macroscopic flaws - voids.
Dewaxing
Sintering
Machine grinding
Ultrasonics and acoustic microscopy. Prediction of failure strength. Measure diameter of spherical inclusions and voids. Measure crack size. Measure density.
Scanning photoacoustic microscopy. Detection of near-surface flaws.
Microwave C-scan. Inclusion detection
Final product
End-product materials characterization and inspection

The inherent brittleness of ceramics makes them less "forgiving" than other engineering materials when flaws are present in a part. Therefore, two important problems in ceramics processing are: to identify conditions early in the processing stages that lead to defective products, and to detect and characterize critical flaws (< 10 μm) in the fine powder. In situ non-destructive (noninvasive) evaluation based on various wave-field techniques is used for process monitoring, characterization, and inspection to ensure the earliest possible removal of defective materials, as well as identification of acceptable parts. (Source: Advanced Materials and Processes, August 1988. Article: "Structural Ceramics: Materials of the Future" by Edward J. Kubel, Jr.)

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CHARACTERISTICS OF ADVANCED CERAMICS

Advantages

High melting point
High stiffness
High hot strength
High compressive strength
High hardness
Wear and corrosion resistance
Low density (light weight)
Good dielectric properties
Thermal/electrical insulators
Semiconductor properties
Ion-conductor properties
Magnetic properties
Biocompatibility
Abundant raw materials

Limitations

Susceptible to thermal and mechanical shock (brittle)
Gaps in understanding and experience
Difficult to fabricate
Poor reproducibility
High cost

POTENTIAL FLAWS DURING MANUFACTURING

Powder production

Unfavourable particle size, shape, and distribution
Off composition
Foreign inclusions
Hard agglomerates

Powder conditioning

Unfavorable agglomerate size distribution
Hard agglomerates
Varying agglomerate density distribution
Varying additive distribution
Insufficient binder
Organic fibre inclusions

Powder shaping (green compacts)

Porosity/voids/cracks
Varying density
Nonuniform binder and additive distribution
Segregation
Residual binder
Organic inclusions

Densification

Porosity/micropore clusters
Voids
Cracks
Nonuniform grain size/grain growth
Harmful grain-boundary phases (glassy phases)
Inclusions
Rough surface

(Source: Advanced Materials and Processes, August 1988. Article: "Structural Ceramics: Materials of the Future" by Edward J. Kubel, Jr.)

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Facility for manufacture of high-performance machinable ceramics

Tokuyama Soda Co., Ltd. has installed a new production facility at its Tokuyama factory that increases the factory's capacity to produce a machinable ceramic "Shapal-M" by eight times the existing capacity. The facility is also designed to manufacture large sintered products to meet recent brisk demand.

Ceramic materials possess various excellent characteristics but their popular acceptance is being impeded by their high machining costs. More recently, the development of machinable ceramics now permits these materials to be worked with ease like iron and brass by using the same kinds of cutting tools, but as yet there are only a few types of easily machined ceramics.

The "Shapal-M" developed by the company is a composite sintered body consisting of an extremely hard aluminium nitride substance and a relatively soft boron nitride substance. Even when cut with a cemented carbide tool, the material does not crack and can be machined into various shapes since the boron nitride particles serve as a cushion.

Regarding the material's characteristics, it displays a strength comparable to that of alumina, also excellent heat transmittivity and a thermal expansion close to that of silicon.

The company installed the new production facility in order to meet the expanding use of ceramic materials for producing jigs and mechanical parts and also heat radiation wafers for electronic components. Reinforcing the facilities for compression sintering and mechanical machining have increased the factory's production capacity to 130 tons/yr. equivalent to about 200,000 units of standard type wafers (1 inch on all sides, thickness of about 0.6 mm) as compared with the former capacity of 25,000 units. Also, while expanding the factory's facilities the company improved its sintering technology, enabling it to manufacture large blocks with a mazimum size of 30 cm on a side (hitherto 10 cm on a side). Now the factory's productivity has been improved and it can produce larger products.

The machinable ceramic material's domestic price is about ¥100,000/kg, roughly 30 per cent higher than that of aluminium nitride, but the production cost is expected to decrease when using this easily machinable material for producing diverse products in small lots. (Tokuyama Soda Co., Ltd., 4-5 Nishi-Shinbashi 1-chome, Minato-ku, Tokyo. Tel.: 03-597-5056. Telex: 2223258 Tokuso) (Source: JETRO, September 1988)

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7. MARKETING

Strong growth predicted for several ceramic markets

Three reports from Business Communications Co., Inc. (BCC), forecast markets for three emerging ceramic technologies: high-performance coatings, ceramic matrix composites and sol-gel processing. According to BCC, the total high-performance ceramic coating service market for 1988 was valued at $310 million, and was expected to grow 9.5 per cent annually to $488 million by 1993. The largest segment of this market is for aircraft engines and aerospace applications. These and cutting-tool applications account for more than 85 per cent of the ceramic coating markets.

The largest growth rate in the ceramic coating market is for engine applications such as automotive, diesel and land-based turbines, with about 22 per cent annual growth. However, the market for engine applications currently accounts for less than 2 per cent of the total market. Also, the diesel engine segment of the engine applications market is very small at present. Although heat-exchanger applications are still only in the developmental stage, there will be a small market by 1993.

Thermal spray and chemical vapour deposition (CVD) techniques dominate the aircraft-engine-component market, producing 2 million parts and 0.5 million parts, respectively. Ceramic physical vapour deposition (PVD) coatings are now emerging for aircraft-engine components because these coatings are the most durable for fan blades. Although aerospace applications constitute only a small market, potential markets include high-emissivity coatings for thermal protection of space shuttles and Aero-assisted Orbital Transfer Vehicles (AOTV).

CVD coatings of TiC, TiN, and Al_2O_3 dominate the current cutting-tool market (totalling $117 million) at 90 per cent, with the remaining market for PVD and ion-assisted techniques. Although only a few companies supply PVD-coated tool inserts, these inserts are in high demand because abrasive resistance is not an important issue with PVD coatings. On the other hand, ceramic coatings for automotive engine applications is still a small market.

The ceramic matrix composites market should have even a higher growth rate (21 per cent) than the ceramic coating market, increasing from a current value of about $77.2 million to $202.5 million by 1993. The development and introduction of ceramic composites is expected to follow the same historical pattern as organic matrix composites, with high-performance applications as the primary focus, followed by more traditional applications.

Wear-resistant parts made of toughened zirconia, along with whisker and other fibre-reinforced ceramic composites, was the largest market segment for 1988, sharing 39 per cent of the market. BCC believes that this market share would be maintained in the future and would reach $272 million by the year 2000. The cutting-tool market would reach $198 million by the same year. Because aerospace applications, such as the space-shuttle tiles, is an established market, the market will only reach $51 million by the year 2000, at a growth rate of 5.5 per cent. Energy-related applications is an even smaller market, which is only expected to reach $6 million by the year 2000. On the other hand, engine applications should have a much higher growth rate, increasing from the current $2 million to $100 million by the year 2000.

The largest market share of materials is held by oxides, with sales of about $45 million. This share will increase from 59 per cent in 1988 to 73 per cent in the year 2000, with sales totalling $144 million and $460 million, respectively. In contrast, BCC predicts that silica and glass-ceramics will have a declining market share, falling from 34.4 per cent in 1988 to 8.3 per cent in the year 2000. Although BCC also believes that the United States is the leader in ceramic composites technology, Japanese competition could be expected in the future.

By far, the fastest-growing market of the three technologies is applications produced from sol-gel processing. These applications promise an overall average increase over the next five years at 117 per cent per year. The existing markets for sol-gel-derived products - high-performance abrasives, ultra-pure ceramic powders, optical and refractory fibres, optical monoliths and coatings - are small, but growing. The total market, including government funding, was estimated at about $9 million, and was predicted to increase to $428 million by 1992.

Short-haul optical fibre has the largest market potential, representing 75 per cent of the total projected 1992 market. The projection of $320 million assumes that the sol-gel process, which is still under development, is accepted as the production method of the next generation. On the other hand, non-metallic abrasives are currently the largest commercial outlet for sol-gel-derived products in the United States. Despite the mature abrasives market, growth is expected during the next decade, reaching $58 million by 1992.

Other applications with market potential are in the electronics and optical areas. The super-conductor market is expected to be $30 million by 1992, but could grow more rapidly if technological breakthroughs are made. Optical device and lens applications depend on technological breakthroughs in solving the problems of cracking and limitations in the sizes of monoliths. Although microelectronics represents the largest dollar potential for sol-gel processing, future acceptance will depend mainly on the success of government-funded research and effective technology transfer of this research. The micro-electronics industry wants to find the most economical process that works, with a minimum of research and development, and if sol-gel technology can achieve this goal, it will become widely used.

According to BCC, foreign companies, particularly Japanese and German companies, are leading in sol-gel technology, with several products already being marketed. These include coated windows that are 1 by 1 m, oxide coatings, continuous silica fibres, high-quality silica glass plates, titania powders for cosmetics, continuous alumina fibres, and silica powder. On the other hand, sol-gel applications are finding very limited commercial use in the United States because of high-cost precursors and shrinkage and cracking problems. Some US companies are involved in long-term development of specialty products, whereas others use sol-gel technology mainly as a source for developing special powders and coatings for in-house use. (Extracted from Ceramic Bulletin, Vol. 67, No. 12, 1988 (© ACerS))

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Ceramics use seen increasing

Demand for advanced ceramics will increase 8.5 per cent a year world wide between 1990 and 1995, with the largest percentage increase predicted in structural ceramics, a research group said.

The 1990s will be a decade during which technology will focus on individual advanced-ceramic parts. The commercial development of the all-ceramic engine that has been touted as a future trend in power plants was still years away.

While the bulk of advanced ceramics currently goes into electronics applications, structural ceramics will be the fastest growing segment of advanced ceramics.

The value of structural ceramics, including cutting tools and dies, wear parts, heat engines and other structurals, totalled nearly $1.55 billion in 1990, or 13.7 per cent of total advanced ceramics demand.

Between 1990 and 1995, however, structural ceramics demand will increase 14.1 per cent annually, reaching nearly $3 billion, or 17.6 per cent of total advanced ceramics demand of nearly $17 billion.

By the end of the decade, demand for structural ceramics will have grown to an estimated $5.2 billion, or 20.8 per cent of total advanced ceramics demand which will then total an estimated $25 billion.

Within the structural ceramics sector, cutting tools and dies account for the greatest demand, totalling $925 million in 1990. Demand is expected to grow 11 per cent annually to $1.56 billion by 1995.

Demand for wear parts such as seals and bearings, the next-largest structural ceramics application, totalled $363 million last year but is expected to grow 12.7 per cent annually through 1995 to an estimated $660 million.

But heat engine applications will show the greatest growth of any structural ceramics segment, growing 29.3 per cent annually to an anticipated $380 million in 1995 from $105 million in 1990.

Automotive engine parts will account for the largest share of heat engine applications for advanced ceramics, but truck, bus and aircraft engine applications will gain ground, too.

Demand for other structurals, including biomedical ceramics and turbine components, totalled $152 million in 1990 but will grow 20.7 per cent by 1995 to an estimated $390 million.

Demand for ceramic coatings, the smallest segment of advanced ceramics overall, totalled $765 million in 1990. That will nearly double to an estimated $1.34 billion by 1995, an annual growth rate of 11.9 per cent.

World Advanced Ceramics Demand
(in millions of dollars)

	1990	1995	2000	Per cent annual growth
Advanced ceramics demand	11 295	16 950	24 900	8.5
Electronics	8 985	12 620	17 540	7.0
Structural	1 545	2 990	5 210	14.1
Cutting tools and dies	925	1 560	2 310	11.0
Wear parts	363	660	1 050	12.7
Heat engines	105	380	1 090	29.3
Other structurals	152	390	760	20.7
Coatings	765	1 340	2 150	11.9
Source: Freedonia Group Inc.				

(Extracted from: American Metal Market, 25 September 1991)

8. PUBLICATIONS

Advanced structural ceramics

Major government-sponsored R and D programmes in the United States, Japan, Germany, the United Kingdom, Sweden and France are surveyed. Major trends and developments in the technology of monolithic structural ceramics and ceramic matrix composites are discussed and end uses are examined. The market for structural ceramics is assessed in the context of other advanced materials and examined in particular for the automotive and cutting tool sectors. 230 pages. 1990. $500. Order from Innovation 128, 24, rue du Quatre Septembre, 75002 Paris, France.

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Concise encyclopedia of advanced ceramic materials

Edited by R. J. Brook, this book provides practical information that gives rapid access to the complex advanced ceramics field. It covers an array of applications and compositional types ranging from the new superconductors to high-temperature turbine components and nuclear waste storage systems. All branches of modern ceramics are treated, including both functional and structural materials. Some 500 references are listed as well as more than 1,000 subjects in a three-level index. 1991. 600 pp. $150. ISBN 0-262-02034-0. Order from MIT Press, 55 Hayward St., Cambridge, MA 02142, USA.

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Structural materials

Edited by George Weidmann, Peter Lewis and Nick Reid. Boston: Butterworth, 1990. 430 pp. $39.95. 620.1'1 TA418.32 89-25456 ISBN 0-408-04658-9.

Contents: Materials and mechanics. Nonferrous metals. Iron and steel. Ceramics and glasses. Polymeric materials. Fibres and fibre assemblies. Composite materials. Cement, concrete and reinforced concrete. Selection of materials. Subject index.

Note: Text for undergraduate students, focusing on load-bearing materials and their applications. Primarily concerned with solid materials. Covers ferrous and nonferrous materials, ceramics and glasses, polymeric and cementitious materials, fibres and composite materials. For undergraduate engineering collections.

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Advances in ceramics and polymers have been included in the updated Handbook of Industrial Materials, intended for engineers, designers and consultants who purchase, use and produce materials for the industrial sector. It costs £95 from Elsevier Advanced Technology, Mayfield House, 256 Banbury Road, Oxford OX2 7DH, UK. Fax 0865 310981.

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World Business Publications Ltd., 4th Floor, Britannia House, 960 High Road, London, N12 9RY, England. Fax: 081-446-3659, has published:

European Advanced Ceramics Directory 1990

The "European Advanced Ceramics Directory 1990" gives invaluable and comprehensive details concerning the advanced ceramics industry in Europe. It contains: 1. An A-Z listing of European advanced ceramics companies - both manufacturers and suppliers - of raw materials, ceramic components and equipment; this detailed section features full address, telephone, fax and telex numbers and a description of the goods and services offered. In addition, there are contact names and company size by turnover and number employed. A clear, easy-to-use product listing is given. 2. An A-Z listing of European universities and research centres carrying out ceramics research; full address and contact details are given together with details of research projects under study at each establishment. 3. An easy-to-use cross reference section. This section is in four parts - raw materials, finished products, equipment and services. In addition to over 400 individual company entries and over 100 university and research centre listings there are two overview articles - one concerning the ceramics raw materials position in Europe, and the other concerning the finished ceramics components position in Europe. (Materials Technology Publications, 232 pp., 01/90. $150 (£90))

and

Advanced Structural Ceramics

Advanced structural ceramics are a new class of materials that create unique opportunities for the engineer because of their special combination of properties. Ceramics in the form of monoliths, composites and coatings are being developed for such diverse applications as engine components, cutting tools, wear components, heat exchangers and aerospace components. Intensive international research activity is being focused on the resolution of technical barriers to their further exploitation, which relate to such areas as high purity raw materials, reinforcements and appropriate processing methods to produce consistently high performance products at an acceptable cost. The report provides an in-depth guide to the current technical and market status of these emerging materials with extensive references to company research and development activities. An international directory of companies involved in structural ceramics is appended to the report. (Innovation 128. 230 pp. 02/90. $500 (£310)).

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The US Market for Ceramic and Metal Matrix Composites

This report examines the advanced composites industry and describes the similarities and differences between the industrial sectors working with CMCs and MMCs. Descriptions of fibre and whisker structures, matrix-reinforcement interaction, and the influence of fabrication method on properties are provided. An assessment of raw materials for CMCs includes alumina, zirconia, carbides, nitrides and carbons. For MMCs, Al, Mg, Ti, Cu, and superalloys are assessed. End uses and consumption are forecast to 1995. 1991. 394 pp. 70 tables and figures. $3,850. Order report No. A2415/P from Frost & Sullivan, Inc., 106 Fulton Street, New York, NY 10038-2786, USA.

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Engineered materials for advanced friction and wear applications: proceedings of an international conference, Gaithersburg, Maryland, USA, 1-3 March 1988.

Edited by F. A. Smidt and P. J. Blau. Metals Park: ASM, 1988. 262 pp. $80. 620.1 TA418.72 88-71490. ISBN 0-87170-331-9.

Contents: Friction and wear mechanisms in engineered materials. Advanced materials and surface treatments for friction and wear applications. Lubrication of engineered materials. Aerospace and defence applications. Computer and electronics industry applications.

Note: Comprising 36 papers delivered at a conference organized to provide a forum for scientists involved with research and applications of new materials designed for high performance and resistance to aggressive environments. Properties and behaviour of new materials such as composites and ceramics, specially designed coatings and surface treatments and other materials were discussed. Needs of aerospace, defence, advanced automotive, computer and electronics industries are compared to available materials. Volume contains keynote review papers and reports of recent research. Papers include references, photographs, figures, tables. For research level collections.

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Advanced materials. The proceedings of the second European Conference on Advanced Materials and Processes, which took place in 1991, are available, price £140 from the Institute of Materials, 1 Carlton House Terrace, London SW1Y 5DB, UK.

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Advanced Materials 1991/1992: Source Book and Directory

This two-volume set provides an up-to-date overview of the advanced materials industry, concentrating on the most important advances in the ceramics, composites and plastics industries. Trends are highlighted, both in terms of technological developments and commercial activities. The Source Book presents information in three cross-reference sections, with a full list of contact names and addresses. The Directory lists the more than 1,000 companies, organizations and R and D centres that are mentioned in the Source Book. Whenever possible, entries contain contact address; telephone, fax and telex numbers; names of contact employees; size of company; products; etc. Source Book: $255. Directory: $170. Set: $382.50. Order from Elsevier Advanced Technology, Attention: Beverley Acreman, Mayfield House, 265 Banbury Road, Oxford OX2 7DH, UK.

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Advances in Ferrites. Vols. 1 and 2

C. M. Srivastava, M. J. Patni (ed.). Aedermannsdorf/CH 1990. 2 vols. 1,220 pp. bound (English). 25 cm x 16.5 cm approx. DM 548.

The "ICF 5" was the fifth ferrite conference since 1970 which took place in January 1989 in Bombay. The proceedings serve for exchanging scientific and technological knowledge in the field of ferrites and adjacent materials. The meeting at Bombay primarily dealt with two aspects: the improved microscopic examinations of the magnetic properties and the developments which have come about in the field of material synthesis and determination. This includes the field super-conductors. Volume 1 comprises the following fields: production of ferrites, sintering, microstructures and physics of the ferrites, thin films and crystal growth, HP-ferrites and testing methods. Volume 2 contains chapters about: high-temperature superconduction, amorphous materials, materials for data recording, magneto-opto and bubbles, microwave materials and appliances, interdisciplinaries.

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Hi-Tech for Profit Business Opportunities in Advanced Ceramics

This report covers the use of advanced ceramics in IC chip carriers/substrates, capacitors, ferrites, sensors, piezoelectrics, cutting tools, automobiles, superconductors, etc. The technology status in India and the world, as well as market assessments/projections for each end product are provided in detail for the Indian and world markets. 170 pp. $100. Order from Technology Exchange Network, 6 Ware Road, Cleveland Town, Bangalore - 560 005, India.

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Acquisition Opportunities in Advanced Materials Section II: High Performance Ceramics

This report provides an overview of the industry, including products and applications, large customers, major suppliers, marketing and technical trends and sources of technology. Detailed evaluations of 35 manufacturers are given. Each company profile includes financial data, marketing policies, technology position, historical and projected sales, manufacturing capabilities, key officers and employees, etc. 270 pp. $3,500. Order from Marketing Consultants, Box 2205, RD2, New Tripoli, PA 18066, USA.

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Chemical Synthesis of Advanced Ceramic Materials

David Segal, Cambridge University Press, Cambridge 1989. xv, 182 pp., bound, £35.00. ISBN 0-521-35436-6.

This book is the first volume of a new series called "Chemistry of Solid State Materials". It is written for chemists, material scientists, physicists and postgraduate students who are mainly interested in the chemistry of advanced ceramics and less in their mechanical properties.

The first chapter gives a short review of the different applications of technical ceramics. Mainly structural ceramics, electroceramics and high-temperature oxide superconductor materials are discussed. The topic of the second chapter is conventional routes to ceramics, namely precipitation from solution, powder mixing, and fusion. Demonstrating that the use of these methods for advanced materials is limited, the author discusses the need for new methods. In the third chapter the fabrication of ceramics is described. The theory of solid-state sintering, pressing of the green body, hot pressing, isostatic pressing (HIP) and reaction bonding as well as slip casting and injection moulding are covered. The significance of strength and toughness in ceramic systems is also explained.

Sol-gel technology is the most extensive section in this book. In chapter four the reader is introduced briefly to the theory of colloids. Using examples from industrial applications particularly in nuclear technology, the possibilities of this method are demonstrated especially for different oxides. The fifth chapter describes the use of metal-organic compounds in connection with sol-gel technology. The synthesis and physical properties of metal alkoxides (Si, Al, Ti, Y, etc.) are shown as well as their application in sol-gel processes.

Chapters six and seven are concerned with the production of nonoxide ceramics. One chapter deals with non-aqueous liquid-phase reactions, the other with the synthesis and properties of polymeric precursors, such as polysilanes, polycarbosilanes and polysilazanes and their pyrolytic conversion to ceramics.

Hydrothermal synthesis, an important method for the preparation of sub-micrometre particles is discussed in chapter eight. The ninth chapter covers gas-phase reactions. Many different heating methods, such as conventional resistance furnaces, lasers, plasmas and electron beams are described. They are used to carry out gas-phase reactions involving solid, liquid and gaseous reactants.

Some methods not described in previous chapters are found in chapter ten, namely the citrate gel process, pyrolysis of metal alkoxides, rapid expansion of supercritical solutions and freeze drying.

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Science of Advanced Materials

Edited by H. Wiedersich and M. Meshil, this is the proceedings of ASM International's 1990 Materials Science Seminar. The first section on amorphous materials covers various methods of solid-state amorphization - interdiffusion of crystalline materials, mechanical alloying, irradiation with energetic particles, and hydrogen-induced amorphization. The second section on artificially structured crystalline materials reviews two types of designed microstructures - artificial superlattices and nonocrystalline materials. The papers on ceramics cover electroceramics and electronic conducting ceramics. Also discussed are toughening of ceramics by martensitic transformation, some theoretical aspects of displacive transformations in ceramic oxides, and characterization of ceramic particles. 1990. 14 papers. 504 pp. $120. $96 to members of ASM. Order ISBN 0-87170-409-9 from ASM International, Materials Park, OH 44073, USA.

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International Directory of Advanced Inorganic Composites 1991/1992

This directory gives detailed information concerning the world-wide advanced inorganic composites industry. It covers ceramic, metal matrix, and carbon/carbon composites. More than 400 manufacturers and suppliers of composites are listed, together with details of more than 100 universities and research centres carrying out advanced inorganic composites research. A detailed cross-reference listing of manufacturers and suppliers by composite type is included. This directory was published by Materials Technology Publications in association with Mitchell Market Reports. 380 pp. $300. Order from Marketing Dept., Materials Technology Publications, 40 Sotheron Road, Watford, Herts., England WD1 2QA, UK.

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Structural Analysis of Composite Beam Systems

A. M. Skudra, Ph.D; F. Ya. Bulavs, Ph.D; A. A. Kruklinsh, Ph.D and M. R. Gurvich, Ph.D; Structural Mechanics Laboratory, Department of Structural Analysis, Riga Technical University

Table of contents: Preface. Structural mechanics of a fabric-reinforced plastic. Structural mechanics of hybrid composites. Thermal strain and stresses. Relative damping. Structural theory of creep. Stress state of reinforced plastics under long-term loading. Structural theory of long-term strength. Transverse bending of beam. Torsion of a laminated beam. Elastic properties of laminated thin-wall beams with open profile. Elastic displacement of laminated beam systems. Viscoelastic displacements of laminated beam systems. Numerical analysis of statistically indeterminate beam systems under long-term loading. Appendix. References. One hundred and nineteen tables and figures. ISBN: 0-87762-837-8. 1991. 312 pp. 6 x 9. Hardcover. $145.00.

Available from: Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604, USA. Phone: 717-291-5609; Fax: 717-295-4538.

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Reference Book for Composites Technology, Volumes 1 and 2

Edited by Stuart M. Lee, this is a comprehensive review of today's composite materials technology. This systematic, in-depth presentation of all major types of advanced composites is illustrated with hundreds of photographs, microphotographs and schematics. Extensive reference data is presented in tables and graphs. Hardcover. Volume 1, 1989. 333 pages. $75. ISBN 0-87762-564-6. Hardcover. Volume 2, 1989. 205 pages. $65. ISBN 0-87762-565-4. The two-volume set costs $119. Order from Technomic Publishing Co., Inc., 851 New Holland Ave., Box 3535, Lancaster, PA 17604, USA.

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Concise Encyclopedia of Composite Materials

Edited by A. Kelly. Pergamon Press, Oxford 1989. xxxix. 317 pp. Hard cover. US$135. ISBN 0-08-034718-5.

The book contains a valuable introductory chapter plus 60 different articles dealing with fibres and whiskers, matrices, composite materials, manufacturing technology, structural and mechanical properties and evaluation, and applications. The articles are written mainly by specialists from the USA and the UK.

This concise encyclopedia on composite materials is recommended to people involved with classical materials science (metallic materials) or ceramic and polymer materials, but it may also serve as a good overview for scientists working in a special field of composite materials.

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Polymer Update: Science and Engineering (Australian Polymer Science Series Volume 2)

Edited by W. D. Cook and G. B. Guise (Royal Australian Chemical Institute, 1989). Approx. 285 pages. ISBN 0-909589-67-4.

This text has seven chapters in which Australian polymer scientists, who are experts in different areas, review the fundamental aspects of polymer science and give their views on the future of these areas. The subjects treated in this book include chain and step growth polymerization, mechanical properties, structure and properties of elastomers, the glassy state, and the morphology of crystalline polymers.

This text should be *quite* useful to those beginning study in polymer science, to those needing a concise discussion of a particular aspect of polymers, or to those wanting a general overview. Since this book originated from a series of lectures, it would serve as an ideal text for an introductory course in polymer science.

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Plasticity and Modern Metal-forming Technology

Edited by T. Z. Blazynski, NY: Elsevier, 1989. 359 pp. $86.50. 671.3 TS213 88-23277. ISBN 1-85166-272-3.

Contents, abridged: Upper-bound solutions and the balance-of-power approach. An outline of engineering dynamic elasticity and plasticity. Utilization of superplastic effects. Analyses of deep drawing. Analytical methods in extrusion. Machining. Index.

Note: Intended for use by practicing industrial engineers and process planners, provides a concise review of the applications of finite element, upper-bound and visioplasticity techniques to analysing material response and modelling of processes. Discusses available methods of analysis with both established and new industrial processes. Also provides an overview of new-material phenomena. Each chapter includes a comprehensive list of references designed to direct readers to more detailed sources. For university and research level collections.

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Surface Engineering and Heat Treatment
Past, Present and Future

Edited by P. H. Morton

Recent advances in materials and new technologies have enabled surface engineering to play an increasingly important role in modern engineering practice from design study through to finished product.

The proceedings of this Conference, which was organized jointly by The Institute of Metals and The Centre for Exploitation of Science and Technology (CEST), presents a balanced overview which sets the scene for surface engineering in the 1990s. The series of invited papers covers: economic and industrial importance of surface engineering; aspects of the development of heat treatment over the last 25 years; advances made possible by new technologies such as plasma, laser and ion-beam. Book 513. 215 x 137 mm. 384 pp. Paper 1992. ISBN 0901716 01 4. £35.00. US$70.00. Orders, with remittance, to: The Institute of Materials, Sales and Marketing Dept., 1 Carlton House Terrace, London SW1Y 5DB. Tel: 071-976 1338. Fax: 071-839 2078. Orders originating in Canada and the United States should be sent direct to: The Institute of Materials North American Publications Center, Old Post Road, Brookfield, VT 05036, USA. Tel: (802) 276 3162. Fax: (802) 276 3837.

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Surface Engineering (quarterly)

Embracing science, engineering, technology and design, Surface Engineering covers the latest developments in surface treatment methods and technology, with particular emphasis on industrial applications. 1992 subscription rate: £122/$239 (members £70/$134). Orders, with remittance, to: Sales and Marketing Department, The Institute of Materials, 1 Carlton House Terrace, London SW1Y 5DB. Tel: 071-976 1338. Fax: 071-839 2078. Telex: 8814813.

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9. PAST EVENTS AND FUTURE MEETINGS

1992

31 Aug. - 4 Sept. Vienna, Austria	8th International Conference on Liquid and Amorphous Metals (Institut für Theoretische Physik, Technische Universität, Wiedner Hauptstrasse 8-10, A-1040 Vienna, Austria)
7-11 Sept. Singapore	CORROSION ASIA (N. Glover, Fulmer [Singapore] Pte. Ltd., Jurong Laboratory, 1 Jalan Terusan, Singapore 2261)
8-10 Sept. Amsterdam, Netherlands	GALVATECH '92: 2nd International Conference on Zinc and Zinc Alloy Coated Steel Sheet (Centre des Recherches Metallurgiques, 11 rue Ernest Solvay, B-4000 Liège, Belgium, Fax: (41) 534064)
16 Sept. Birmingham, UK	Design against corrosion (The Institute of Materials, 1 Carlton House Terrace, London SW1Y 5DB, Fax: 071 839 3576)
17-24 Sept. Singapore	Third ASEAN Science and Technology Week (ASEAN Committee on Science & Technology; Conference and Exhibition Management Service, 1 Maritime Square # 09-43, World Trade Centre, Singapore 0409, Fax: 2784077)
21-25 Sept. Cancun, Mexico	First International Conference on Nanostructured Materials (Mexican Academy of Materials Science and Acta Metallurgica. For Information: Miguel Jose-Yacaman, Instituto de Fisica, UNAM, Apartado postal 20-364, C. P. 01000 Mexico, D. F. Mexico. Fax: (525) 548-31-11)
22-24 Sept. Genoa, Italy	EUROMAT '92 Materials development in rail, tyre, wing, hull transport (Org. by the Associazione Italiana di Metallurgia [Piazzale Rodolfo Morandi 2, I-20121 Milano, Italy, Fax: 02/78.42.36] under the auspices of the Federation of European Materials Societies)
22-26 Sept. Telford, UK	ISFEC '92 - Surface Finishing (Exeter House, Holloway Head, Birmingham B1 1NQ, UK)
29 Sept. Birmingham, UK	Surface Technology - Developments for Tools and Dies (One-day technical workshop at the University of Aston, Birmingham, UK)
29 Sept. - 2 Oct. Tokyo, Japan	6th International Conference on Ferrites (ICF-6). (Professor Masahiko Naoe, General Secretary, ICF-6, Department of Physical Electronics, Tokyo Institute of Technology 2-12-10-Okayama, Meguro-ku, Tokyo 152, Japan. Fax: +81-3-3729-1399)
12-15 Oct. Göttingen, Germany	4th European Conference for Laser Treatment of Materials (Deutsche Gesellschaft für Materialkunde EV. Adenauerallee 21, 6370 Oberursel, Germany)
13-16 Oct. Cracow, Poland	Metallurgy '92: modernization of iron and steel industry and new processes of steel production (Metallurgy '92, SITPH, ul. Podgorna 4, 40-954 Katowice, Poland)
14 Oct. Warwick Castle, UK	Managing materials information for profit (The Institute of Materials, 1 Carlton House Terrace, London SW1Y 5DB, UK, Fax: 071-839-3576)
26-28 Oct. Budapest, Hungary	High-Tech Exhibition EUROTECHNICA (For more information: Mr. Simon Kenna, 29 Havelock Close, London W12 7NG, UK. Fax: 4471 925.0470)
1-5 Nov. Chicago, Illinois, USA	6th International Conference on Surface Modification Technologies (Dr. T. S. Sudarshan, Materials Modification Inc., 2929-P1 Eskridge Center, Fairfax, Virginia 22031, USA)
17-20 Nov. Kyoto, Japan	8th International Congress on Heat Treatment of Materials (Research Institute for Applied Science, 49 Tanaka Ohi-cho, Sakyo-ku, Kyoto, 606 Japan)
23-26 Nov. Dubai	Arab Plastic and Rubber Industry Trade Show (Al Fajer Information and Services, P. O. Box 11183, Dubai. Fax: 622 802)

26 Nov. London, UK	Surface Engineering Of and With Polymers (The Institute of Materials, 1 Carlton House Terrace, London SW1Y 5DB, UK. Fax: 071-839-3567)
30 Nov. - 1 Dec. Solihull, UK	The Biennial International Conference on Plastics and Rubber in Automotive Technology (The Plastics and Rubber Institute, 11 Hobart Place, London SW1W 0HL, UK. Fax: +44(0)71 823 1379)
1-4 Dec. Houston, Texas, USA	Magnetism and Magnetic Materials (Institute of Electrical and Electronic Engineers, 655 15th Street, Suite 300, Washington, D. C., 20005, USA)
14-31 Dec. Kharagpur, India	QIP Short Term Course on Polymeric Materials Product Technology (Materials Science Centre, Indian Institute of Technology, Kharagpur-721 302, India)

1993

9-11 March Bremen, Germany	International Conference on Surface Engineering (Deutsche Gesellschaft für Materialkunde EV, Adenauerallee 21, 6370 Oberursel, Germany. Fax: (06171) 525 54)
27-29 April Brighton, UK	PVC'93, The Future (The Plastics and Rubber Institute, 11 Hobart Place, London SW1W 0HL, UK. Fax: +44(0)71 823 1379)
4-6 May Atlanta, Georgia, USA	5th Symposium on Composite Materials: Fatigue and Fracture (ASTM, 1916 Race Street, Philadelphia, PA 19103-1187, USA)
26-28 May Plymouth, UK	ICF-8 Satellite: Structural Integrity and Fracture of Advanced Composites (Prof. David Taplin, Trinity College, Dublin, Eire)
7-10 June Paris, France	3rd European Conference on Advanced Materials and Processes (Soc. Française de Métallurgie et de Matériaux, Immeuble Elysées la Défense, Cedex 35, 92072 Paris La Défense, France)
12-16 July Madrid, Spain	The Ninth International Conference on Composite Materials (ICCM/9). (Professor Antonio Miravete, Department of Mechanical Engineering, University of Zaragoza, Maria de Luna, 3, 50015 Zaragoza, Spain. Fax: 34(76) 512 932)

PREVIOUS ISSUES

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