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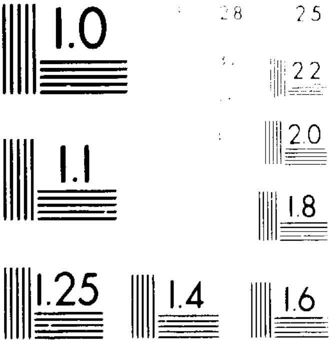

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NEW CERAMICS

by

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Abstract

New ceramic materials with desirable properties based on special microstructures and careful control of purity and composition offer great technical and market potential but require difficult and sophisticated technologies which are still under development. Market prospects are reviewed. Advanced ceramics are classified by function. Ceramic processing is reviewed with emphasis on processes critical for the new ceramics. Some leading families of the new ceramics are reviewed and contrasted. The impact of the developing ceramic technologies on established as well as new ceramic industries is contrasted. Opportunities for participation by developing nations are discussed. Examples of successful transfer of ceramic technology to developing nations are given.

1. Introduction

A new era has opened in the manufacture and use of ceramics. Throughout the industrialized world advances in products and competition in performance, cost, and reliability are driving materials, including ceramics, to new levels of sophistication. The new ceramics have their roots in the past, of course. In many cases their promise was seen two decades ago and research has been underway for a long time. The flowering of new ceramics results from a confluence of research results, market conditions, and a worldwide attempt by many firms, aided by governments in many cases, to stake out future positions in high-technology products.

The new ceramics go under several names. In the United States they are frequently called "high-performance ceramics" or "advanced ceramics". In Japan they are called either "new ceramics" or "fine ceramics". In all cases the terms refer to a broad and diverse group of ceramic materials which are not easy to embrace in a simple definiton. Their distinguishing features in general are: a substantially higher level of performance, much more stringent requirements on composition control and processing, and a market value based on unique performance delivered which justifies a much higher cost and higher value added per kilogram than is characteristic of traditional ceramics. Within this broad overall definition many families and subfamilies of advanced ceramics exist and continue to grow and multiply in number and kind. The total range of new ceramics is bewildering in its complexity. To establish economic perspective we begin with a discussion of probable future markets. To provide an organized sequence of themes we then begin with a discussion of applications classified by the function which the ceramic performs. This allows us to develop a list of the principal families of advanced ceramics by chemical type. Next we discuss the most important processes by which ceramics are made. This is a critically important subject. The outstanding properties which make advanced ceramics attractive are achieved by close control of microstructure and distribution of chemical species within a ceramic. Next we give a brief description of each of the major advanced ceramics families including the most important properties and the special aspects of composition and processing control needed to produce the microstructure required to give these properties. Then we consider how development of technology for the new ceramics is likely to impact established types of ceramics. With this as background we consider the most favorable circumstances for participation in future ceramic markets by developing nations. Finally we give two examples of successful transfer of ceramic technology to developing nations.

2. A Market Estimate for Advanced Ceramics

Comprehensive statistics on ceramics, especially advanced ceramics, are difficult to obtain. Conventional economic statistics concentrate on the older families of ceramics such as building materials. Much of the activity on new ceramics is included in economic totals for organizations in other econonic categories and can only be partially broken out if at all. One can use surveys by various market research organizations as a rough guide. A broad overall feeling for the size of this market is provided by the estimate in Table 1 prepared by H. K. Bowen for the Committee of the U. S. National Academy of Engineering on High Technology Ceramics in Japan and based on familiarity with several such surveys. This estimate assumes success in a limited range of ceramics for heat engines but does not assume a full ceramic engine. Electronic ceramics and structural ceramics take roughly equal shares in this market estimate. Other estimates vary widely especially with regard to timing of future growth. For example, C. Stevens of the U.S. Department of commerce estimates that the U.S. market for ceramic-based electronic components will be $ 19.7 billion in 1990 but is more conservative about the growth of structural ceramics placing the greatest growth in this field after 1990. All that can be said with reasonable assurance is that the future market for advanced ceramics is large with a high growth rate and offers good opportunities. This market prospect has attracted the attention of many aggressive firms especially in the United States and Japan. The low estimate in Table 1 for the probable future market outside these two countries reflects the concentration of current activity in producing and using advanced ceramics in these two countries plus the view that future growth will require mastering very difficult production technology while competing fiercely on price. There would seem to be no inherent reason why firms in other countries should not take a larger share of this growing market provided they can bring the technical and financial resources together in an organization which can deliver reliable products on time at a competitive price and simultaneously move with the developing technology. Joint ventures in new ceramics by firms in developing countries in conjunction with firms in developed countries would appear very promising.

3. Advanced Ceramics Classified by Function

New ceramics are generally used as parts in devices because they can perform some function better than competing metals or polymers. Many of these applications rely on ceramics' special electromagnetic properties, their relative chemical inertness, their hardness and strength, and their high temperature capabilities, sometimes in combination. A systematic classification, developed by the Yano Research Institute and adapted by Kenny and Bowen, is given in Table 2.

The first classification, electric functions, is a broad one and requires discussion in terms of more detailed categories. Electrical insulation materials are descendants of traditionsl electrical porcelains in a sense but the properties required and the size and complexity of the integrated ceramic parts makes them a new family of materials. Aluminum oxide, ranging in purity from 99.5 to 90 percent depending on the application, is the dominant ceramic electrical insulator. Refinement of the tape casting process in the early 1970's made it possible to produce unfired tapes with sufficient strength for handling including punching of holes, inking, stacking, etc. When fired these tapes produce ceramics typically 50 to 100 microns thick with bending strength values greater than 275 MPa. These ceramics compete with polymers and coated metals as supports for electronic chips and dominate in applications where high heat dissipation and high hermeticity are required. This technology is highly developed and includes multilayer substrates having more than thirty layers with tens of thousands of interconnections by thin metal layers applied as inks and fired with the ceramic. Excellent as alumina is for this application, alternate materials are being studied in an attempt to lower the dielectric constant to permit higher frequency operation and a better match for the thermal expansion of silicon. Multiphase ceramics in the aluminum oxide - silicon dioxide - magnesium oxide family may be the next generation and beyond them silicon nitride may eventually be the third generation.

This situation illustrates both the opportunity and the difficulty for a developing nation to produce one of the new ceramics and gain a market share. The opportunity for ceramic substrates for electronic chips appears to be very good. The immense growth of industrial and consumer applications of microelectronics indicates a doubling and redoubling market for ceramic substrates and packages over the next decade. Table 3 from Stevens gives her estimate of the future U. S. market potential for ceramic IC packaging and shows an impressive annual growth rate of 9 percent. The difficulties for a new producer are equally impressive. First, a complex existing technology must be mastered and products must be sold in competition with outstandingly expert and efficient producers. Second, the existing technology is likely to be outmoded in a few years by alternate, advanced and proprietary ones.

Ferroelectric ceramics, primarily barium titinate and related materials, have a high dielectric constant making them excellent as the dielectric in capacitors which are an indespensible component in electronics. Some are made by a process similar to the multilayer substrates discussed above.

Vast numbers (tens of billions) are required at a low unit cost and great efforts are being made to lower cost by using cheaper metals (which must survive firing) as electrodes. Stevens estimates that in 1982 a total of 6530 million capacitors were shipped in the United States. Of these 5100, or 78 percent were ceramic-based, but these had a value of $ 452 million which is 38 percent of the total of $ 1190 million for all capacitor shipments. Table 4 gives her estimate for the future U.S. market potential for ceramics in capacitors.

Piezoelectric ceramics, such as lead zirconate titanate, are used in a wide variety of applications to convert motion into electrical signals and vice versa. Vibrators, oscillators, filters, speakers, etc. are essential parts of many industrial and consumer products.

Ceramic semiconductor materials include titanates, silicon carbide, zinc oxide, vanadium oxide, nickel oxide, iron oxide, and cobalt oxide. In some cases they are used as thermistors, i.e. as strongly temperature dependent resistors, for termperature control. In other cases, they are used as varistors, i.e. as voltage sensitive resistors, to protect against voltage surges as in lightening. In still other cases they are used as chemical sensors by relying on the large changes in electrical conductivity which absorbed chemicals can change on the surface of thin films. In still other cases they are used as miniature heaters.

Ionic conducting ceramics, such as beta-alumina and stabilized zirconia, are finding important uses as oxygen sensors in automobiles and as electrolytes in fuel cells.

Magnetic ceramics, such as ferrites made of iron oxide in combination with one or more of the oxides of barium, lead, strontium manganese, nickel, and zinc, can be tailored to be either hard or soft magnets. They find wide application in speakers, motors, transformers, recording heads and the like. Ceramic ferrites are sometimes considered to be a relatively mature market, but they might be of particular interest to developing countries as their economies develop and they begin to experience the enormous use of small electric motors characteristic of highly developed countries.

Stevens has attempted to estimate the U.S. market for electronic ceramics other than integrated circuit packages and capacitors. Her conclusions are given in Table 5.

In the category of optical functions a special form of pore-free alumina is widely used as the inner envelope for high pressure sodium vapor lights whose characteristic orange glow lights so many of the highways of the world. Lead zirconate titanate (PLZT) ceramics are a specialty material finding increased use in light modulation and displays.

Modern high-transmission optical fibers are a material of enormous future technical and economic importance. These are currently silica-based glasses and as such are a type of new ceramic. This field is just taking off economically. In 1982 some 373 km of low loss fiber was sold with a value of $ 335 million. For 199 sales of 5271 km with a value of $ 4000 million is forecast. The additional field of fiber optic sensors is in an even earlier stage of development. Sales in the U.S. in

1981 have been estimated at $ 12 million and forecast for 1991 to be $ 180 million.

Ceramics play important roles as sensors for fuel/air mixtures, for humidity, and have potential for wider application in the chemical process industry. Semiconducting ceramics (e.g. ZnO) and ionic conductors (e.g. stabilized zirconia) are generally used. Ceramics serve to promote chemical reactions also as in the case of ceramic catalyst carriers and ceramic electrodes.

One of the oldest uses of ceramics is as thermal insulators at high termeratures and they continue this role in modern form, e.g. as super insulators such as the silica tile used on the space shuttle. Modern ceramics such as silicon carbide and silicon nitride are increasingly attractive as heat exchangers as are the low-expansion ceramics such as cordierite.

Much of the excitement over new ceramics centers on their inproved mechanical properties and their potential use in industrial processes and in heat engines. Major families include silicon carbide, silicon nitride, transformation toughened airconia and alumina, and composites involving ceramic fibers.

A potentially important market for new ceramics is as implants to replace teeth, bone, and joints.

Ceramics have long been used in the nuclear field as fuels, cladding material, and shielding material. They are leading candidates as matrices to contain radioactive wastes for long term storage.

4. Ceramic Processing

The outstanding properties possessed by advanced ceramics are achieved through special compositions and microstructures which require very careful control throughout the successive stages of ceramic processing. These stages are summarized in Table 6 for the most important type of ceramic processing which involves production of a powder, consolidation into an unfired blank (called a green ceramic), sintering, and final finishing. It is impossible to go into ceramic processing in depth in this paper but a brief sketch will help in understanding the challenge in making advanced ceramics.

Fine grain size is generally desirable in finished ceramics to impart high strength and to permit the making of small parts or where smooth finishes are required, for example. in substrates for electronic chips. Some chemical systhesis processes yield fine powders directly. Other chemical processes give larger size powders and require an additional step of size reduction through milling or grinding.

Traditional ceramics are largly made from natural raw materials which are physically separated and reduced in size. The new ceramics generally require chemical conversion of raw materials into intermediate compounds which lend themselves to purification and subsequent chemical conversion into the final form desired. The details of these processes are sometimes trade secrets. An extreme example of production of pure oxide powder would involve refinement of pure metal from an oxide followed by reoxidation under controled conditions. More typically for oxide powders a soluble intermediate, such as a carbonate, hydroxide, or metal-organic compound is formed, purefied and then transformed into an oxide. For the carbide and nitride ceramics high temperature reactions are generally used. At one extreme a mass of silica sand and coke is heated by current from carbon electrodes (Acheson process) to produce a large mass of silicon carbide crystals which must then be broken up and sized. At another extreme, very fine and uniform silicon nitride particles can be produced by a laser-driven reaction between silane and ammonia.

Traditional ceramics are made using powders which have a distribution of particle sizes. For the new ceramics one experimental line of work aims at producing very strong and reliable ceramics by working from very fine spherical, monodisperse powders (powders having a very narrow distribution of particle sizes). These monodisperse powders are made typically by techniques of colloidal chemistry for oxides and by controlled nucleation and growth in gas phase reactions for the carbides and nitrides. However, most of the new ceramics are still made from powders with a broad distribution of particle sizes but with smaller average particle sizes (less than one micrometer) than the traditional ceramics.

Typical processes for particle size reduction and/or selection are listed in Table 8. Air classification and elutriation (settling in a liquid) are processes which separate powders into different size range fractions. Attrition milling and ball milling are typical of processes which reduce the average particle size but leave a very broad distribution of particle sizes. Thus a two-stage process for reduction followed by separation of particle size fractions may be required. Contamination during these processes is sometimes a problem.

Powders are difficult to handle and this difficulty increases as the particle size decreases. The powder must be compacted into a shape approximating the final part before sintering (final compaction by heating to high temperature). This compaction requires flow which is impeded by agglomeration of the powder particles into clusters. Such clustering can cause pores of sufficient size in the green part such that large flaws can remain in the final ceramic with sometimes disasterous results for strength. Control of the rheology (flow characteristics) of the powder is essential. The powder is effectively made into a more or less viscous fluid by the addition of substances which will subsequently decompose and escape as gases during the early stages of heating before appreciable sintering takes place. Table 9 lists types of additives and the functions which they perform.

Ceramics are typically very hard and expensive to machine after the sintering stage. It is therefore of overriding economic importance that the green ceramic be shaped into an oversized approximation of the final part desired. If this is done well and shrinkage during sintering is properly taken into account, little or no final machining will be required. Table 10 lists some of the most important consolidation processes for making the shaped green parts.

In uniaxial pressing a powder-additive mixture is compacted in a die by applying pressure along a single direction. This typically produces density gradients in the green piece which can persist in the sintered part with undesirable results. The process is also limited in the complexity of green shapes which can be made. More complex parts and more uniform green densities can by made by the more expensive process of isostatic pressing. This process involves the application of pressure uniformly on all sides by enclosing the powder in a liquid-tight rubber mold and immersing the mold in an essentially incompressible liquid which is then pressurized. The powder can first be formed by one of the casting or plastic forming processes and subsequently isostatically pressed so that great flexibility is possible.

Variations of these two processes can be carried out at high temperature in which case the shaping process and the sintering process are combined. In hot pressing a heated die, typically graphite, is used. In hot isostatic pressing a gas such as argon is used in conjunction with a specimen container, typically metal or glass, which softens at high temperature and transmits pressure uniformly but prevents gas entry into the pores of the partially-compacted ceramic.

Casting is another family of consolidation and shaping techniques. A suspension, called a slip, of the powder in water or organic liquids is prepared with suitable additives for rheology control (frequently one of the critical trade secrets). This slip is cast into a mold having very fine pores. Enough of the liquid is removed into these pores by capillary attraction or external pressure to convert the remaining powder-liquid mixture into a green body having sufficient strength for subsequent handling. The shape is then removed from the mold and further liquid is extracted by drying at a rate which must be carefully controled to avoid cracking.

Plastic forming constitutes another, somewhat similar family of consolidation and forming techniques. In this case a mixture which is deformable under pressure is made using suitable additives. This is extruded into dies or pressed into molds, usually with some heating to facilitate plasticity. The binders must be removed by decomposition and evaporation in carefully controlled heating before heating to higher temperatures for sintering.

The sintering action itself is complex. Two processes are generally taking place simultaneously. The desirable process of densification takes place under the action of surface tension forces. The undesirable process of grain growth takes place under the action of differential grain boundary energies. Some of the additives used in the forming stage of processing are high temperature materials themselves (such as small amounts of other oxides) introduced to reduce grain growth in normal sintering or to give some high-temperature plasticity in those cases when hot pressing is used. In addition to helping with the processing stage, these additives sometimes affect final properties. Their effect can be beneficial (e.g. electrical conductivity control in grain boundaries) or harmful (e.g. promoting slow creep at high temperatures). The interrelated fields of sintering-additive design and grain-boundary engineering for property control are in themselves complex and critical aspects of ceramic processing.

There are additional processes which combine several steps and avoid or greatly modify the powder processing aspects of conventional ceramic processing. Glass-ceramics are made by melting the components together as a glass-forming liquid, forming the articles by glass-forming techniques and then crystalizing the glass with a subsequent heat treatmert using the aid of a nucleating agent which causes many small crystals to grow simultaneously resulting in a largly-crystalline, fine-grain ceramic of high strength. The process is limited to glass-forming systems. Sol-gel processing begins with metal ions in metal-organic compounds which can be put in solution and mixed on the molecular level thus achieving homogeneity in multi-component systems on a fine scale which is difficult or impossible to achieve by powder mixing. These metal-organics are reacted, typically with water, to simultaneously form oxides and to form polymers which develop strength and so become a gel. These are dried (with large attendant shrinkage, a problem with the method) and then heated to sinter into the final product.

A central problem in ceramic processing is to avoid the formation of flaws during any of the early stages. For high strength applications flaws with a maximum dimension of 100 micrometers may be unacceptable. This is the origin of the famous reliability problem of ceramics which produces the requirement of proof testing every part for the most demanding applications. Improvement in reliability through improvement in processing control is perhaps the greatest challenge for advanced structural ceramics.

5. Some Major Families of Advanced Ceramics

With these facts concerning uses of advanced ceramics and the nature of ceramic processing in mind, let us turn to a somewhat closer look at some of the leading families of advanced ceramics.

Silicon nitride has been attracting great attention and is one of the front runners for great growth. It occurs in both alpha and beta phases so that phase purity as well as purity in the ordinary sense becomes important. Powders with alpha phase content around 90 percent and with mean particle size around 0.7-1.0 micrometer are available from several manufacturers. These powders are difficult to sinter, in part because of the high dissociation pressure at high temperature, so that pressurized sintering methods are used to produce either hot pressed silicon nitride (HPSN) or gas pressure sintered silicon nitride (GPSSN). Small amounts of oxides are usually added to facilitate sintering and allow the production of ceramics with high strength and very attractive short term properties. Table 11 compares basic physical properties of competing structural ceramics and Table 12 gives typical values for some properties of these materials which are strongly dependent on the microstructure formed during sintering and so can vary considerable for the same nominal material. Unfortunately, the oxide sintering aids cause long term loss of strength at high temperature (above 1000 C). A different approach is to form a green ceramic from silicon powder by cold pressing a porous part and then to convert the part to silicon nitride by reacting with nitrogen at high temperature. This results in a body which has lower itital strength but which retains this strength for long times at high temperature. Evidently the choice of the type of silicon nitride to use must be tailored to the conditions of application. Intense research is directed toward effective sintering aids which allow good strength retention at high temperature. Production of better powders is also being attempted but the market, although potentially large, is still a market for research material primarily so that investment in production capacity for powders is risky.

Tables 11 and 12 give perspective on the relative advantages and disadvantages of the competing advanced ceramics. Thus silicon nitride has low thermal expansion (good for resisting thermal shock but bad for use in conjunction with iron-based alloys).

Silicon carbide is a major competitor with silicon nitride for the first generation of advanced structural ceramics. Long used as an abrasive and available as a silicon-bonded material, it entered a new era with the discovery of methods to sinter to full density with suitable sintering additives. It occurs in both alpha and beta phases, both have now been sintered to full density. Table 12 compares the properties of these materials. Both silicon carbide and silicon nitride possess excellent strength and moderate toughness. The properties of either appear adequate for many industrial and heat engine applications. Work centers on reliably achieving these properties in complex shapes in one of the great technological contests of the world.

Partially stabilized zirconia (PSZ) has been in limited use for decades. Without stabilization, zirconia rapidly transforms from a monoclinic to tetragonal form and back again upon heating and cooling. Addition of a sufficient amount of a stabilizing oxide (e.g. 10 percent magnesium oxide) keeps it in the cubic phase. Partial stabilization yields a cubic phase with inclusions of a transforming phase. The discovery some ten years ago that if the particles of transforming phase were kept well below one micrometer in size the strength and toughness were dramatically improved. This opened a new period in structural ceramics. As Table 12 shows, strength values above 700 MPa and toughness above 8 MPa mexp(1/2) are commercially available and still better PSZ materials are in the research stage. The good thermal expansion match for iron-based alloys, the reasonable hardness, and the low thermal conductivity makes this an outstanding candidate structural material. Its use will probably be limited to moderate temperatures however because the strength typically drops to half at 700 C and to one fourth at 1000 C.

Aluminum oxide is available as a powder with 99.99 percent purity and average particle size of about 0.5 micrometer. The existing markets for sodium vapor lamp tubes, and electronic ceramics make this a well-supplied, competitive business. Strengths above 350 MPa can be obtained by conventional sintering and values around 700 MPa by hot pressing but the latter are expensive and limited in shape. However, the low toughness of this material limited its consideration as a structural material. The extension of the transformation-toughening mechanism used in partially stabilized zirconia to make transformation toughened alumina (TTA) is dramatically changing this picture. As Table 12 shows, strength and toughness values comparable to PSZ are being achieved in TTA in research specimens. Only some 15 percent of the more expensive zirconia is needed in TTA together with the cheaper alumina so that the prospects for TTA seem very good.

As our final example of an advanced structural ceramic we consider the so-called ceramic-ceramic composites. These consist of ceramic fibers (typically silicon carbide) in a glass or glass-ceramic matrix. Excellent strengths up to 1000 C and high toughness values (in the range of metals) have been achieved as Table 12 shows. These materials are currently made by hot pressing which is expensive and shape limiting. Also, oxidation problems associated with cracking of the matrix have emerged. They will undoubtably find important specialty uses and as such form the third generation of advanced structural ceramics.

6. Potential Impact of New Ceramics on Developing Nations

We have so far concentrated our attention on families of advanced ceramics which are new and are still undergoing rapid change. These are the families which are attracting the most attention because of the new markets which they promise to serve and because of the excitement associated with their rapid technical progress. However, a predominant part of the present market for ceramics is made up of better established and more traditional ceramics. Some of these established ceramics are sophisticated, high-technology materials such as sparkplug porcelains. Other portions of established ceramics are likely to develop more high technology products as materials and processes improve. For this reason and because the established ceramics appear to offer the best prospects for developing nations we now examine the interplay between the high ceramic technologies being developed for the new ceramics and future possible improvements in established ceramics.

Some established ceramic industries are compared with new and rapidly changing industries in Table 13. The refractories industry has been concerned with ceramics for insulation, chemical erosion, and resistance in high temperature furnaces for steel making, glass melting, and similar uses. The new ceramics intended for service in heat engines are in one sense special types of refractory with the added need to carry substantial loads in some engine application. They are being developed primarily by scientists and engineers outside the traditional refractories community but the new technologies which they require will also undoubtedly lead to improvements in traditional refractories.

As Table 14 shows schematically, an established industry is subject to two kinds of forces to modify products in addition to the normal pressures of economic competition in their established product line. One force comes from changes in the requirements of the market which they serve, such as, the increasing use of continuous casting by the steel industry and the associated need for special refractories for this casting technology. The other force comes from developments in ceramic technology which can be used to produce improvements in their traditional products or in products for their new markets. As ceramic technology advances, giving products with higher performance and longer life, the value of these products per unit weight increases. This makes shipping over long distances economically possible and increasingly makes ceramic industries subject to world-wide competition. A manufacturer of an established type of ceramic product cannot afford to ignore developments in high technology ceramics which could be applied to improve his type of product. It may seem that such a gap exists between the complex and expensive technologies used with the new ceramics and the relatively low cost of many traditional ceramics that the former would have no impact on the latter. It is believed that there will be many significant impacts from fundamental aspects of the new technologies although these will require adaptation to traditional products.

Table 15 gives more detail on recent changes in the steel-making refractories industry. The special refractories required for the new steel-making processes listed are sophisticated, high-technology products in their own right even though they are typically not as costly or difficult to make as some of the newest ceramics.

Table 16 lists some of the fundamental ceramic technologies whose development is being pushed by the new ceramics. Some of these technologies very likely can be adapted to give better products in many of the established ceramic industries listed in Table 13. For example, the work on fine powders, chemical routes to green bodies and better rheology control way well lead to the development of bulk ceramics made with a bonding phase of very fine particles in a material made up predominantly of larger grains of a relatively inexpensive ceramic.

We conclude that developing nations should study the progress in new ceramics from two points of view: First, to find a portion of the process of making one or more of the new ceramics which they could profitably perform. Second, to find portions of the new technologies associated with the new ceramics which they can adapt to the production of the more well established types of ceramics. Table 17 shows overall judgement of the liklihood of success classified according to whether the market is domestic or export and whether the nation involved is developed or developing. A developed nation with strong technical capability presumably can exploit fully the economic potential of existing ceramic technologies as they apply to that nation's particular raw materials and market conditions when the market is domestic. Excellent possibilities also exist for the new ceramics for domestic markets. A developing nation has a strong likelihood of being able transfer new ceramic technologies in existing industries as they are adapted to these industries, at least for domestic markets. Their chance of being able to develop profitable industries for the new ceramics for their domestic markets appears quite small, in part because the whole user industry for the new ceramics would have to be developed as well.

Turning now to the potential for new ceramic technologies to make products for export markets, a somewhat different situation appears probable. Developed countries again have excellent prospects for application of new technologies to established products appropriate to their raw materials and economic circumstances. For the new ceramics the prospects are good but hazardous due to the difficulty of the new ceramics and the fierce international competition that is likely to develop. Developing nations would seem to have only fair prospects on average for adapting new technologies to traditional ceramics for export because they would probably be later in coming to market than the developed countries. This generality may have important exceptions when a cost advantage for the developing country can be combined with a joint venture with a multinational firm which has already mastered the technology and which has marketing arrangements outside the developing country. For the new ceramics themselves, some developing countries may be able to offer labor cost advantages but the complexity of the new ceramics technologies probably makes a joint venture with an outside leader in the field almost essential. It is appropriate, therefore, to consider the lessons of experience in the transfer of ceramic technologies to developing nations.

7. How Ceramic Technology is Transferred to Developing Nations

For the transfer of technology in ceramic materials to occur in any nation there must be a basis for utilization of those materials within those countries or an export market. Therefore, this is likely to be an evolutionary process rather than a revolutionary process. In a "truly" developing nation the transfer of the highest technology of ceramic materials can only occur if the transferring agent or country were to act as the recipient of the produced materials from the developing country or as the distributor of these materials for that region. Of course, the incentive here would be for the transfer of technology to occur because of the favorable labor rates and essentially the more economical production of those materials. However, there are many considerations even in this scenario such as the culture, the work ethic, and the ability of the people to assimulate the technology.

As stated previously, the term high technology should include the advances in technological state of the more mature ceramic industries. These industries could supply technology for the pattern of developing needs in each of those nations. Examples might be refractories, whitewares, cements, ceramic metal systems, structural clay materials, glass, electrical ceramics, etc. Many examples could be given of developing countries who have had technology transfer in ceramics to implement their existing and growing industry. Perhaps two case histories will suffice to show how technology may be transferred to a developing nation. These two cases involve southeast Asia and South America.

Example number one would be the transfer of refractory technology to a southeast Asian country. In this country there were many raw materials available for refractory use but the existing industry was extremely poor and certainly not well managed on a scientific and engineering basis. In this instance, an American manufacturer surveyed the needs around the world for possible technology transfer and licensing arrangements and selected this country as a target. First contact was made in 1970 and after a round of negotiations an agreement was signed in

1973. This company had thirty different products as candidates for technology transfer. For transfer to occur it was necessary for a whole round of educational process to be initiated. This included instructing the engineers of that country in the various methods of material characterization and the technology of modern production techniques. By 1974 one product of low technical importance was transferred and was on the market. At this point geologists were employed to search the country for additional raw materials and to develop an even better characterization laboratory and beneficiation techniques. During the next ten year period, most of the thirty different products were transferred to the developing nation but all along the way this required support from the licensing company with respect to laboratory analyses, guidance in technological assessment, and a slow equipage of a modern laboratory in that country. Initially, the materials were transferred from southeast Asia to the United States for evaluation and developed in actual pilot plant operations to prove the feasibility of the product. After feasibility was determined with those materials, the technology was again transferred to southeast Asia.

Perhaps the most important thing to understand is that in this evolutionary development the overall time frame was minimum of fourteen years. In actuality this is a relatively short period for transfer of technology and speaks well of the technical abilities and assistance programs generated by the licensing corporation.

Example number two, in South America, had an even longer time frame in developing the technology transfer. In 1965, an emerging ceramic industry in that country was totally dependent upon imported raw materials. In fact 95% of all materials used in their whiteware plants were from overseas. Of course, this was an intolerable position both from an economic standpoint and a technology standpoint. Here again, the geologists from the corporations began a search for available and useable raw materials for their industry. Using outside consultants and licensing arrangements from the United States, technical criteria and characterization techniques were determined and were used as specifications for the whitewares industry in that country. Over time the characterization techniques of the materials became part of the every day existence of the company and resulted in the greater utilization of the indigneous materials of the country. In fact, as of today 95% of all material used in the whiteware industry are indigneous material as opposed to imported. As this technology was transferred it was certainly considered high technology to that developing country. Once the basis of a good ceramic industry was developed, the next levels of high technology ceramics were installed. These were in the areas of spark plugs, ferrites, special glasses, etc. There was now an evolutionary base which had matured to the point where the higher technologies could be transferred. It should be pointed out again that this effort started in 1965 and that we are only now seeing the emergence of some truly high technolgy products in that developing country.

There is another scenerio which should be examined and might best be termed the off-shore operation. In this case, a major high technology corporation may be looking for the exploitation of a highly intelligent work force in a country whose economy is such that their labor rates are much more beneficial to the manufacture than those of the developed nations. In this instance, transfer of technology can be accomplished either by a partnership or by utilizing the low labor rates of the country. The developing nation could share in the marketing of the product produced by acting as a regional distribution center for high technology products and also sending product to its partners.

Probably the transfer of the ceramic high technology to a developing nation which can assimulate the products into its own infrastructure on an evolutionary basis is the preferable model to be followed. There are many partners that might be assembled to give the greatest spectrum of skills to implement the transfer. These partners might include major corporations whose technologies can be sold or licensed on appropriate terms. The process could include the assistance of Unido or other such organizations. One effective group is the retired executives organization (I.E.S.C.) that operates out of Washington, D. C. This organization recommends highly skilled and qualified people to work in the developing nations that require assistance in particular ceramic fields. Many of the leaders of the American ceramic industry have participated in such programs all around the world. The results of this type of input have been enormous and again this has been an evolutionary process. Unido can also send consultants into the various countries to help determine the feasibility of any potential industry in that country. After determination of feasibility a body of experts should be sent to physically implement the construction of the plants and laboratories. It should be followed up by experts who can act as the engineers in constructing industry.

It should be reiterated that no technology is going to be able to be transferred until there is a solid core of technically trained people available within the developing country. Once this core of people is available, the transfer technique may come from a government motivated process or by entrapreneurial action by individuals or corporations. The driving force for transfer is the need for the specific technology within that country. These mechanisms may be licensing of technology, purchase of technology, joint venture, or development of technology through research in the countries laboratories. In some instances, there can be international bartering, that is, the country can trade raw material resources to a major corporation for the technology either for the production of that material or other technologies which that corporation can license. Unido development funds may be necessary. Perhaps another vehicle is the international monetary fund for co-development of industries between the developing nations and the highly developed nations.

Not enough can be said about the cultural heritage of the developing nation with respect to the ability to assimulate new highly technologically oriented industries. Once a good basis of industry in that country has evolved there has to be an interaction of the industrial community with the government and the developing educational system in that country. In many of these countries there are industrial czars who are politically influential and can have great effect on the educational system and the direction their countries will take. These national leaders and the government leaders must want this technological progress to occur or it is unlikely to happen. Even with dedication to the process the technically oriented ceramic industry cannot evolve quickly.

8. Conclusions

New ceramics constitute a commercially important set of materials with good prospects for rapid market growth. The full extent of future growth depends upon further technical developments. Intense competition exists between different families of new ceramics, between ceramics and other materials, and between firms in many developed countries for shares of the new markets.

The new technologies deing developed for synthesis and production of the new ceramics will have important impacts in upgrading types of ceramics already made by established industries. International competition among suppliers of these ceramics will probably increase.

The low labor costs of developing countries gives them potential for sharing in markets for both new ceramics and improved forms of established ceramics. However, the technical difficulties and need for marketing arrangements strongly favor joint ventures with firms in developed nations which have mastered the technology and are already suppliers. Labor force training and acceptance of the long time frame typically involved are important requirements to understand.

Table 1. World Market for Advanced Ceramics

Sales by Free World segment

	1980	1990	1995
Japan	1900	6500	9000
United States	1500	5000	7000
Other	700	500	1000
Free World total	4100	12,000	17,000

Table 2 Classification of High Tech Ceramics by Function

Electric functions	Insulation materials (Al_2O_3, BeO, MgO)		IC circuit substrate, package, wiring substrate, resistor substrate, electronics interconnection substrate
	Ferroelectrics 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 arrestor, etc.
		Sintered CdS material:	solar cell
		SiC heater:	electric furnace heater, miniature heater, etc.
	Ion conducting materials (β-Al_2O_3, ZrO_2)	Solid electrolyte for sodium battery	
		ZrO_2 ceramics:	oxygen sensor, pH meter fuel cells
Magnetic functions	Soft ferrite		Magnetic recording head, temperature sensor, etc.
	Hard ferrite		Ferrite magnet, fractional horse power motors, etc.
Optical functions	Translucent alumina		High pressure sodium vapor lamp
	Translucent magnesium, mullite, etc.		For a lighting tube, special purpose lamp, infrared transmission window materials
	Translucent Y_2O_3-ThO_2 ceramics		Laser material
	PLZT ceramics		Light memory element, video display & storage system, light modulation element, light shutter, light valve
Chemical functions	Gas sensor (ZnO, Fe_2O_3, SnO_2)		Gas leakage alarm, automatic ventilation fan, hydrocarbon, fluorocarbon detectors, etc.
	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, sulfides, borides)		Electrowinning aluminum, photochemical processes, chlorine production
Thermal functions (ZrO_2, TiO_2 ceramics)			Infrared radiator
Mechanical functions	Cutting tools (Al_2O_3, TiC, TiN, 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, others)		Ceramic engine, turbine blade, heat exchangers, welding burner nozzle, high frequency combustion crucibles
Biological functions	Alumina ceramics implantation		Artificial tooth root, bone, and joint
	Hydroxyapatite bioglass		
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)		

Table 3. U.S. Market Potential For Ceramic IC Packaging (U.S. $ million, current dollars)

Year	Total IC Shipments	Ceramic Based	%	Ceramic Package Value
1980	6768	1692	25	220
1985	13000	5200	40	676
1990	27000	13500	50	1755

Table 4. U.S. Market Potential For Ceramics in Capacitors
(U.S. $ million, current dollars)

Year	Total Shipments	Ceramic Based	%	Ceramic Value
1980	1085	390	36	234
1985	1450	580	40	348
1990	2000	1000	50	600

Table 5. U.S. Market Potential For Ceramics In Other Electronic Components
(U.S. $ million, current dollar)

Year	Total Shipments	Ceramic-based	%	Ceramic content
1980	15,600	1,560	10	80
1985	20,000	3,000	15	150
1990	26,000	5,200	20	260

Table 6. Stages in the Processing of Crystalline Ceramics

- Powder Synthesis
- Powder Sizing
- Rheology Control
- Consolidation and Forming Processes
- Sintering
- Final Machining
- Inspection

Table 7. Powder Synthesis

- Natural raw materials
- Metal purification followed by reaction
- Carbonate or hydroxide purification followed by thermal treatment
- Precipation
- Gas phase reaction
- Use of metal-organic precursers
- Many others

Table 8. Powder Sizing Processes

Air Classification

Attrition milling

Ball milling

Calcining

Elutriation

Fluid energy milling

Freeze drying

Hammer milling

Precipitation

Vibratory milling

Table 9. Function of Additives to Mixtures for Rheology Control and Other Purposes (after Pincus and Shipley).

Additive	Function
Binder	Green strength
Lubricant	Mold release, interparticle sliding
Plasticizer	Rheological aids, improving flexibility of binder films, allowing plastic deformation of granules
Deflocculant	pH control, particle-surface charge control, dispersion, or coagulation
Wetting agent	Reduction of surface tension
Antistatic agent	Charge control
Antifoam agent	Prevent foam
Foam stabilizer	Strengthen desired foam
Chelating or sequestering agent	Deactivate undesirable ions
Fungicide and bactericide	Stabilize against degradation with aging
Sintering aid	Aid in densification

Table 10. Major Techniques for Powder Consolidation and Shape Forming (after Richerson)

Pressing	Plastic Forming
Uniaxial pressing	Extrusion
Isostatic pressing	Injection molding
Hot pressing	Transfer molding
Hot isostatic pressing	Compression molding
Casting	Others
Slip Casting	Tape forming
Thixotropic casting	Flame spray
Soluble-mold casting	Green machining

Table 11. Comparison of Some Basic Properties of Selected Compounds Used in Advanced Ceramics

Compound	Density g/cm^3	Hardness kg/mm^2	Melting Point C	Thermal Conducitivity cal/cm s C
Aluminum Oxide	3.98	2100	2050	.07
Zirconium Oxide*	6.27	1200	2715	.005
Silicon Carbide	3.22	2500	2220**	.16
Silicon Nitride	3.17	2400	1900	.04
Silica Glass	2.20		---	.002

* Stabilized in cubic form
**Decomposes

Table 12. Comparison of Properties Important to Structural Use for Some Advanced Ceramics

Material	Strength MPa	Toughness MPamexp(1/2)	Thermal Expansion 10exp(-6)/C
	Types of Silicon Nitride		
RBSN	300	3.6	3.3
HPSN	1100	6.6	3.5
GPSSN	440	2.9	3.5
	Types of Silicon Carbide		
Alpha SSC	420	2 to 3	4.1
Beta SSC	533	2.4	4.1
HPSC	800	3.9	4.2
	Types of Transformation Toughened Ceramics		
PSZ	700+	8+	10.2
TTA	900	8	7
	Ceramic-Ceramic Composites		
SiC-LAS	620	15	1 to 4

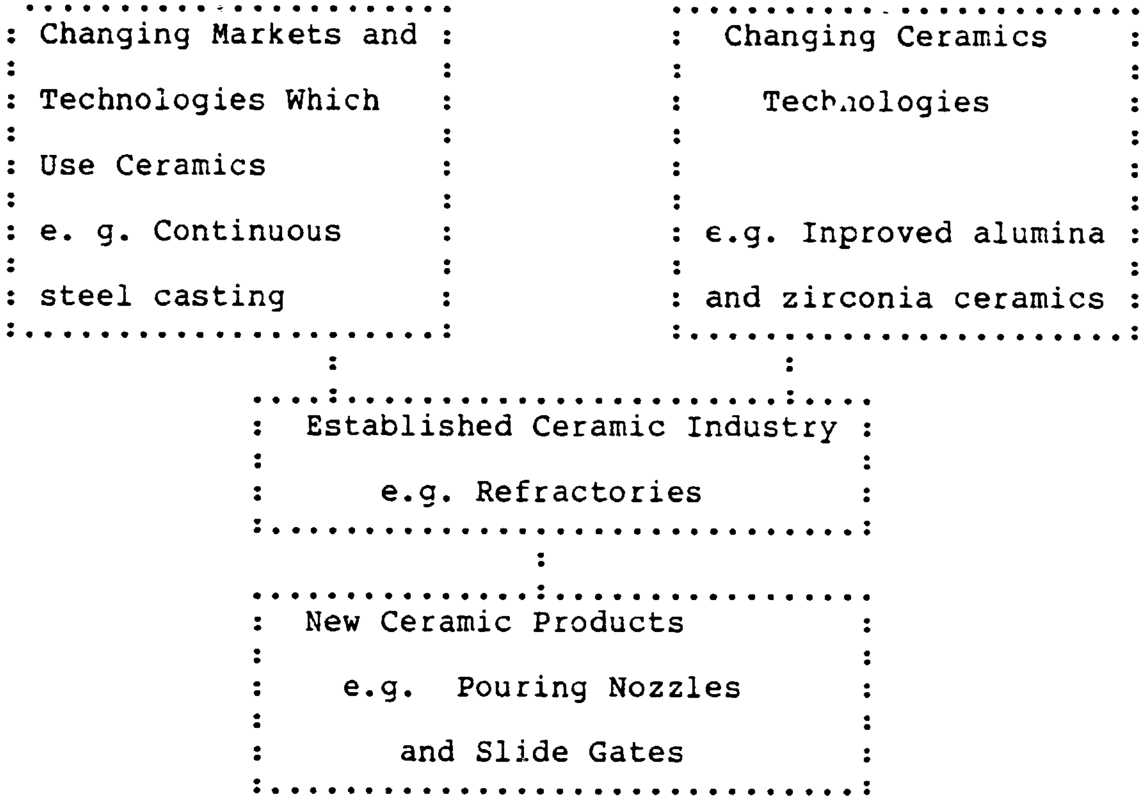
Key:

RBSN	Reaction bonded silicon nitride
HPSN	Hot pressed silicon nitride
GPSSN	Gas pressure sintered silicon nitride
Alpha SSC	Alpha-phase sintered silicon carbide
Beta SSC	Beta-phase sintered silicon carbide
HPSC	Hot pressed silicon carbide
PSZ	Partially stabilized zirconia
TTA	Transformation-toughened alumina
SiC-LAS	Silicon carbide fibers in lithium aluminosilicate glass

Table 13. Typical Established Ceramic Industries Compared with New Ceramic Industries

Established and and Evolving	New and Rapidly Changing
Refractories	Structural Heat-Engine Ceramics
Whitewares	Wear-Resistant Specialty Ceramics
Electrical Ceramics	Electronic Ceramics
Flat and Container Glass	Optical Communication Glass
Cement and Concrete	Composite Involving Cement
Mineral Resources	Synthetic Powders and Fibers
Enameled Metals	Ceramic Fiber Reinforced Metals
Co-WC Cutting Tools	Ceramic Cutting Tools
Ceramic Nuclear Fuels	Nuclear Waste Disposal Ceramics

Table 14. Forces of Change Acting on Established Ceramic Industries



Changing Markets and Technologies Which Use Ceramics

e. g. Continuous steel casting

Changing Ceramics Technologies

e.g. Inproved alumina and zirconia ceramics

Established Ceramic Industry

e.g. Refractories

New Ceramic Products

e.g. Pouring Nozzles and Slide Gates

Table 15. Examples of New Ceramics Requirements for the Steel Industry

Steel Industry Process Change	Ceramic Material Changes
Direct Reduction	*Tar-bonded dolomite *Carbon magnesite refractories use in reduction vessel
Electric Melting Furnace	*Newest chrome-magnesite brick grain for brick *New graphite and composite electrodes
Continuous Steel Casting	*Alumina-carbon tubular shrouds for pouring steel from ladle to tundish and the tundish to column. *Zirconia and alumina slide gates for control of steel flow from tundish
Billet Transfer	*Fused cast chrome magnesite slabs for wear resistance

Table 16. Fundamental Ceramic Technologies Being Developed for New Ceramics

Ultra-fine, ultra-pure ceramic powder production

Improved powder size distributions

Chemical routes to green ceramics (e.g. sol-gel)

Chemical routes to final ceramics (e.g. CVD)

Improved dispersion and rheology of slips and injection molding mixtures

Pressure-assisted slip casting

Injection molding

Hot pressing and hot isostatic pressing

Improved sintering aids

Grain-boundary engineering

Toughness control through second phases

Ceramic composites technology

Finer-grain thin-layer ceramics for electronics

Thermal expansion matching ceramics for silicon

Ultra-low optical absorption glasses

Protective ceramic thin-films and coatings

Composites and gradient-composition ceramics for ceramic-ceramic and ceramic-metal joining

Table 17. Estimates of the Potential for Technology Transfer in Developing and Developed Nations to Serve Their Domestic and External Markets.

Countries	Existing Ceramic Industries	New Ceramic Industries
Percent Potential Use for Domestic Markets		
Developed	100	80 to 100
Developing	80	0 to 5
Percent Potential Use for External Markets		
Developed	80 to 100	40 to 80
Developing	25 to 50	40

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