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NATURE, STATUS, AND SELECTION OF CERAMIC MATERIALS

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SUMMARY

Ceramic materials are identified as having ionic-covalent bonding, being composed of compounds, and being either crystalline or glassy. The oxides are of particular interest because of their chemical stability up to high temperatures. Limited or no ductility, i.e. brittle behavior, make them sensitive to flaws either intrinsic or extrinsic, thus requiring a uniform distribution of uniform flaws to achieve reliability. Intrinsic flaws can be correlated with character features. Extrinsic flaws in themselves are character features. Both of these features can be correlated with mechanical properties and behavior. A number of applications of ceramic materials based on their unique properties of chemical resistance, high strength/density ratios, high modulus of elasticity/density ratios, hardness, optical transparency, and electrical resistance are reviewed.

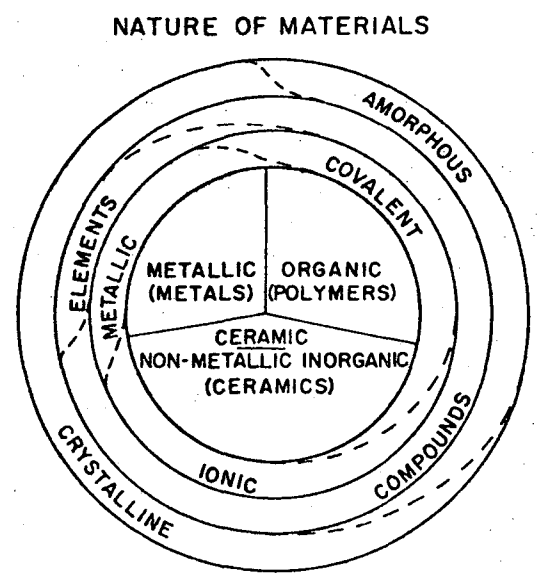
Ceramic, frequently referred to as non-metallic inorganic, materials are of general interest to the engineer because of their potentially greater high temperature stability—both chemically and mechanically, high strength/density ratios, high modulus of elasticity/density ratios, hardness, optical transparency, and unique electrical properties. The principal difficulties in the use of ceramic materials, on the other hand, are normally associated (a) with their brittleness characteristic which is responsible for the lack of toughness in terms of limited resistance to impact and thermal shock, (b) with lack of reliability represented by a large scatter of values for a given property, (c) with fabrication problems in terms of shaping and sizing, and (d) with joining difficulties. Nevertheless, the unique properties are so attractive and desirable, and the progress in their development has been so great since World War II, that the potential for industrial ceramics appears very bright.

Basic questions arise as to the cause of brittleness and lack of reliability, and as to whether there are character features that can be modified to improve this situation. A great deal of research activity within the areas of materials science and ceramic processing science is thus directed toward the understanding of these problems. Concurrently, there is considerable activity among the design engineers in developing techniques for the use of brittle materials, particularly in areas where the performance requirements can only be fulfilled by the unique properties of ceramic materials.

Nature of Ceramic Materials

A certain amount of orientation as to the nature of ceramic materials may be useful. The term ceramics was first applied to clay-based products which included pottery, dinnerware, sanitaryware, porcelain, wall tile, fireclay refractories, and structural clay products. In the United States, glass and porcelain enamels were also included. Since silica is a common ingredient in these products, these industries were frequently referred to as the silicate industries. The latter classification, however, is no longer used synonymously with ceramics as a whole because of the development of non-silicate products such as magnesia and alumina refractories, and the so-called industrial ceramics which include oxides in general, carbides, borides and nitrides. The basic unifying characteristic of all these products is that they are non-metallic and inorganic in nature. All non-metallic inorganic processed materials, thus, come under the heading of ceramic materials, and the indicated changes in the nature of the products with time are a reflection of the progress of ceramic science and ceramic technology.

A further orientation as to the nature of ceramics (non-metallic inorganic materials) in relation to metals (metallic materials) and polymers (organic materials) is illustrated in Fig. 1. In general, the principal and most differentiating feature, since it is fundamental, between the materials is the type of chemical bonding or electronic structure: ceramics are primarily ionic-covalent with a complete range of relative amounts, polymers are covalent, and metals are metallic by definition. Ceramics and polymers are thus primarily composed of compounds that are either crystalline or amorphous/glassy depending on the amount and nature of covalent bonding. Polymers are thus essentially always amorphous and metals, crystalline. Ceramics can be crystalline or glassy.



XBL 6912-6706

Figure 1

Materials are also classified or discussed on the basis of properties: mechanical, optical, and electrical-magnetic. Since all properties are dependent on the atomic and electronic structures of the materials, it is logical that materials could be classified in this way at least in a general way. Thus, ceramic materials have differentiating characteristics of high electrical resistivity, high dielectric strength at high voltages, chemical inertness, optical transparency, hardness and poor ductility.

From the viewpoint of engineering materials, mechanical properties are always of prime interest. This is the case with respect to the oxide types of ceramic materials despite their brittleness because of their high strength/density and modulus of elasticity/density ratios, hardness, and because of their oxidation resistance at elevated temperatures. In this discussion, then, primary attention will be directed to the problems and approaches associated with the understanding and development of desired mechanical properties and behavior characteristics for ceramic oxide materials.

Nature of Brittleness

The principal difficulties in the engineering or mechanical use of ceramic materials are normally associated with their brittleness characteristic. It thus becomes desirable to explore this phenomenon as to its nature and the difficulties generated by its existence.

One way to define "brittle" is to say that it means "nonductile." The extreme case of a brittle material then is one that is completely elastic, or shows complete absence of plastic strain, on loading and fracture. Its stress-strain diagram consists of a straight line to failure; all the energy absorbed is recovered upon removal of the load, if failure has not occurred. No permanent set of the material is possible; there is then no change in shape on fracture.

On the basis of this description, brittleness in itself is not bad. Theoretically, the ultimate tensile stress should coincide with the value required to pull the atoms apart. Such extremely high values, however, are not attained in load tests. The reason is that on loading, the presence of flaws or irregularities in a brittle material, i.e. in the absence of plastic deformation, permits high stress concentrations to develop at these sites without any alleviation. Tensile stresses under these conditions result in the nucleation and propagation of a crack, or just propagation if the flaw is already a crack, in a catastrophic manner when the stress exceeds the critical value according to the Griffith relationship.

This behavior in itself also is not bad. If the "flaws" were reliably uniform in size, shape and distribution, the stress at fracture would be constant and the designer could use this value as a limit with confidence. The difficulty is that the flaws are not uniform within a specimen and from specimen to specimen. This leads to scatter of data, and consequently, lack of reliability.

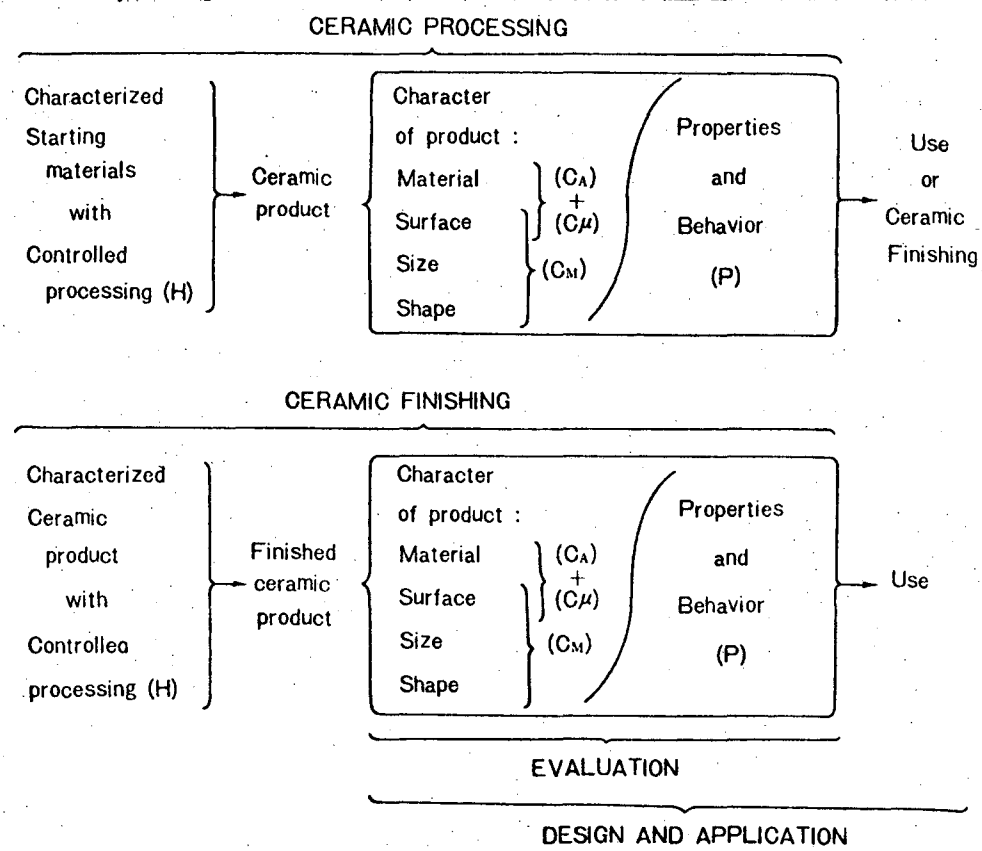
Presence of ductility in metals assists in the dissipation of energy at points of stress concentration by localized plastic deformation. Even though some ceramic materials, like MgO, exhibit some dislocation motion they are handicapped since the necessary five independent slip systems for general ductile deformation are not readily available because of a large difference in the yield stresses for different slip systems, particularly at normal temperatures. Also, additional difficulties arise because of intersection problems of slip planes. Such interactions of slip systems in many cases are bad in that they lead to the nucleation of cracks with subsequent propagation leading to fracture.

A simple conclusion can then be drawn that, in general, the best situations would exist when either good ductility or no ductility was present. Research studies toward the improvement of strength are concerned with the correlation of character features or parameters with mechanical behavior. They should, however, be more than just a statistical cataloging; the reasons or mechanisms should also be understood so that logical procedures could be followed toward the improvement of properties. The objectives, either knowingly or unknowingly, in the case of realizing high strength would be to control character parameters that play a role in the nucleation of a crack and, in the case of realizing ductility, that permit the buildup of sufficient stress to realize plastic flow without the nucleation of a crack. Characterization of materials is thus imperative.

Characterization

The systems approach as indicated in Fig. 2 indicates the logical sequence of processing the starting material to form a material with a given character which determines its properties which, in turn, determine the material's use and application. A fundamental treatment involves the coupling of adjacent factors, e.g. properties from an ideal viewpoint should not be correlated with processing parameters but with the character of the material. Likewise, processing should be correlated with the character of the produced material and not with its property directly. The character of the material is then the heart of the systems approach, and also of materials science and ceramic processing science.

The complete characterization of a material involves a description of the atomic and micro characteristics of the bulk and of the surface, and of the macro characteristics of size and shape ($C_T = C_A + C_\mu + C_M$). Ideally, it should be possible to quantitatively correlate or evaluate the critical features of character with a specific property or behavior (P). In current practice, however, these capabilities are inadequate and incomplete. Consequently, properties have been used as an additional means of characterization. It has thus been suggested that an interim use be made of the term Description and of the formula $D = f[xC_T] + f[(1-x)(P + H)]$ in order to keep the need for characterization in focus. The term (H) for history of the processing is included only when the known features of character and known properties are insufficient to completely describe a material for purposes of reproduction. Ideally, properties also would not be included as part of the Description if they could be correlated with known features of the character. It thus becomes evident that, as our knowledge of character and our ability to quantitatively correlate character with properties increases, x in the formula will approach one and the need for the term Description will disappear.



Description ≡ D = $\times C_T +$ $(1-x)(P+H)$ $C_T = C_A + C^{\mu} + C_M$

Figure 2 XBL 711-141

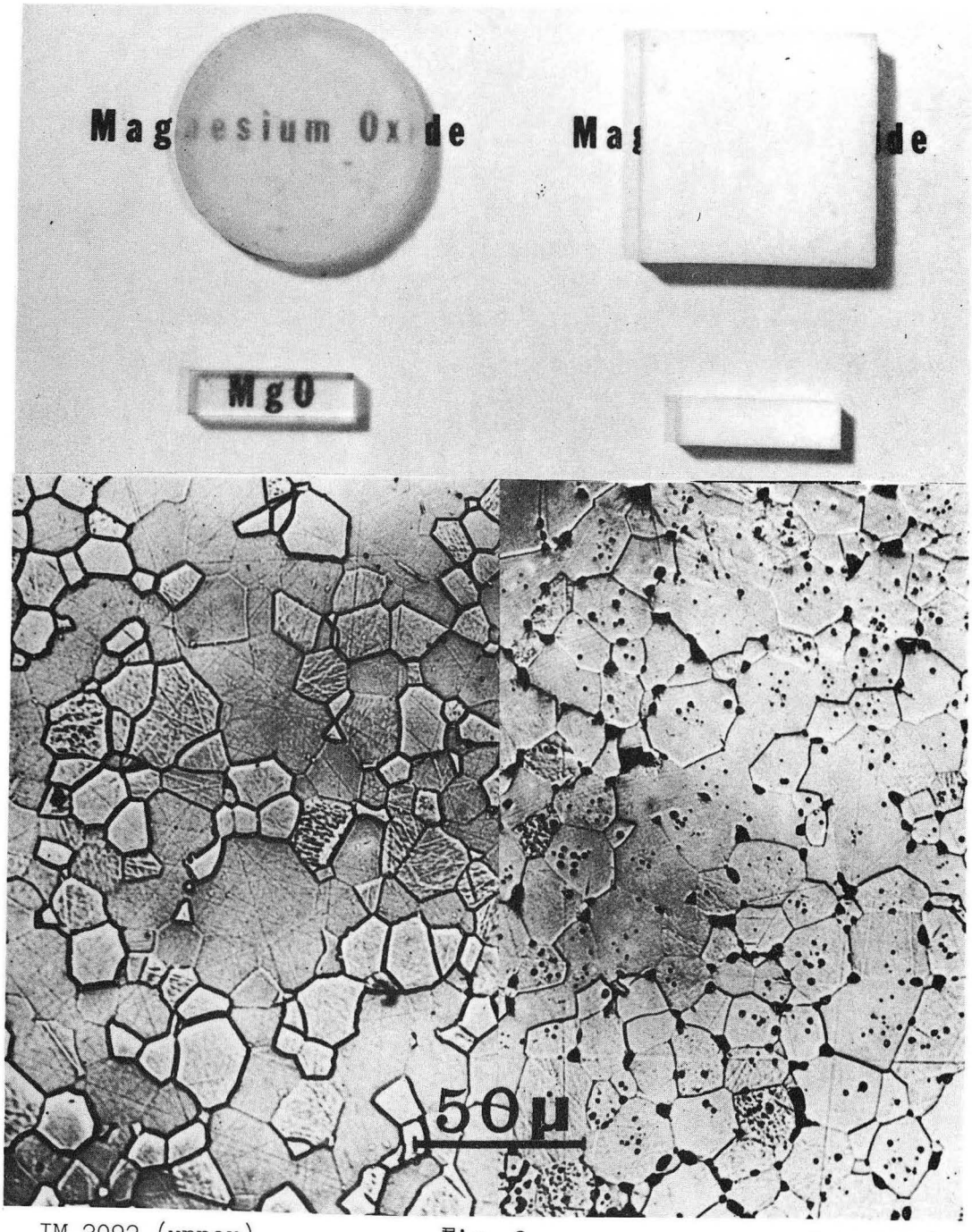
Correlation of Character with Properties

Several microstructures of polycrystalline magnesia, both in the range of 99.9+% MgO, are shown in Fig. 3. The one on the left is completely transparent (the hazy appearance of the disk is due to a lack of a surface polish); its microstructure is pore-free and similar in appearance to that of an overetched polished section of a metal. The one on the right is macroscopically opaque because of the presence of pores; otherwise the microstructures appear to be similar. Unfortunately, with today's technology, the presence of pores is typical for most single phase oxide ceramics; the specific gravity or density of these ceramics is then in the range of about 95 to 99% of the theoretical density. There is now considerable processing research in progress and, as can be seen, microstructures are being dramatically improved. Good progress is being made in developing processing procedures for obtaining theoretically dense polycrystalline alumina (Al_2O_3) which is already commercially available, and spinel ($MgAl_2O_4$). The former is slightly translucent because sapphire is crystallographically anisotropic, and the latter is transparent because of its cubic or isotropic structure just like magnesia.

From a mechanical behavior viewpoint, however, the nature of the pore structure is important as well as the volume fraction of pores. This opinion is based on mechanical behavior studies at elevated temperatures. Figure 4 shows compression stress-strain curves at 1000°C for six types of polycrystalline MgO. Type 1 is the transparent theoretically dense specimen shown in Fig. 3, and type 2 is the opaque specimen. Types 2 to 5 had a density of about 98.5% of theoretical or about 1.5% porosity, but showed variations in the average pore size and distribution. It can be seen that types 1 to 3 fractured with little significant plastic deformation at stresses in the range of 29,000 to 45,000 psi, but types 4 to 6 deformed to strains >0.02 before fracturing at stresses greater than 45,000 psi. All types were ductile with strains in excess of 0.02 at 1200°C.

The marked differences in behavior between types 2 to 6 of similar density, and the relatively poor performance of type 1, indicate that the character features influencing the stress-strain relations in polycrystals are fairly complex. Careful examinations of microstructures of the opaque types have indicated that the overall pore structures varied as to population of pores, location of pores, and relative sizes of pores and grains. Correlations with the indicated mechanical behavior shows that for some ductility to be realized below 1200°C the grain boundaries should be relatively pore-free and, if boundary pores exist, they should be small with respect to the grain size. Presence of very fine pores distributed within the grains appears to be beneficial, probably because they permit some mass accommodation when limited slip occurs.

These deductions, however, were not satisfactory in explaining the behavior of the types 1 and 3 specimens. Analysis of the type 1 specimen indicated a LiF content of about 75 ppm. Although electron microscopy showed that no second phase existed at the grain boundaries, the occurrence of much intergranular fracture at low temperatures (as seen in the left photograph of Fig. 5) in comparison with intragranular fracture for the other types (as shown in the right photograph), suggested that the LiF was probably preferentially segregated at the boundaries in solid solution and thus weakened the boundaries.



IM 2092 (upper) Fig. 3 IM 2379 (lower)

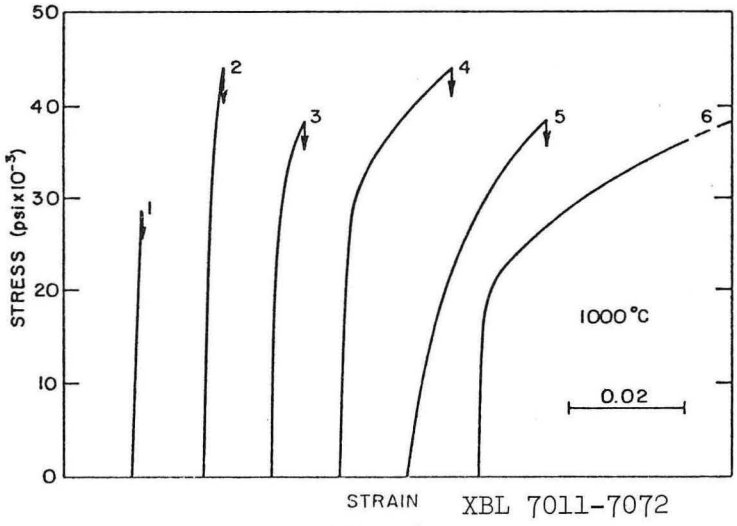


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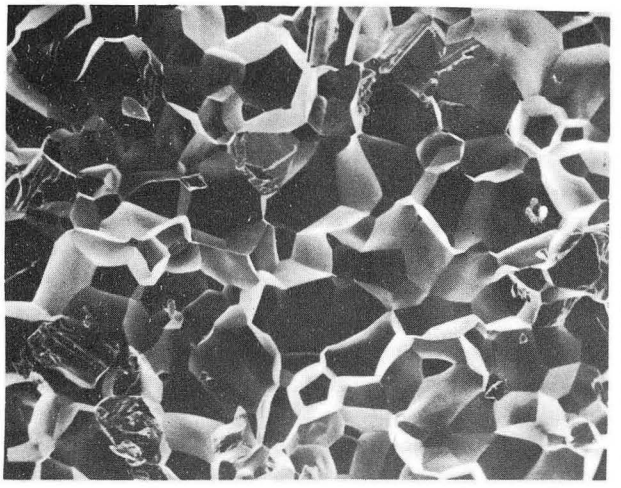
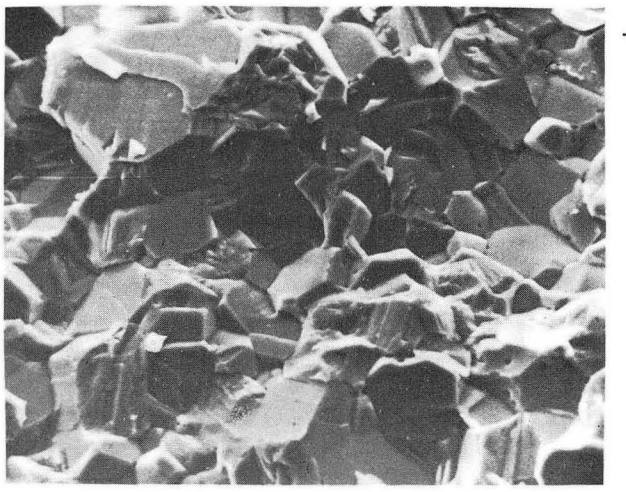
Fig. 4





XBB 688-4706 Figure 5 XBB 688-4710

Also, type 3 did not show as much ductility as was expected from its pore structure. A spectroscopic analysis indicated a larger amount of SiO_2 and CaO which was primarily segregated along grain boundaries in solid solution. It was concluded that these impurities did not weaken the grain boundaries but that they did interfere with dislocation motion. The general conclusion relative to grain boundaries was that they should be sufficiently strong to allow the build-up of stress concentrations to realize slip on the necessary five independent slip systems and to permit extension of slip bands across grain boundaries.

Sufficient reports have appeared in literature to support the correlations that strength at normal temperatures increases with decrease in porosity and decrease in grain size. Systematic experimental correlations with control of other variables such as pore structure, however, are limited. Figure 6 shows data indicating an exponential increase of strength with a decrease of the volume fracture of pores for polycrystalline alumina. A general explanation for these relationships is based on the concept that grain boundaries are favored sights for crack nucleation; the grain size then approximately represents the potential microcrack length. The chemical and physical nature of the grain boundary determines the stress level at which it becomes a microcrack. The type of impurity determines its relative concentration at the grain boundary and in the bulk. The presence of sufficient amounts of impurities to form an identifiable phase in the grain boundary region results in a different material whose property/behavior characteristics will be different, particularly at higher temperatures where the second phase may behave as a liquid. Mechanical properties are then generally adversely affected in the sense of becoming weaker. At lower temperatures when the second phase may behave as a rigid glass, the material becomes stronger but less ductile.

Correlations of creep behavior at elevated temperatures with character features have been even less documented. Most of the studies that have been reported have been concerned with understanding the nature of the mechanisms for creep. The same situation generally applies to mechanical shock.

As indicated earlier, complete characterization should include the surface, especially for ceramic materials because of their brittle nature and because the shaping of ceramic pieces involves the use of grinding methods. The difficulties here are associated with the fact that microcracks can be easily introduced into the surface which then are readily propagated under tensile stresses. The problem then is one of realizing a surface character that is resistant to the introduction of damage during the finishing process.

At this point it becomes of interest to discuss the current objectives that are being followed in character development of single phase oxides to realize maximum mechanical capabilities. On the basis of current publications and statements, the desired character appears to be one of extremely fine grain size and free of pores; a requirement for strong grain boundaries, however, should be included. This type of character should lead to maximum strength at low temperatures whether there is limited plastic deformation or none. The present indications are that metal-like ductility will not be realized at low temperatures for polycrystalline ceramic materials because of the lack of a sufficient number of active or mobile mechanisms at the stress levels that could normally be attained before the nucleation and/or propagation of a crack. It should be added, however, that the single crystal deformation studies of materials such as MgO have been necessary for the understanding of the behavior of materials, e.g. the limited movement of dislocations in polycrystals is a principal mechanism for the nucleation of microcracks. Because of this brittle behavior, one additional feature should be included, and emphasized, with the above specified character objective. This is that there should be complete uniformity and reproducibility of the character, whatever it may be, at the microscopic level without any occasional or unusual flaws or defects. The effect of the uniform and uniformly distributed flaws is incorporated into the measured property value of the material that the designer can work with; the occasional irregular large flaws or variations are detrimental in that they are responsible for the scatter of data generally exhibited by brittle materials. The latter could generally be avoided by good engineering practice in processing.

At temperatures above about half the melting point, when diffusion processes become active, many ceramic materials become ductile. Some of the character features that play a significant role in realizing good ductility have already been discussed. A great deal of work is necessary to evaluate these and other factors more extensively and quantitatively. It should again be pointed out that the desired optimum behavior of a material of a given composition under given conditions is dependent upon some specific character, and that this character will generally have to be different for that composition under some other conditions, e.g. grain size, density.

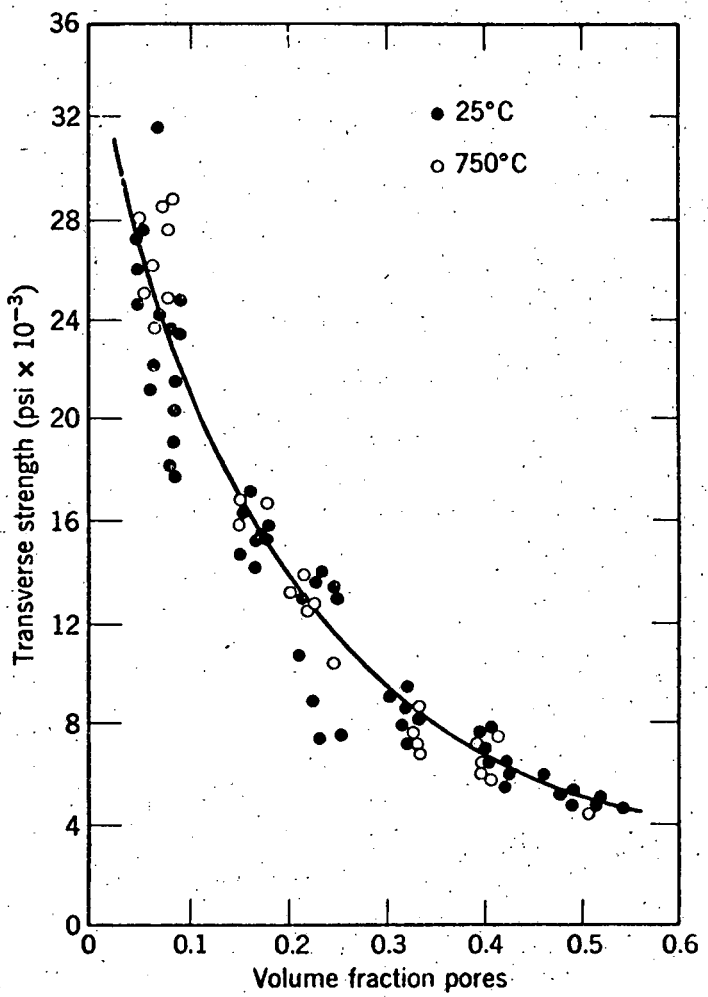


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Figure 6

In any case, the most important factors are uniformity and reproducibility in order to realize reliability. We are thus dependent on a science of ceramic processing and good engineering practice to realize this objective and also to be able to develop and produce some desired character presently unattainable or economically unfeasible.

Selection of Ceramic Materials

The potential list of compounds that could serve as the basis of ceramic materials for engineering applications includes oxides, borides, carbides, nitrides, silicides and sulfides. The cost factor in their development and production still limits most of them to the laboratory level. Some of them have very specific properties which make their use mandatory in certain applications and tend to justify or counteract the cost factor. As an example, boron carbide is the hardest man-made material next to diamond; it is harder than α-Al_2O_3, the hardest easily available ceramic material. The need for such hardness would justify its cost. Another illustration is related to strength at very high temperatures. Borides, carbides and nitrides exhibit much higher strengths than oxides at temperatures above about 1300°C, some having good strengths up to about 2500°C, but their use at these temperatures is restricted to a reducing atmosphere or vacuum because of poor oxidation resistance.

From an engineering viewpoint the oxides have thus been of greater interest because of their oxidation resistance, and availability. The common oxides that comprise the industrial ceramic group are alumina, beryllia, magnesia, spinel, zirconia, zircon, thoria; of these, alumina is used most extensively. Its growing production volume and expanding use as an engineering material have created a need for standardization, and the industry is moving in this direction. The rest of this discussion will therefore be based primarily on references to this material for examples.

Technically, high alumina ceramics have become the principal industrial ceramic materials because they as a class have characteristics of hardness, dimension stability and strength at elevated temperatures, virtual chemical inertness, oxidation resistance up to their melting point, and high electrical resistivity. They are also more readily available, and more attractive economically.

High alumina ceramics are specified on the basis of their alumina content, ranging from about 80% to 99.9%. Most manufacturers will have at least four types having about 85, 90, 95 and 99.5% Al_2O_3. Other compositions are also available that have been made with specific characteristics for special applications. The densities are generally in the range of 96 to 99% of the theoretical density, but it is expected that as our basic knowledge or processing techniques improve theoretical densities will be achieved more extensively with corresponding improvements in properties. The balance of the composition is made up of fluxes, commonly SiO_2, CaO, and MgO, which are added to improve fabrication and firing characteristics;

to control the size of, and to bond, crystals; and to develop specific properties. These fluxes are not specified and vary among the manufacturers. The strength and other properties generally improve with increase of Al_2O_3 content and density, and decrease of grain size. The processing costs also show a parallel increase, and thus economic factors play a role in the selection of a material.

The compressive strengths are reported to have a range of 280,000 to 400,000 psi with increase of Al_2O_3; and the tensile strengths, 22,500 to about 40,000 psi (roughly about 1/10 of the compressive strength). The compressive strengths at 1000°C range from 1/5 to 1/2 of the corresponding compressive strengths at normal temperatures depending on the amount of added fluxes. These strengths should certainly be adequate for many structural applications, but there are actually very few such applications, if any. The engineering designer always has that concern about a potential failure due to a statistically low value which is a deterrent to the use of the ceramic material. On the other hand, since these materials may be susceptible even to one critical flaw under tensile stress conditions because of their brittle nature, suppliers are reluctant to set a lower safe limit which is necessary for structural applications. If a sufficiently strong material were to be developed so that a safe lower limit of strength could be set, the field of structural applications would be opened up.

Most applications of ceramics are thus based primarily on the utilization of their favorable properties, and strength, although it may be important and critical, becomes secondary, e.g. panels or windows. A review of some applications will illustrate the use of favorable properties.

If a ceramic is to be used as a structural component or is to be exposed to mechanical stresses, the design should be such so that these stresses are compressive since flaws under such conditions are not critical and the high strength of the ceramic can be realized. An example of a design is shrink fitting a metal adapter over a piece of ceramic. A more dramatic example currently under study is the thin-wall hollow sphere designed to be used as a deep-water submersible.

Many applications of alumina materials are based on their hardness and wear resistance. High-alumina grinding media and lining brick have been used for years in ball and pebble mills. Shaft seal rings are common in automobile engines and home appliance water pumps. High-alumina plungers are used in reciprocating pumps for corrosive and abrasive liquids at pressures to 3,000 psi. High-alumina tool bits are now becoming common. Wire drawing has been improved by the use of alumina drawing capstans.

Air bearings for navigational gyroscopes have been made of high aluminas because the material has the required mechanical strength, dimensional stability, and electrical insulation properties, in addition to being lighter than most other materials considered.

Alumina materials have high electrical resistivity, high dielectric strength, and low dielectric energy losses. This enables them to be used as bases for thick and thin-film circuits, hybrid microelectronic circuits, integrated circuits, and various semiconductor devices. The hardness of the material allows the attainment of the needed extremely flat surfaces by mechanical polishing.

The non-galling characteristic of ceramic against ceramic, plus its strength and dimensional stability, are utilized in journal bearings for high temperature service. The additional resistance to oxidation or corrosion makes its use as a precision valve under severe conditions possible.

The refractoriness of alumina ceramics allows their use at high temperatures as furnace tubes and thermocouple sheaths. They have also been used to make nose cones because of their RF transparency, density, and rain-erosion resistance.

In summarizing this discussion on selection of materials, the efforts of the industry to standardize alumina materials on the basis of alumina content should be encouraged, but it should be emphasized that other features of the character will in time have to be included. Materials with equivalent alumina contents from different producers are not equivalent in property values. This situation is another indication of the sensitivity of the properties to the character of the material; it also indicates the sensitivity of the character to the processing procedures and controls. Selections of material thus should be based on descriptions that include required properties as well as compositions; in some cases the description should also include the history of the material, although highly unscientific, on the basis that a certain treatment introduces some unknown but critical character feature. This state of affairs is even more true for other ceramic materials that are produced in smaller quantities.

Lastly, uniformity and reproducibility in production is reflected in the absence of the irregular flaws that are responsible for the scatter of data. Achievement of this performance on the part of the producer is based on a foundation of a science of ceramic processing and good engineering practice. The reliability and confidence in a given producer that results is certainly a major factor that plays a role in the selection of a specific material.

This work was done under the auspices of the United States Atomic Energy Commission.

FIGURE CAPTIONS

Figure 1. Classification of man-made materials into three broad groups on the basis of the nature of bonding, formation of compounds, and crystallinity.

Figure 2. The progressive sequence of a ceramic material from its production to its final use or application; ceramic finishing involves subsequent treatments such as grinding. The function of evaluation is within the field of Materials Science; design and application, Materials Engineering; and ceramic processing, Ceramic Engineering.

Figure 3. Transparent polycrystalline MgO produced by hot pressing and subsequent annealing, and opaque polycrystalline MgO produced by sintering. The corresponding microstructures as obtained from polished cross-sections are shown below the respective specimens.

Figure 4. Stress-strain curves for six types of polycrystalline MgO at 1000°C obtained in compression under a constant rate of loading of 20 psi/sec, based on the initial specimen cross-section.

Figure 5. Scanning electron photomicrographs of fracture surfaces of specimens broken at room temperature. The one on the left (approximately 250X) corresponds to the transparent specimen of Fig. 3; the one on the right (approximately 500X), to the opaque specimen of Fig. 3.

Figure 6. The effect of porosity on transverse strength of alumina at 25°C and 750°C.

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