SCIENCE

Ceramics Today

Ceramics made from pure substances may be controlled to have a variety of useful properties.

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Ceramics today is much changed from the ceramics of 20 years ago. Over this period the ancient art that produced mostly pottery and building materials has been transformed into a sciencebased branch of materials engineering. Today ceramics have precisely controlled properties and critically important functions in many modern technological devices.

A wide variety of nonmetallic inorganic substances are now called ceramics. Some of them, such as uranium dioxide, beryllium oxide, the magnetic iron oxides, and the piezoelectric titanates and zirconates were little used 20 years ago. Others, such as aluminum oxide, zirconium oxide, and many glasses, have been so improved in purity, composition, or structure that they may be considered to be new materials for technology. In all cases, they possess unique combinations of properties that have led to important uses, for example, in production of nuclear energy, in electronics, high-temperature devices, new sources of light, and new electrochemical devices. An improved understanding of behavior also improves the ability to fabricate ceramics, at a reasonable cost, into desired shapes, to regulate the manufacturing process so that it will yield a product with narrowly controlled properties, and to predict behavior of the product during use. To be able to do these things for a variety of nonmetallic inorganic substances is the goal of ceramics today. This requires the ability to control not only the chemical composition of the product but also its 20 SEPTEMBER 1968

structure on an atomic and microscopic scale, and an understanding of the relation between structure and properties so that desired structures can be specified.

For silicate ceramics, such as porcelain or refractories, there is a guiding background lore extending into prehistory and scientific information that goes back at least 50 years to aid in processing. No such background existed for the newer materials; hence it had to be developed, partly empirically, but to a great extent by investigating the physics and chemistry pertinent to the behavior of these materials, and by using the knowledge obtained to guide the development of processing, to control properties, and to predict behavior. The accumulation of such knowledge is continuing at the present time, and quite a broad understanding of the behavior of ceramic materials now exists. The intent of this article is to give some typical examples of important new ceramic materials, of the kind of understanding that has been obtained, and of the ability to control the properties of these materials.

Relation to Physical Metallurgy

The development of ceramic science has drawn heavily on physical metallurgy not only for techniques and directly transferred information but also for guidance in understanding the factors that control the combinations of properties in ceramics which differ from those in metals. The fundamental rationale of both fields is that many important properties can be varied over wide limits by altering the chemical composition in order to control the structure on an atomic scale and by regulating the thermal and mechanical processing to control the microstructure. The parallels are much closer in crystalline ceramics than they are in glasses, but even in glasses many concepts can be carried over. Two examples will be given to illustrate the close relation; others will be implied later in this article.

Both crystalline ceramics and metals, in their commonly used forms, are polycrystalline aggregates. Many properties, but especially strength, are related to the size and shape of the crystalline grains. At elevated temperatures the grains grow, and the change in the size of the grains can be followed by microscopic measurement on polished and etched surfaces. Figure 1 shows the similarity in microstructure of polycrystalline yttrium oxide and a single phase metal, alpha iron. In both cases the configuration of grain boundaries is that of a foam, because grain boundaries have a surface tension (of the order of 500 dynes per centimeter) exactly as foam cell walls do, and their configuration is a consequence of the local balancing of the surface tension forces of these boundaries. In both metals and nonmetals the average size of the grains increases upon heating at temperatures at which there is sufficient atomic mobility. The driving force for crystal growth is provided by the surface tension of the boundaries. As shown in Fig. 2, the growth laws are similar in metals and ceramics, and much of the current understanding of grain growth in ceramics stems directly from the earlier work on metals.

It is more difficult to find good parallels between physical metallurgy and the science of glass. Perhaps the best are found in the monumental work of Griffith on the stress necessary for propagation of a crack in brittle ma-

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Fig. 1. Grain structure of polycrystalline (a) yttrium oxide ceramic (15) and (b) alpha iron. Since similar surface tension forces operate, both materials have grain boundary configurations similar to that of a foam (\times 500).

terials, particularly glass—a reverse contribution that has been studied extensively by metallurgists. In 1921, Griffith deduced, and demonstrated in glass, that the minimum stress, S, necessary for the propagation of a sharp crack in a brittle solid is

$$S = \left(\frac{4\gamma E}{\pi l}\right)^{\frac{1}{2}}$$

where γ is the surface energy of the newly formed surface; *E*, Young's modulus of elasticity; and *l*, the length of the crack. This relationship has long provided one of the limiting conditions for fracture in metals, which are usually more ductile than glass, absorb more energy than is required to produce the new surfaces, and hence require somewhat higher stresses for crack propagation.

Important Uses of Ceramics

A brief discussion of a few of the modern technological uses of ceramics will illustrate their importance and some of the practical combinations of properties.

Uranium dioxide, in the form of sintered cylinders about 0.5 inch (1.25 centimeters) in diameter and 1 inch long, contained in tubes of a zirconium alloy is almost the exclusive fuel for producing power in nuclear reactors. It combines a melting point of 2400°C and inertness toward superheated water or steam with reasonably high thermal conductivity and, of course, an acceptable concentration of uranium. About

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300 pounds (135 kilograms) of UO_2 enriched to about 3 percent of uranium-235 is required for each megawatt of reactor power and this must be replaced every 3 years. There is currently being built, or on order, some 50,000 megawatts of reactor capacity, so the market for this ceramic is large and is growing rapidly.

A major current problem with UO_2 is that of predicting its behavior under the conditions of use in a reactor. Several percent of the atoms in the ceramic will undergo fission during the life of the fuel element, giving rise to fission products, an appreciable fraction of which are krypton and xenon. These inert gases can separate into pores at the high temperatures of operation. The pores may migrate, under the extreme temperature gradients that exist (Fig. 3), to coalesce and cause swelling or to release the fission gas directly. A complete prediction of behavior involves knowledge of the mechanisms of migration and release of fission gases, and a knowledge of the deformation mechanisms of UO_2 . All of these are active current areas of investigation (1).

The magnetic oxides, particularly the ferrites, have been the subject of a tremendous amount of work since World War II, and their magnetic behavior is now understood better than is ferromagnetism in metals. The fact that they are ferromagnetic and are also electrical insulators (with the result that no eddy currents flow when the direction of magnetization is reversed) makes them most serviceable for use at high frequencies, because the direction of magnetization can be reversed in short times.

Development of the fundamental understanding of ferromagnetism in these substances is, of course, in the realm of physics. As Smit and Wijn (2) point out, however, "many of the properties of the ferrites are strongly dependent upon their exact chemical composition and microscopic physical structure. These factors in turn are determined by the method of preparation." The



Fig. 2. Grain growth in alpha brass and in ThO₂-doped Y_2O_3 ceramic (15). Note that in spite of a difference in size of grain and in temperature, the growth laws are similar.

same general principles of the control of composition and structure that apply to other ceramics also apply to ferrites —to control their properties intelligently, it is necessary to understand the influence that composition and structure have on properties, and it is also necessary to be able to control processing in order to produce the desired composition and structure.

An important application of ferrites is their use in computer memories, which contain an array of as many as a million small ferrite rings, each of which can be magnetized in a positive or negative direction to store one bit of information. The magnetic properties, that is, the shape of the hysteresis loop for these tiny toroids, must be controlled with extreme precision. At the present time, the diameter of the toroids has been reduced to about 0.5 millimeters, the cycle time to store or retrieve one bit of information to less than 0.5 microsecond, and the cost to about 10 cents each.

High-strength glass filaments are used increasingly in polymer-bonded composites with a very high ratio of strength to weight. The filaments are strong because glass does not flow plastically at room temperature, and because they have very smooth surfaces and no stressraising notches that can initiate fracture. The smooth surface is produced by surface tension forces when the fiber is drawn from molten glass, and it is preserved by the protective coating of polymer, which also serves to bond the fibers together. Even the most microscopic roughening will drastically reduce the strength of the individual fiber.

A quick calculation with the Griffith equation displays the tremendous importance of surface perfection. Assuming a Young's modulus of 10 million pounds per square inch $(7 \times 10^{11} \text{ dyne})$ cm²), a crack depth of 5 Å, and a glass surface energy of 2000 ergs per square centimeter, one computes a fracture stress of about 2.3 million pounds per square inch, in reasonable agreement with the maximum of 2 million pounds per square inch which has been observed experimentally. If the crack is at the limit of microscope resolution (a depth of about 1 micron) the fracture stress computed on the same basis is only about 50,000 pounds per square inch-still several times the commonly observed strength of bulk glass, but only 2.5 percent of the maximum observed. The use of composite materials also offers the further advantage that 20 SEPTEMBER 1968



Fig. 3. Pores in UO₂ ceramic exposed to steep temperature gradient migrate up the temperature gradient to the top and "drag" columnar grains behind them. [Photomicrograph courtesy Dennis M. Rooney; \times 200]

the total load-bearing capacity of the member is reduced only to a very small extent by the accidental fracture of a few fibers, because the concentration of local stress is distributed to adjoining fibers through the bonding resin with a lower modulus (3).

It is convenient to point out two additional facts here. First, glass fibers are among the strongest engineering materials available. Strengths up to 500,000 pounds per square inch are readily obtained in undamaged com-



Fig. 4. Fused silica rod about 1 millimeter in diameter, bent elastically to a 12-millimeter radius of curvature. Stress in surface fibers is about 500,000 pounds per square inch (4).

mercial fibers. Similar strengths have been obtained in metals only in dislocation-free "whiskers," because in bulk metals plastic deformation occurs by dislocation movement. Dislocations cannot exist in the aperiodic structure of a glass, hence no plastic deformation can occur by dislocation movement, and independent evidence indicates that no other mechanisms of plastic flow operate either. Second, these high strengths are not confined to filaments with small diameters. The only requirement is that the glass surface be almost atomically smooth. Figure 4 shows a fused silica rod, with a diameter of about 1 millimeter, bent elastically to such a radius that the tensile stress in the outer layer of the convex surface is about 500,000 pounds per square inch-an elastic strain of about 5 percent. Hillig (4) has observed strengths up to 2 million pounds per square inch in such rods.

The final example of technological use involves the combination of optical transparency with a high melting point, chemical inertness, and moderate strength at high temperatures. Most ceramics are intrinsically transparent, but are opaque because the included pores scatter light. A greatly improved understanding of the mechanism of sintering, set forth below, led to techniques for producing pore-free polycrystalline ceramics, particularly aluminum oxide, which would transmit over 90 percent of the incident light. The high melting point and chemical inertness of this pore-free polycrystalline alumina permitted the invention of a new class of high-intensity sodium-vapor lamp that used an Al₂O₃ envelope in place of more conventional glass (Fig. 5). This lamp has a continuous spectrum and a luminous efficiency of about 110 lumens per watt, compared with about 17 for an incandescent lamp and perhaps 75 for the quite different fluorescent lamp (5).

Atomic Transport in Ceramics

A remarkable number of important and interesting phenomena in ceramics involve the movement of atoms, or more usually ions, from one site to another, under the driving force of a concentration or temperature gradient, a mechanical stress, or an electric field, The rates of such important but diverse phenomena as sintering, grain growth, formation of new phases, dielectric loss in glass, ionic conductivity, metal oxi-



Fig. 5. High-intensity sodium-vapor lamp with inner envelope of pore-free polycrystalline aluminum oxide.

dation, high-temperature creep, and the swelling of nuclear fuels are controlled by the transport of matter. The study of transport phenomena has engaged the attention of a number of ceramists over the past few years; the understanding of mechanisms and the measurement of quantitative values now constitute important parts of the field of ceramic science. There have, of course, been important investigations in other areas: thermal and electronic conductivity, plastic deformation and dislocation movement, vaporization processes, static fatigue in glass, determination of large numbers of phase diagrams, and the collection of other thermodynamic data of importance in processing and in predicting behavior during use. I shall not discuss these further, in order to permit a more detailed discussion of the phenomena associated with atomic transport, together with some indication of their technological impact.

Solid-State Diffusion

Solid-state diffusion in metals has been known and studied for nearly 100 years. Excellent quantitative data on mechanisms and kinetics were obtained, and more recently the work has been greatly facilitated by the availability of radioactive tracers. Formally, the same theory applies in ceramics, and the same techniques of measurement are applicable; but there are major differences. In metals, at least in most substitutional solid solutions, only one crystallographic lattice is involved in atom movement. In ceramics, two different species of ions diffuse, often at greatly different rates, although the necessity for local electrical neutrality in the system usually requires that the diffusion of the two species be coupled. Experimental determination of the diffusion coefficients is difficult because no radioactive isotopes of the elements of interest (for example, aluminum,



Fig. 6. Some recent values from the literature for the diffusion coefficients observed in some simple oxides. Note particularly the marked difference in diffusion coefficients for oxygen and uranium in UO_2 .

beryllium, silicon, magnesium, and, particularly, oxygen) have suitable halflives.

In spite of these difficulties, there has been developed, over the past 10 to 15 vears, a considerable body of knowledge about the diffusion rates of important elements through various compounds of interest. Investigations have delineated not only the self-diffusion rates in nearly perfect crystals but also the effects of temperature, deviations from stoichiometry, grain boundaries, and foreign ions. Some important values are shown in Fig. 6. The scatter in the reported results for BeO indicate that there is still an opportunity for greatly improved accuracy in the determinations.

Ionic Conductivity

The electrical conductivity associated with the ionic movement in ceramics may exceed the electronic conductivity by several orders of magnitude. The ionic conductivity (σ) may, in principle, be computed from the known diffusion coefficient (D) of the more rapidly moving ionic species by the Nernst-Einstein equation:

$$\sigma = \frac{DnZ^2e}{kT}$$

where n is the number of charge carriers per cubic centimeter; Z, their valence; e, the charge on an electron; k, the Boltzmann constant; and T, the absolute temperature. There are many ambiguities in the use of this relationship, however, with reference to the variety of structures and diffusion mechanisms available. If direct current is used, polarization will of course occur and increase the apparent resistance, unless the moving species can be applied at one electrode and be liberated at the other.

In general, diffusional transport occurs by the movement of ions into neighboring unoccupied lattice sites. In pure stoichiometric compounds the concentration of such vacancies at thermal equilibrium is exceedingly small, hence the conductivity is low. In a number of substances, however, this concentration can be increased by orders of magnitude by suitable doping or alloying.

The outstanding example is zirconium oxide alloyed with about 15 mole percent of calcium oxide (CSZ in Fig. 6). The divalent calcium ions substitute for tetravalent zirconium in the cation lattice, and charge is compensated by the

creation of vacancies in the anion lattice. The addition of calcium oxide also stabilizes the cubic phase, and in such stabilized zirconia, at 1000°C, the diffusion coefficient for oxygen is 10^{-7} square centimeter per second, corresponding to an ionic conductivity of 0.02 reciprocal ohm-centimeter. The electronic conductivity is negligible. Attempts are being made to exploit this high ionic conductivity by using stabilized zirconium dioxide ceramic as the electrolyte in various electrochemical devices.

One such device, now becoming commercially available, will determine the thermodynamic activity of oxygen in a gas. It consists of a nonporous tube of ceramic with suitable electrodes, a furnace, and potential measuring equipment (Fig. 7). The unknown gas is admitted to one side of the tube and a reference gas (for example, air at atmospheric pressure) is admitted to the other side. The potential (V) of the galvanic cell is then given by

$$V = \frac{RT}{nF} \ln P_{o_2} / P'_{o_2}$$

(where R is gas constant; F, faraday; and P, pressure), and, because of the logarithmic scale, activities of oxygen ranging over several orders of magnitude can be read.

A closely related, but not yet commercially feasible, use for stabilized zirconia is as the electrolyte in a hightemperature fuel cell. The device is schematically similar to the oxygen sensor and consists of a plate or tube of zirconia ceramic coated on each side with a porous electrode. Oxygen or air is admitted to one side of the electrolyte, is ionized there, and transported through the electrolyte to the other side as oxygen ions. Hydrogen or carbon monoxide admitted to that side combine electrochemically with the oxygen ions, and electrons return through an external circuit to give the desired electric current. A potential of about 1 volt is obtained when hydrogen is burned, and power densities of 250 watts per square foot (0.25 watt per square centimeter) of electrolyte have been obtained.

The most recent example of such devices utilizes the extraordinarily high diffusion rate of sodium ions through the substance beta alumina, Na₂O-11 Al₂O₃ (8). At 300°C, the ionic conductivity associated with the transport of sodium ions can be as high as 0.1 ohm⁻¹ cm⁻¹, which leads to a computed diffusion coefficient for sodium ions of



Fig. 7. Device for measuring the partial pressure of oxygen. It utilizes the transport of oxygen ions through the ceramic for the thermodynamic measurement (7).

about 10^{-5} , approximately as high as the observed values in liquids. Storage batteries are contemplated in which molten sodium is supplied to one side of tubes of beta alumina ceramic and molten sulfur to the other side. The overall reaction

$Na + (X)S \rightarrow NaS_x$

will produce a cell potential greater than 2 volts. The free energy released in this reaction is thus high, and both reactants are of low density. The potential is for a battery that will surpass the ratio of energy to weight of a lead-acid battery tenfold.



Fig. 8. Microstructure of typical electrical porcelain (\times 500). Untransformed particles of quartz are bonded by a glassy phase that contains a very fine dispersion of mullite crystals. [Photomicrograph by Edith Raviola]

Sintering

It was indicated at the beginning of this article that the term ceramics has been extended to include most nonmetallic inorganic materials, because most of the classical and new ceramics are prepared from powders by sintering at elevated temperatures. Although superficially similar, the reactions that accomplish the consolidation are quite different in the two classes of materials. In clays, decomposition occurs during heating and results in a glass phase that undergoes viscous flow, producing shrinkage and bonding of the residual crystals and yielding the structure shown in Fig. 8. In most of the new substances, no liquid phase forms. The transport of matter occurs solely by solid-state diffusion to produce a single solid-phase product without a bonding glass. The development of a thorough knowledge of the mechanisms of this process and an ability to control the preparation of powders and the sintering conditions in order to produce the desired structures have been and continue to be major concerns of ceramists. The basic understanding of the mechanism stems from the initial work of Kuczynski (9) on the sintering of metal powders, but the work of ceramists, starting with that of Kingery and Berg (10), has greatly extended that understanding.

Figure 9 summarizes the presently accepted concept of the process. The three circles represent three crystalline particles with point contacts. Their free surfaces toward the center define the boundaries of a pore, and the surface tension of the pore-vapor interface tends to make the pore shrink. On an atomic scale this can be accomplished by transporting matter from the grain boundaries at the points of contact to the inner surface of the pore. As a result the grain centers approach each other, the pores become smaller, the area of contact between the grains increases, and, as observed externally, the specimen shrinks. An equivalent way of stating this phenomenon is that the pores disappear to form lattice vacancies in the surrounding crystals, and that these lattice vacancies diffuse to grain boundaries where they are annihilated by the movement of grains together. Obviously, to fill up a pore with a compound AB, both species A and B must diffuse, and the rate of the sintering process should be governed by the diffusion rate of the slowermoving species.

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Fig. 9. During sintering, matter is transported by diffusion from the points of contacts between crystalline grains to the voids between grains. Grain boundaries are formed, and the centers of the particles approach each other until the pore finally disappears.

Quantitative comparison of sintering kinetics with diffusion data requires a geometrical analysis of the shrinkage process. Several such analyses have been made, and in general they predict a shrinkage law of the following form:

$$\frac{\Delta L}{L_0} = B \left(\frac{\gamma a_0^3}{kT} \quad \frac{D}{r^3} \quad t \right)^{1/2}$$

The linear fractional shrinkage $\Delta L/L_0$ is controlled by the surface tension γ of the solid-vapor surface, the diffusion coefficient for the more slowly moving species D, and the particle radius r. The other terms are a geometrical constant B (of the order of unity), the molecular volume a_0^3 , the Boltzmann constant and absolute temperature kT, and the time t.

The time necessary to produce a given fractional shrinkage is thus proportional to r^3/D . It is common to speak of a "sintering temperature" in the processing of ceramics—usually the



Fig. 10. Interaction between the pore and grain boundary. The downward migrating boundary is restrained by the pore that lies on it. The boundary may remain fixed, break away from the pore, or pull the pore along with it, depending upon detailed circumstances.

temperature at which a given specimen will densify to the desired value, say 95 percent of theoretical density, in firing times of 1 to 4 hours. While many factors may influence this temperature slightly, in most materials a sintering time of a few hours is found when the value of the ratio of r^3 to D is approximately 1. For a particle size of 1 micron, the required diffusion coefficient is about 10⁻¹² square centimeter per second. The diffusion coefficient varies with temperature as D = $D_0 e^{-Q \nearrow RT}$ (where D_0 is the temperature-independent part of the diffusion coefficient) and, for many common oxides, Q (activation energy) is of the order of 100 kilocalories per gram atom. Hence, at sintering temperatures in the neighborhood of 1500°C, an increase in temperature of 100°C will reduce the time for a given amount of shrinkage about fivefold. A twofold increase in particle diameter will increase the required time eightfold, however, which illustrates the tremendous importance of fine powders for rapid or low-temperature sintering.

Grain Growth

In spite of the fact that it is possible to predict the course of a reaction such as sintering under ideal circumstances, difficulties arise in practice because perfect substances and postulated behaviors are rarely dealt with. For example, a particle radius r was assigned in the equation for sintering, and the assumption was made that the particles were spheres of uniform size. In fact, most powders are composed of irregularly shaped particles with a range of sizes, often in clumps or aggregates. This variable can markedly affect the rate of sintering and the resulting structure.

Furthermore, during sintering, other simultaneous reactions may occur in addition to the transport of matter from grain boundaries to pores; for example, the grain boundaries themselves may move. This will change the microstructure by causing an increase in the average grain size, and, more importantly for sintering, may cause a separation of pores from grain boundaries. The latter effect will drastically increase the diffusion distances above those that prevailed when the pores were located on the grain boundaries and hence will increase the time for pore removal (11).

Grain growth in nonporous poly-

crystalline aggregates is well understood, particularly from studies on metals, and, as was indicated earlier, the same general laws apply to ceramics. To state it simply, the excess free energy associated with the region of disorder where two crystals of different orientation meet manifests itself as a surface tension. At temperatures that allow sufficient atomic mobility, the boundary will migrate toward its center of curvature-the concave crystal will grow, the convex one will shrink. When viewed on a sectioning plane, all sides of grains with fewer than six sides are convex. These grains thus disappear as the grain boundaries move.

Breakaway of a Pore from

a Grain Boundary

The driving force that the surface tension of grain boundaries provides for movement of these boundaries is approximately $F_{\rm b} = 2\gamma_{\rm b}/R_{\rm b}$, where $\gamma_{\rm b}$ is the surface tension of the grain boundary, and $R_{\rm b}$ its radius of curvature, approximately equal to the grain diameter. This driving force is reduced if a grain boundary intersects a pore, because the pore exerts a drag on the grain boundary, as shown in Fig. 10. The grain boundary intersects a pore of radius r_p in a circle of circumference $2\pi r_{\rm p} \cos\theta$, and the pull, $F_{\rm p}$, exerted by the pore on the boundary in the y direction is $\pi r_{\rm p} \gamma_{\rm b} \sin 2\theta$. If the maximum force, at θ equals 45°, is exerted by boundary movement, the boundary will pull away. For this to occur, the driving force movement of the grain boundary must be sufficiently high to move the boundary up to θ of 45°, and the pore velocity $v_{\rm p}$ must be sufficiently slow, relative to velocity of the grain boundary at stresses up to those when θ equals 45°, so that the pore does not just move with the boundary and prevent breakaway.

The maximum retarding force imposed by an array of pores (θ equals 45° at all pores) is $n\pi r_p \gamma_b$, where *n* is the number of pores per square centimeter of grain boundary area. If the pores are uniformly dispersed through the solid, the number per square centimeter on a plane 2 r_p thick is $3f/2\pi r_p^2$, where *f* is the volume fraction of pores in the solid. The total retarding force is hence $3f\gamma_b/2r_p$.

The two conditions that must be fulfilled for a boundary to pull away from a pore are: (i) The size of the grain



Fig. 11 (left). In the discontinuously growing large grain to the right, pores are far removed from the grain boundary and diffusion distances are long, hence little further pore shrinkage will occur upon heating longer (\times 500). Fig. 12 (right). Polycrystalline aluminum oxide in which discontinuous growth is complete. Note pores included in the grains (\times 500).

must be small enough so that the driving force for grain growth exceeds the restraint imposed by the pores:

and

$$R_{\rm b} < \frac{4r_{\rm p}}{3f}$$

 $F_{\rm b} > F_{\rm p}$ so $\frac{2\gamma}{R_{\rm b}} > \frac{3f\gamma}{2r_{\rm p}}$

a relationship first derived by Zener (12) for grain boundaries and inclusions in metals. If $R_b \equiv 4r_p/3f$, and inclusions are immobile, grain growth stops. (ii) The pore must not move along with the boundary

$v_{\rm b} > v_{\rm p}$ hence $F_{\rm b}M_{\rm b} > F_{\rm p}M_{\rm p}$

where $v_{\rm b}$ and $v_{\rm p}$ are the velocities and $M_{\rm b}$ and $M_{\rm p}$ the mobilities of a boundary and a pore. Substituting from above, then, the second condition for pullaway is

$$\frac{M}{R_{\rm b}} > \frac{3fM_{\rm p}}{4r_{\rm p}}$$

Both calculations are made for a uniform dispersion of pores. If the pores are confined to grain boundaries smaller volume fractions than those shown will produce the same retardation.

Since sintering requires the diffusional transport of matter from grain boundaries to pores, it will occur at a maximum rate when the pores lie on the boundaries. Elimination of pores will be slower, and may almost cease, if they become separated from grain boundaries by movement of the boundaries.

During the early phase of the sinter-20 SEPTEMBER 1968 ing of any specimen, the volume fraction of pores is high, little movement of grain boundaries occurs, and pores remain on these boundaries. An essential part of the sintering process is that pores disappear, so that at some stage condition (i) above is fulfilled, and even in the presence of immobile pores, grain growth will occur.

In many materials this takes the form of "discontinuous" or exaggerated grain growth. When pores that have been preventing the movement of certain grain boundaries disappear, some grains can grow. It is a geometrical consequence of the configuration of grain boundaries that the boundary curvature, and the growth force for a large grain in a fine-grained matrix, is larger than that which exists for individual grains in the fine-grained matrix. Hence, when such large grains appear they are able to grow in a solid that has a concentration of pores sufficient to prevent uniform or continuous growth of the fine grains of the matrix. Condition (i) is fulfilled for the fine grains but not for the coarse ones. The result is that at the interface between fine and coarse grains the boundary moves to consume the fine grains, along with pores at their boundaries, which yields an array of coarse grains with pores far removed from boundaries. This phenomenon is shown in Fig. 11, a nickel-zinc soft ferrite in which discontinuous grain growth has occurred.

A similar phenomenon occurs in most ceramics. Figure 12 shows a specimen of sintered aluminum oxide that has undergone such discontinuous grain growth, yielding an array of large porous grains. Several years ago it was discovered that discontinuous grain growth could be prevented in aluminum oxide by the addition of about 0.1 percent MgO in solid solution. After this discovery aluminum oxide powder could be sintered to theoretical density, with no light-scattering pores in the structure. The microstructure is very similar to that shown for Y_2O_3 in Fig. 1. The optical transmission of this material is very high, and, as was indicated earlier, it is useful as an envelope for hightemperature light-generating devices.

The role of the added MgO can probably be understood in terms of condition (ii) for the breakaway of a grain boundary from a pore. If the pores in the material are able to move at some low velocity, and if the role of MgO is to reduce the grain boundary mobility, then, condition (ii) would explain why pores would remain on the grain boundaries. The essential feature of discontinuous grain growth is the breaking away of boundaries from pores (or other second-phase inclusions), so it too would not occur.

There is little doubt that this explanation is correct. Aust and Rutter (13) have shown that small additions of solute to high-purity lead can greatly reduce the mobility of grain boundaries in zone-refined lead. Jorgensen (14) has shown that the rate of grain growth in MgO-doped Al₂O₃ is measurably less than that in pure Al₂O₃. Finally, recent studies of the behavior of nuclear fuels have focused attention on the possibility of the movement of

pores, and in a number of theoretical studies the effect of the size of the pores on their mobility has been investigated in detail. In general these studies show that the mobility of pores increases rapidly with a decrease in their size. Depending upon the mechanism postulated, the velocity is computed to be inversely proportional to the third or fourth power of the radius of the pore. Since fine pores can be obtained only with fine powders and since high mobility of pores will inhibit discontinuous grain growth, this establishes the great importance of the sizes of fine particles if high densities are sought in sintered materials.

Quite recently, Anderson and Jorgensen (15) have exploited the importance of decreasing the mobility of grain boundaries to produce pore-free yttrium oxide (Fig. 1). Pore-free aluminum oxide is not transparent because the individual grains are doubly refracting, and each grain boundary is a lightscattering interface. Yttrium oxide is cubic, and optically isotropic, so that the polycrystalline ceramic is as transparent as glass, with the additional advantage of good transmission in the infrared and a melting point of 2400°C.

Future Trends

Only a partial view of the importance of ceramics in today's technology and of the existing knowledge of the behavior of ceramic materials has been possible in this brief review. Much of the emphasis here, and by ceramists generally, has been to understand the thermodynamics, kinetics, and mechanisms of the structure-controlling reactions used for processing powders, because such understanding is necessary in order to regulate the processing. As new materials and new structures are needed, emphasis will shift to other methods-direct solidification from the melt and vapor-deposition techniques, for example. In the fabrication of products from powder, more attention will be paid to the control and characterization of the powder.

The need is for even more extreme properties-higher thermal conductivity coupled with low electrical conductivity, lower evaporation rates at high temperatures under reducing conditions, higher strengths, higher stiffness, higher electrical breakdown strength, and so forth. Some of these goals will be met by using materials that have not yet been exploited to any great extent, but many of them will be met by minor modifications of the structure and composition of materials already well known. The future progress of ceramic science will be to provide the knowledge and understanding of this class of materials which will support these developments

References and Notes

- See, for example, AIME symposium on gas bubbles in solids, J. Metals 20, 3a (1968).
 J. Smit and H. P. J. Wijn, Ferrites (Wiley, New York, 1959).

- A. Kelly, Sci. Amer. 217, 160 (Sept. 1967).
 W. B. Hillig, J. Appl. Phys. 32, 741 (1961).
 W. C. Louden and K. Schmidt, Illum. Eng. 60, 696 (1965).
- 6. W. Rhodes and R. E. Carter, J. Amer. Cer. Soc. 49, 244 (1966).
- H. S. Spacil, in preparation.
 Y. F. Yu Yao and J. T. Kummer, J. Inorg. Nuc. Chem. 29, 2453 (1967).
 G. C. Kuczynski, Trans. AIME 185, 169 (1949).
- 10. W. D. Kingery and M. Berg, J. Appl. Phys. 26. 1206 (1955).
- 11. R. L. Coble and J. E. Burke, in Progress in C. Zener and C. S. Smith, Trans. AIME 175, 15 (1949).
- 13. K. T. Aust and J. W. Rutter, in *Recovery* and *Recrystallization of Metals* [Interscience (Wiley), New York, 1963].
- 14. P. J. Jorgensen, J. Amer. Cer. Soc. 48, 207 (1965). 15. and R. C. Anderson, ibid. 50, 533
- (1967). I thank A. Holik, E. Raviola, and J. Stafford 16.
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Hydrodynamic Studies of Structure of Biological Macromolecules

Experimental and theoretical advances yield structural details of proteins, DNA, viruses, and polysomes.

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Hydrodynamic measurements have been prime sources of information on the molecular weight, size, shape, and configurational mobility of biological macromolecules. The quantities measured typically include sedimentation and translational diffusion coefficients, rotational diffusion coefficients, and intrinsic viscosities. Each such measurement gives a single number. Thus, even if all currently known or conceivable hydrodynamic techniques were brought to focus on a single protein or nucleic acid molecule, the handful of parameters thereby obtained would be grossly inadequate to determine the thousands of atomic positions in the molecule. For atomic details, only x-ray diffraction studies will suffice. However, hydrodynamic studies are extremely useful for elucidating overall, long-range aspects of biopolymer structure.

This article reviews some of the developments which have forged hydrodynamics into a sharper and stronger tool for the study of biopolymer structure. The greatest experimental advances have been made in ultracentrifugation, where improved optical systems and density-gradient techniques have enabled measurements of a precision, sensitivity, and diversity never before possible. Viscometry, long a key technique in the characterization of synthetic polymers, has been adapted to the very low shear stress situations necessary for studying DNA of high molecular weight. Methods for the study of rotational motion and relaxation, notably fluorescence depolarization and flow and electric birefringence, have provided insight into the dynamical behavior of proteins and nucleic acids.

Concurrent with the experimental advances has come a flurry of significant theoretical activity. The number of types of model structures in terms of which hydrodynamic experiments can be interpreted has expanded sub-

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