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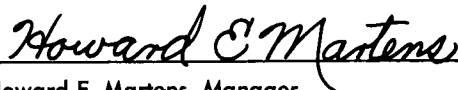
*The Effect of Grain Boundaries on Mechanical
Behavior in Polycrystalline Ceramics*

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Abstract

The importance of grain boundaries to the mechanical behavior of ceramics and the importance of mechanical strength to the overall usefulness of ceramics are discussed. The need for more direct knowledge of the nature of grain boundaries in ceramics is emphasized.

The research involved many facets, as follows: (1) direct observation of the atomic structure of grain boundaries, (2) the chemical nature of the grain boundary and the development of applicable techniques, (3) suitable techniques for production and characterization of specimens, and (4) the development of suitable mechanical test data and facilities.

Because of the premature termination of this activity, all phases of the program are essentially incomplete. However, many conclusions could be drawn and future directions indicated, although the overall interrelationships could not be determined.

The Effect of Grain Boundaries on Mechanical Behavior in Polycrystalline Ceramics

I. Introduction

Ceramic materials are used for a variety of engineering applications. These uses generally rely on the unique properties of ceramics, such as high thermal and electrical resistivity, hardness, chemical inertness, and a wide range of specific electronic and magnetic characteristics. Often substitution of other materials is totally impossible because the desired characteristics are a function of the chemical bonding in ceramics, and so cannot be simulated. In spite of this diversity of applications, the major shortcoming of ceramics appears to be brittle failure. Electrical insulators fail in service, although the failure is totally unrelated to voltage breakdown, and components often fail during installation and are therefore never even exposed to service conditions. These mechanical failures are undoubtedly the most widespread problem with real ceramic materials today.

There has been considerable research on mechanical failure in ceramics, and indeed considerable information is available. However, much of this research has been concerned with the behavior of single-crystal ceramics,

particularly with dislocation motion. Indeed, much of the single-crystal research has been justified on the basis of explaining the behavior of polycrystalline ceramics. However, when this extrapolation is attempted, considerable difficulty is encountered. Thus, dislocation behavior in single crystals is one factor in the mechanical failure of ceramics, but there are undoubtedly other unknown or unproven factors equally as significant.

The complexity of the microstructure in real ceramics is one factor which undoubtedly makes the step from single-crystal behavior to polycrystalline behavior so difficult; even so-called pure research samples of ceramics contain porosity, impurities, and other structural anomalies that complicate interpretations. These anomalies cannot be neglected in the interpretation of results since there is evidence to support the theory that they may indeed be the controlling factor (Refs. 1 and 2).

One rather obvious structural inhomogeneity in polycrystalline ceramics is, of course, the grain boundary itself. The grain boundary is known to interact with dislocations (Ref. 3). Evidence suggests that it has a strong

effect on the propagation of cracks (Ref. 1), that it is a site for the generation of apparently impurity-controlled porosity (Ref. 4), and that at higher temperatures it is the site for the principal mode of deformation in polycrystalline ceramics (Ref. 5).

The grain boundary is also critical in terms of other properties of ceramics. Diffusion at moderate temperatures is a grain-boundary-controlled process (Refs. 6-8). This diffusion, of course, is important to applications of ceramic materials, as it then controls mass and charge transport. In addition, such properties as hardness and chemical stability are related to the existence of grain boundaries, since the grain boundary generally behaves in a manner different from that of the single crystal.

In spite of the importance of the grain boundary to the mechanical behavior and almost all other observed properties of polycrystalline ceramics, practically nothing is known of its basic nature. In metals, many grain boundaries may be adequately represented by an array of dislocations, especially grain boundaries of small angles of misorientation. However, in ceramics, there is evidence to suggest (1) that the grain boundary occupies a finite volume (it is not an interface between two lattices) (Refs. 7-9), and (2) that small-angle boundaries in real materials may be nearly as complex as large-angle boundaries (Ref. 6).

Against this background it became clear that in order to understand the mechanical behavior of real polycrystalline ceramics, considerably increased knowledge of the nature and composition of the grain boundary was required. Information was needed on the atomic structure of the grain boundary, the chemical composition, the existence of vacancies and defects, and the volume in which such effects were significant. Such information, when correlated with precisely determined mechanical property data, should permit the development of a comprehensive theory for mechanical failure in ceramics. Such a theory would permit optimization of properties through control of grain boundary volume, composition, and structure.

The effort directed towards such a program at the Jet Propulsion Laboratory (JPL) was divided into three parts: (1) the generation of mechanical property data, including the production and characterization of appropriate specimens, (2) the determination of the chemical nature of the grain boundary, as it may differ from the lattice, and (3) an understanding of the structure of

the grain boundary in terms of coordination, defects, and vacancies. Because of the termination of this entire research program before completion, all phases are essentially incomplete, and certainly no comprehensive theory may be developed. However, significant portions of each phase of the activity do permit some conclusions and provide suggestions for continued work toward the desired comprehensive theory.

II. Mechanical Behavior

A. Causes of Mechanical Failure

The process of mechanical failure in a polycrystalline ceramic involves many, but, in any particular case, not necessarily all, of the following processes:

- (1) Generation of dislocations
- (2) Motion of dislocations
- (3) Pile-up of dislocations at barriers
- (4) Nucleation of cracks
- (5) Propagation of cracks
- (6) Stoppage of cracks by barriers or blunting
- (7) Repropagation of cracks to fracture

In many cases, certain of these processes are eliminated in the course of failure. For example, in materials with pre-existing flaws (as proposed to be the case in most ceramics), dislocation pile-up is not necessary to nucleate cracks, since they already pre-exist as part of the fabrication process or prior treatment. In other cases, crack impediments may not exist, and a crack may be nucleated and thereafter accelerate until a limiting velocity is reached and failure occurs immediately.

The early phases of the problem involving dislocation sources, propagation, and pile-up have been studied to varying degrees. In the case of magnesium oxide, a clear picture of the process is available. It may be summarized as follows (Ref. 3): "Fresh" dislocation sources are needed to generate dislocations within the lattice, and, although the actual difference between fresh and locked-in dislocations is not clear, the very minor mechanical action required to produce fresh dislocations assures that all real ceramic materials must contain significant numbers of them. Next, these dislocations glide at relatively low yield stresses in magnesium oxide and pile up at such barriers as grain boundaries. Such a pile-up may induce slip in the next grain, but generally it does not,

and cracks are nucleated. These then propagate immediately to failure, or until they are stopped by some barrier such as additional grain boundaries. As was stated previously, this process may be short-circuited by the existence of such cracks from fabrication procedures. It is the continuation of this series of events involving the propagation and stoppage of cracks in which it is felt that the next major effort in explaining the behavior of real ceramics need be placed, and it is in this area that the majority of this research is concentrated.

Since one very significant source of flaws in ceramics is the surface of the material, the effect of surface pretreatment has occupied considerable attention. For example, surface heat-treatment removes fresh dislocations and produces marked increases in strength (Ref. 3). However, these defects are part of the failure process in real ceramics, and a part that has not been extensively studied. Consequently, surface pretreatment in an attempt to improve the surface of the specimens was not made, in that there was no desire to remove these defects.

B. Relation of Fracture Stress to Grain Size

The behavior of cracks in materials has often been discussed in terms of the work of Griffith (Ref. 10) and later workers (Refs. 11-13). This discussion appears to be entirely valid when applied to such homogeneous materials as glasses, although attempts with polycrystals have been less successful. Using the Griffith-Orowan relationship and taking values for MgO on 100 planes, one obtains

$$\sigma_f = \left[K \frac{E \gamma}{a(1-\nu)} \cdot \frac{\rho}{C} \right]^{1/2}$$

where

K = a constant usually taken as $1/4$ or $2/\pi$

E = the modulus of elasticity (2.54×10^{12} dyn/cm²)

γ = surface energy (1200 dyn/cm), assuming that plastic work is zero. If not, then γ_p (plastic work) must be added to γ .

ν = Poisson's ratio (0.233)

a = interplanar spacing (2.1×10^{-8} cm)

$2C$ = the crack length (assumed to equal grain size)

ρ = crack-tip radius ($2.1 \times 10^{-8} n$, where n is the number of lattice spacings)

We can plot the σ_f versus (grain size)^{-1/2} for crack-tip radii equal to different numbers of lattice spacings (see Fig. 1). A plausible theoretical basis for this analysis has been reported (Ref. 14).

An analysis of this type requires that the fracture stress be proportional to grain size to the $-1/2$ power, a finding not universally agreed upon, although recent theoretical evaluations, correlated with existing data, do give this relationship significant basis for acceptance. However, one of the basic tasks of this particular program was to ascertain this relationship over a wide range of grain sizes.

If one assumes that the fracture stress does vary as the grain size to the $-1/2$ power and compares experimental data with the theoretical relationship in Fig. 1, a crack-tip radius of five to ten atomic distances is needed to

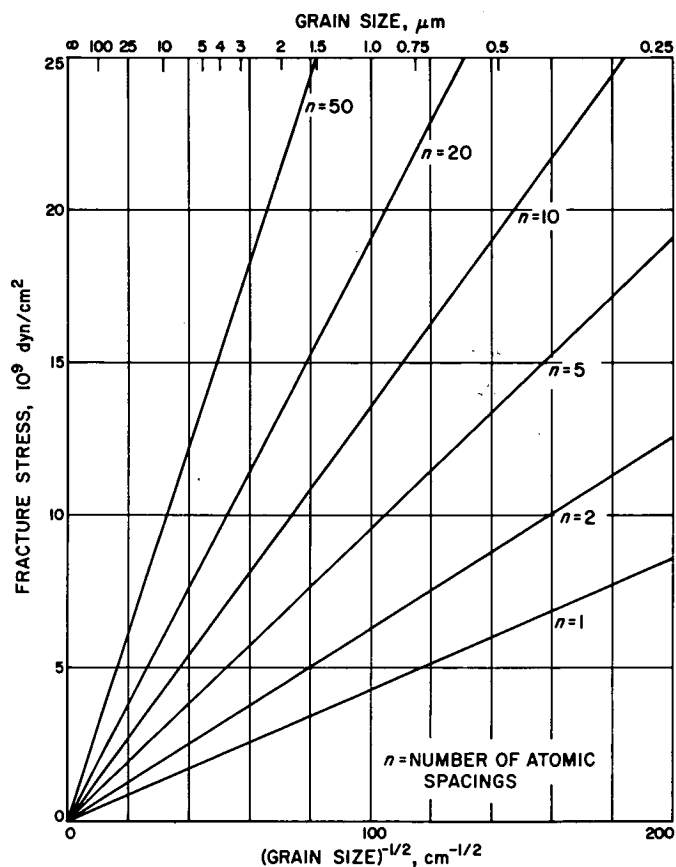


Fig. 1. Fracture stress versus grain size for various crack-tip radii (the crack-tip radius is expressed as n interplanar spacings in MgO). Plastic work equals zero

reconcile these results. Such radii require significant atomic mobility in the grain boundary over a volume that is inconsistent with the dislocation array model, and this fact lends credence to other theories.

Examination of the variables involved in the Griffith-Orowan relationship reveals that there is significant question concerning the magnitude of γ , ρ , and C . The half-crack length C is assumed to be directly related to the grain size, and such an assumption is the basis on which this formula is applied to polycrystals. The surface energy γ in itself is fairly well known, but there are two sources of error in the selection of values for use. One is the existence of multiple cracking, thus preventing accurate determination of the new surface area developed, and the second is the inclusion of plastic work in conjunction with the propagation of the cracks. For cleavage cracks in a single crystal or a single crystallite of a polycrystal, multiple cracking is generally ignored. The inclusion of plastic work generally must be considered dependent upon the material under consideration. The crack-tip radius ρ is generally considered a variable and is treated as such in Fig. 1, with the surface energy being held constant (that is, there is no plastic work). Figure 2 reverses the situation.

Clearly, separation and definition of these variables from an experimental standpoint would be one of the major requirements of understanding mechanical behavior in ceramics. It is in this region that much emphasis was to have been placed.

C. Testing to Determine Mechanical Behavior

The generation of precise mechanical data on ceramic materials is a substantial problem. A variety of techniques are available; for example, uniaxial tension, uniaxial compression, modulus of rupture, diametrical compression, and hydrostatic ring testing. Many of these techniques, such as the last three, are ideally suited to room-temperature brittle-failure evaluation, but are not usable for deformation at higher temperatures. In modulus of rupture, the effect of surface behavior is over-emphasized and stress distribution is very nonuniform. Because of the desire to study crack propagation under the influence of known stresses, the uniaxial tension technique seems to be ideally suited to the broad requirements of this program. However, testing ceramics in uniaxial tension is a significant technical problem because of the high modulus of elasticity and the lack of a yield point at room temperature. On the other hand,

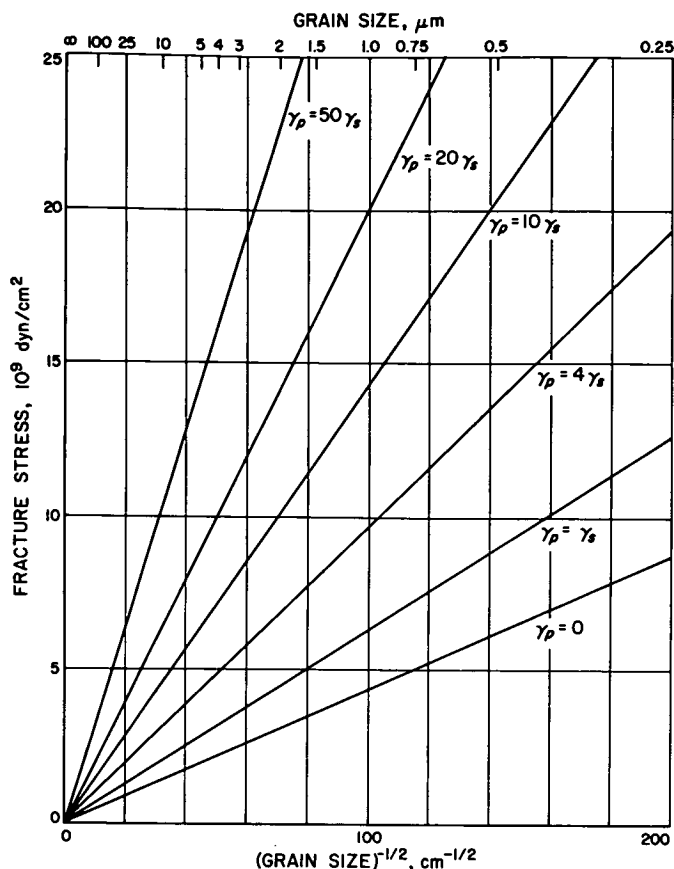


Fig. 2. Fracture stress versus grain size for various amounts of plastic work (the plastic work is expressed as a ratio to the surface energy). Crack-tip radius equals one interatomic distance. The notation γ_p represents the energy of plastic work, and γ_s is surface energy

these are problems that are capable of being minimized through proper design and dimensional control.

It was felt that the scientific advantage of tensile testing was overriding, and a facility was designed, constructed, and evaluated with the purpose of precisely testing ceramic materials under uniaxial tension over a wide range of temperatures. The considerations made in such a design and the end product are thoroughly described in a separate report (Ref. 15). Consequently, no details will be presented here, but only the following brief description. The specimen consisted of a 3.8-mm-diameter gauge section in a cylindrical dog-boned configuration. A special streamlined contour was used at the shoulders to reduce notch effect. The specimen was held in a rigid grip system placed between spherical air-floated bearings to improve axiality of loading. Strains

were determined by optical trackers not requiring contact with the specimen. Strain sensitivity was approximately $1 \mu\text{m}$ and permitted modulus-of-elasticity measurements. Stresses were determined by a relatively conventional, although special, load cell unit. Environment and temperature control was also provided.

This mechanical testing facility was used to generate precise mechanical property data on ceramics which would be useful in developing a comprehensive theory of behavior, rather than in providing engineering data; consequently, the selection of materials for study was based only partly on engineering usefulness. The other, and generally more heavily weighted considerations, were (1) ability of the selected material to represent ceramics as a class, (2) availability of background information, (3) simplicity and ease of understanding on a fundamental basis, and (4) availability. Careful consideration of these factors finally led to the decision that studies could be effectively made on magnesium oxide and tantalum carbide, with the greatest emphasis on the magnesium oxide. Magnesium oxide was emphasized over tantalum carbide because more background knowledge is available and it more nearly represents ceramics in present applications. (Although carbides are proposed for extensive applications, present ones are rather limited.) Further, because of the limited information available on the carbides and also because of finite research resources, the preliminary goal of the carbide program was to ascertain whether the mechanical behavior of polycrystalline carbides was ceramic in nature, and to provide usable engineering information.

D. Preparation of Materials

Conventional sources of high-purity ceramics for research are undependable. This difficulty stems partly from the high affinity for impurities in ceramics, and from poor and incomplete analytical procedures (this is discussed more fully in Section III). Consequently, a process was developed for the production of pure polycrystalline ceramics in a configuration suitable for machining into test specimens. These results have been extensively reported (Ref. 16).

The following changes in the as-reported (Ref. 16) material preparation of MgO were made. The chelate extraction purification step was discontinued, since chemical analysis showed that this step did not significantly decrease the cation impurity content and showed

a slight increase in anion impurities. Anhydrous ammonia was substituted for the chemically pure ammonium hydroxide previously used, but no change in purity was noted. Such changes were evident only with the advent of improved chemical analyses. In addition, the precipitation of the hydromagnesite from the $\text{Mg}(\text{NO}_3)_2$ solution was carried out at room temperature instead of the previously used 80°C . This change in procedure increased the yield of MgO per batch by 20 to 40%. The drying temperature of the filtered material was limited to 75°C to increase the filter life.

Evaluation of other material sources and fabrication procedures also continued with low emphasis in an attempt to improve the product or increase efficiency. The consideration of hot isostatic pressing, as a means of fabrication, was evaluated and results have been reported (Ref. 17). An alternative source of MgO^1 was evaluated and the results are included here.

A quantity of fully prepared MgO was obtained from Kanto (see Table 1) and attempts were made to hot-press it under conditions designed to produce theoretical density easily. Densities of 3.16 to 3.34 g/cm^3 were obtained, and it was surmised and later confirmed that the particle size was approximately one micron. This apparently resulted from air calcining at temperatures above the 650°C in vacuum used here. Consequently, a quantity of uncalcined material, $\text{Mg}(\text{OH})_2$, was obtained (see Table 2) and calcined under vacuum at 650°C . Although particle data were not available, the ability to attain theoretical density at normal conditions (13 kpsi and 1000°C) indicates particles approximately $0.05 \mu\text{m}$ in diameter. Although corroborative analyses were not obtained, this $\text{Mg}(\text{OH})_2$ would appear to be a valuable source of pure research-grade MgO.

E. Mechanical Behavior Test Results

With the availability of specimen fabrication techniques and a testing facility, a testing program was begun. Because of the limited time, specimen parameters could not be varied as was desired nor procedures completely refined. The tests that were conducted are reported elsewhere (Ref. 18) and provide, in general, few data that can be properly introduced into the general theory of polycrystalline behavior. The conclusions that

¹No. 73 Chrome Honcho Nihonbashi, Kanto Chemical Company, Inc., Tokyo, Japan.

Table 1. Impurity content of Kanto MgO

Element	Impurity content, atomic parts/10 ⁶			Element	Impurity content, atomic parts/10 ⁶		
	A ^a	B ^b	C ^c		A ^a	B ^b	C ^c
H	10,000	—		S	200	—	
Li	2	—		Cl	350	—	40
B	10	4		K	10	—	
C	1,000	—		Ca	120	10	30
N	100	—	180	Mn	1	0.7	3
F	20	—		Fe	10	4	10
Na	3	—		Ni	2	14	
Al	3	15	60	Cu	2	0.6	
Si	60	140	30	Zn	4	—	10
P	30	—	10	Ba			6

^aBy the mass spectroscopy method.
^bBy the emission method.
^cAs reported by the vendor.

Table 2. Impurity content^a of Kanto Mg(OH)₂ (based on MgO)

Element	Impurity content, atomic parts/10 ⁶
N	15,000
Al	30
Si	80
P	15
S	24
Cl	25
Ca	20
Mn	2
Fe	5
As	0.5
Pb and other heavy metals	2

^aAs reported by the vendor.

may be reached from the limited amount of data generated are as follows:

- (1) Fracture in tantalum carbide at room temperature is primarily a transgranular process, with fracture stresses of approximately 25 kg/mm² in material with 20- μ m grain size.

- (2) No evidence of extremely high strength in sub-micron dense magnesium oxide was noted.
- (3) Improved understanding of the hot-pressing characteristics of tantalum carbide is necessary for reproducible specimen production.
- (4) Improved procedures are necessary for hot-pressing magnesium oxide to preclude the presence of macroscopic failure sources and cracks.
- (5) The mechanical testing facility at room temperature provides superior mechanical data for these purposes, although requiring a large investment of time and money.

III. Nature of the Grain Boundary in Ceramics

If the grain boundary is indeed so controlling in the behavior of polycrystalline ceramics, then to explain this behavior it is necessary to know in detail the nature of such grain boundaries. However, the present knowledge of such grain boundaries is poor. Attempts to select explanations from existing theories on grain boundary structure, such as dislocation arrays, islands of "fit," or viscous layers, have not been generally satisfactory. Further, attempts to correlate such theories with observed data on the behavior of polycrystalline ceramics lead to some unacceptable conclusions. For example, diffusion

data in polycrystalline MgO suggest a grain boundary width of approximately one micron (Ref. 6), while micro hardness data indicate an even larger zone of influence (Ref. 19).²

Early investigations of the behavior of ceramics at this Laboratory (Ref. 4) suggested that one reason for the existence of significant grain boundary volumes might be the separation of the impurities to locations near the boundary interface. They would, however, extend for finite distances into the lattice on either side, and most certainly they could explain the observed behavior.

Attempts to analyze ceramic oxide for impurities quickly revealed that methods were not available for analysis for the wide range of impurities that might be expected in ceramics, either in terms of bulk analysis or in terms of distribution. It was noted that at levels below hundreds of parts per million, even techniques for bulk analysis of conventional metallic impurities were not reproducible, and techniques available for analysis of non-metallic impurities had not been sufficiently confirmed (Ref. 20). Consequently, a subcontracted program for the development of approved analytical procedures for use with ceramics was begun. The initial phase of the program was to confirm the bulk analysis of almost all impurities in ceramics with the additional proviso that the technique used could be developed into a distribution-sensitive procedure. This phase of the research has proceeded to the point where mass spectroscopy has been selected as a usable technique for the bulk analysis of all impurities in ceramics (Ref. 21). It has been confirmed in almost all cases (exceptions being hydroxyl and carbon, which are under study) and certainly this technique can be developed into a distribution-sensitive procedure. This latter development is expected to continue under JPL contract 951578 as a fundamental contribution to ceramic science (Ref. 24).

Results on the distribution of metallic impurities by previously existing techniques have been reported (Ref. 22), and the conclusion is evident that certain metallic impurities are segregated to grain boundaries in polycrystalline oxides to the limits of detectability. The inference of this conclusion is that the grain boundary in a ceramic must be considered chemically different from the lattice; consequently a polycrystalline oxide is perhaps better represented as crystals joined by a boundary

volume and the properties of such a boundary must be known in detail before the behavior of the boundary-interior composite can be evaluated. Another inference of this finding is that theoretical models of "pure" grain boundaries may be meaningless from a practical point of view since it is not possible at this time to obtain polycrystalline ceramics with less than hundreds of parts per million total impurity, and impurities to this level generally still reside at the grain boundary.

There is continued need for improvement in the purity of such ceramic materials to permit understanding of the effect of such impurities on the behavior. This is not to suggest, however, that purity per se may be a prerequisite for satisfactory performance. To the contrary, the advantageous effects of impurities as grain growth inhibitors are well known, and it may be proposed that impurities at grain boundaries facilitate blunting of cracks as they enter the grain boundary region. However, blunting of cracks would appear to correspond to a "softer" structure, and so care must be taken that such a structure does not also promote deformation of the ceramic at higher temperatures. Consequently, a selected distribution of certain impurities at the grain boundary may well be the answer to improved behavior of polycrystalline ceramics.

A further complication of the existence of impurities at grain boundaries is the production of volatile components when the material is exposed to moderate-to-high temperatures. Extraction of such impurities has been suggested as an explanation for the increase in strength exhibited by fine-grained ceramics after thermal treatment (Ref. 23).

Once detailed knowledge of the chemical composition of the grain boundary is available, it will be necessary to ascertain the manner in which these atoms are put together into the grain boundary structure. If the grain boundary is indeed a region containing large amounts of different kinds of atoms other than those of the host lattice, it is then also likely that such a region is highly disordered, and undoubtedly contains a large number of defects. It is certainly necessary to determine how closely the regular crystal lattice of the grains approaches the interface or, conversely, how far the influence of the interface and its associated impurities and defects extends into the grains.

Little is available in terms of efforts to apply direct structure evaluation techniques to grain boundaries in

²Also, private communication on MgO from J. H. Westbrook, General Electric Research Laboratory, Schenectady, New York.

ceramics. Consequently, the approach was taken to apply conventional structure analysis methods, such as X-ray diffraction, electron microscopy, etc., and to attempt to localize the region under study to the grain boundary. Little more than preliminary results were obtained, and these indicated that the techniques were applicable to the study of the grain boundary, but that considerable improvement was needed to develop the necessary resolution. The concepts on which the selections of techniques were based, the nature of the preliminary results, and the conclusions and recommendations are more extensively discussed in a separate report (Ref. 24).

IV. Conclusions

Because this effort was ended before any of the major phases were completed, no definite conclusions have been made concerning the interrelationship of grain boundary composition and structure with mechanical behavior in polycrystalline ceramics. However, within each phase, conclusions may be drawn concerning the success of the techniques applied, the results of these techniques, and the directions and approaches to be taken in the continued effort to solve this problem.

In the area of mechanical testing, the following conclusions are evident. First, although it was shown to be feasible to design and construct a "universal" testing machine for brittle ceramics over a wide range of temperature and environments, the difficulty encountered and the sophistication required for the solution of the

problems involved suggest that a larger number of facilities, each individually designed for a specific phase of the problem, might be more efficient in terms of total time and money expenditures. Part of this problem lies in the difficulty in producing sound, satisfactory specimens for testing. A simpler test configuration requires simpler, more easily produced specimens.

Studies of the chemistry of grain boundaries in ceramics suggest that real ceramics in which grain boundaries can be considered uncontaminated do not exist. (Polygonized deformed single crystals are a likely temporary exception.) Conventional metallic impurities at levels as low as tens of parts per million when referred to the bulk are located at the grain boundary. The segregation of anion impurities is presently not known, except that the quantities are usually larger than those of metallic impurities. The location and influence of these anion impurities need to be determined before a clear picture of the grain boundary can be proposed.

Further effort is required to delineate the atomic structure of the grain boundary in ceramics. Preliminary results obtained here indicate a high degree of complexity, showing the existence of several regions of misorientation within a single boundary, zones within a boundary where the optical behavior of the zones differs from that of the rest of the boundary region, and significant interaction of lattice substructure in regions near the grain boundary. Moreover, a high level of crystallographic orientation is developed in polycrystalline ceramics after the material has undergone relatively conventional heat treatment.

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