DEFORMATION PROCESSES IN FORGING CERAMICS

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ABSTRACT

The program objective is to investigate the deformation processes involved in forging of polycrystalline oxide ceramics. A combination of mechanical testing and forging are planned.

An extensive review of the literature on the deformation and high temperature fracture of the refractory oxides was made; this suggested that initial efforts be directed toward forging of fine grained Al_2O_3 and on MgO at high temperatures.

Initial mechanical test results on Al_2O_3 revealed more extensive strain hardening than had been anticipated, a strong Bauschinger effect and a suggestion of a yield effect. The implications of these results are discussed with regard to grain boundary sliding and dislocation mechanisms.

FOREWORD

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I. INTRODUCTION

There have been several investigations into the hot working of crystalline ceramic oxides in the last several years. Although several of these have been moderately successful, there are still significant problems resulting from limited understanding of the high temperature deformation and fracture of the oxides. It is the objective of this program to investigate the forging of several refractory oxides in order to provide a greater capability in their deformation processing. Therefore, the particular objectives of the program can be stated briefly as follows:

1) Understanding of the deformation and fracture behavior necessary for forging ceramic oxides,

2) Successful forging of flaw-free bodies with useful properties,

3) The possible development of unique or otherwise difficult to obtain properties as the result of hot working.

Hot forging, extrusion and rolling have been utilized by several investigators.* Successful extrusions of several oxides have been made by Hunt and co-workers at Nuclear Metals and with Rice of Boeing. Although crack-free extrusion of MgO and other relatively ductile oxides have been obtained, the high strain rates and rapid cooling rate are problems and have contributed, in part, to the failure to obtain sound extrusions of the less ductile materials such as Al_2O_3. Vasilos and co-workers[2] at Avco have demonstrated the successful upset forging (press forging) of many refractory oxides, including several, such as Al_2O_3, which have not been successfully extruded. Promising results have also been obtained in shape forging of Al_2O_3.[3] Hot rolling has been more limited although some success has been obtained in densification of MgO powder[4] and with materials with a glassy phase.[1] In addition, the extrusion of refractory carbides has been accomplished by Dolloff and Probst.[5]

The results of the initial efforts have been encouraging and have indicated that hot working should provide an extension of present forming capabilities and also can provide improved properties in the refractory oxides. Property improvements can be reasonably expected in a number of areas as a result of high density, microstructural and crystallographic texture and perhaps retained dislocation substructure. Moderate increases in strength resulting from extrusion of MgO[1] and upset forging of Al_2O_3[3] have been demonstrated. Upset forging has been used to obtain theoretical density resulting in transparency in a number of oxides.[2] Crystallographic texture from forging results in transparency in Al_2O_3[2] and in high values of magnetic permeability in barium ferrites.[6]

Although results of this type are encouraging significant problems still exist. Hot tearing and cracking severely limit reductions on extensions.

* Good reviews of efforts in the hot working of ceramics can be found in the articles by R.W. Rice.[1]

obtainable and result in flaws in hot worked pieces. Lack of complete understanding of the mechanical behavior of ceramics and the response to combined thermal and mechanical treatments limited property improvements obtainable by hot working.

The basic approach of this program will be to correlate controlled forging experiments with the basic mechanical properties of ceramic materials. Although existing information on the deformation and fracture of ceramics will be used where it exists, there is only a limited amount of information available on the deformation of ceramics at high strains and on high temperature fracture. Therefore, basic mechanical testing will be done in conjunction with forging. The initial effort will be on mechanical testing using the results of previous forging efforts to indicate necessary information.

The primary effort will be with Al_2O_3 and MgO since these are available in high quality bodies and there is considerable experience in fabricating them, and comparative base-line information is available on properties and microstructures resulting from conventional fabrication techniques. Limited consideration will be given to $MgAl_2O_4$ (spinel) and other compositions in the MgO-Al_2O_3 system to provide information about mixed oxides and multiphase systems.

II. TECHNICAL APPROACH

Much of the work to date on the hot working of ceramic oxides has necessarily been of an empirical nature. Although results have been encouraging, there has by now been enough work done to suggest a number of problem areas which must be given basic consideration in order to allow a more sophisticated approach to deformation processing of oxides and to the development of desired properties. The most critical problem areas have been identified and will be discussed briefly followed by an outline of the basic approach to be used in the program.

A. Problem Areas

Most of the critical problems can be divided into three broad areas for consideration. The first, and most serious, is the problem of hot tearing, cracking and cavitation; this is related both to the problem of limited ductility of some materials and to a limited knowledge about ductile fracture in even the most ductile ones. The second area for consideration is the rather broad area of microstructural control resulting from grain growth, strain induced boundary migration and recrystallization. The third area includes the engineering and equipment problems associated with high temperature processing including chemical compatibility, tooling design and temperature control.

The problems of limited formability, high rejection rates and microstructural degradation from flaws and cracks have been particularly severe in hot working to date. The application of basic metal working technology is severely limited by incomplete understanding of the flow and fracture mechanisms and of reliable data on the properties of particular oxides. Although the basic deformation mechanisms have been identified for the oxides there is still considerable controversey concerning the relative importance of various of them over broad ranges of temperature, stress and strain. Much of the work has been done at low strains and the behavior at high strains has not been characterized. General conclusions about deformation mechanisms have been drawn from this low strain work and the danger of extrapolating this behavior to high strains has not been given sufficient attention.

The problem of high temperature fracture of ceramics has received less attention than yielding behavior. Although fracture associated with limited ductility involving failure to satisfy the von Mises condition requiring five slip systems has been observed, the broad conditions for which this condition dominates are not yet clear, especially for Al_2O_3. In addition, intergranular cracking has been frequently observed under conditions where the problem of insufficient slip systems was not thought to be dominant. Although the obvious embrittlement resulting from weak or low temperature second phases has been frequently seen, the effects of smaller amounts of impurities within the nominal solubility limits are not known. The result is that some of the potential failure mechanisms have been identified; however, there does not yet exist a broad understanding of failure in ceramic oxides nor are there available fracture criteria relating the variables of temperature, stress, strain and strain rate to microstructural variables. Although it is expected to be many years before a unified fracture criteria is developed for these materials, a greater understanding than is presently available is essential at this time.

The type of information which must be made available for application to forging problems includes definition of the conditions under which ductility is too limited to be useful, understanding of the cause and prevention of grain boundary cracking and cavitation which result in eventual hot tearing of the material and degradation of subsequent material properties, rates of strain hardening and the effect on neck resistance and fracture, and finally the effectiveness of strain rate sensitivity in providing neck resistance. This type of information is necessary in order to develop constituitive equations which can be used in subsequent analysis of the flow conditions in the forgings. Therefore, both mechanistic understanding and reliabile data for the particular materials to be used are necessary.

The problem of grain boundary cavitation may prove to be one of the most serious and difficult to prevent. Examples have been seen at Avco in the shape forging of cones and hemispheres of Al_2O_3 where intergranular cracking and cavitation lowered the density from nearly theoretical to as low as 60-65%, but caused only very limited macroscopic tearing or cracking; forging of a similar piece under nominally similar conditions resulted in no loss of density. The causes for the differences are not known, but cannot be simply written off to lack of ductility. This problem is particularly severe in that small amounts of intergranular cracking may be quite deleterious to the low temperature properties of forged materials.

A final problem relating to fracture behavior which should be mentioned is the effect of intermediate anneals and multiple step processing on extending formability. This problem is ultimately related to the broad area of resultant microstructure and its influence on subsequent properties. It is likely that intermediate heat treatments and multiple loading will have some influence on formability and this area will be considered both with respect to extending formability and developing final properties.

The entire problem of microstructural control during and after deformation processing is not well understood; however, it is of importance both with respect to multiple step processing and to final properties. Both recrystallized and unrecrystallized Al_2O_3 have been produced by upset forging;[7] the unrecrystallized material having retained dislocation networks and twins.[2] In addition, effects such as polygonization[8], recovery and apparent strain aging[9] have been observed in tensile studies of MgO. Therefore, it should be possible to obtain a wide variety of resultant microstructures. There is, however, relatively little information concerning the exact conditions under which these various phenomena occur, and frequently reliable predictions whether or not recrystallization will occur cannot be made.

The problem of retention of extremely fine grain sizes may be particularly bothersome because of the high rates of grain growth in many systems at the high temperatures necessary for adequate ductility, this is aggravated by the fact that concurrent straining may enhance growth rates, particularly at low strain rates.[10] This has been a problem in both upset forged Al_2O_3[2] and extruded MgO[1] in which grain sizes have not been obtained as fine as can be produced by hot pressing. Because of the highly desirable properties associated with fine grained ceramics, this problem will be given serious attention. Both recrystallization with grain refinement and lower temperature forging to produce unrecrystallized, fine grained materials will be considered.

The engineering problems associated with forging are not expected to be limiting, although continued attention to them will be required. Graphite tooling and modified hot pressing equipment will be largely used. The most serious limitation will probably be that of chemical reaction; however, techniques and separating media have been developed in hot pressing which will be useful. Tool design will, of course, be a significant area and techniques from metal working technology will be utilized to optimize tool design; this is an area where feedback between analysis of forging experiments and mechanical test data can be particularly valuable but reliable constituitive equations are necessary for effective analysis.

B. Mechanical Testing

In order to obtain the mechanical property data which is necessary, mechanical testing will be combined with a thorough review of the literature for information and data which are applicable to the problem. As mentioned, testing and forging will be primarily confined to Al_2O_3 and MgO with limited consideration given to $MgAl_2O_4$ and perhaps other compositions in this system.

Areas to be investigated include the dependence of flow stress on temperature, strain, strain rate and microstructure and similarly the dependence of fracture upon these same variables so that the areas of maximum ductility can be identified. Both accurate data which can be used to develop constituitive equations and mechanistic understanding will be sought. Testing will be done in several modes including flexure, tension and torsion in order to assess the effect of deformation mode upon ductility. Where feasible, testing will be to failure to provide information on both flow and fracture. Investigation in the range of 1400-1900°C is planned for Al_2O_3 and $MgAl_2O_4$ and 1400-2200°C for MgO over rather wide ranges of strain rate for both. Microstructural analysis will be utilized to provide information on mechanism. Multiple loading, with and without intermittent annealing will be utilized to provide information on recrystallization and recovery behavior which may affect formability.

C. Forging

The conditions for forging experiments will be dictated by the results of the mechanical property tests in order to optimize formability. Shape forging will be used extensively with deep drawing of a hemisphere to be studied initially. Shape forging is felt to be desirable in comparison with upset forging or extrusion because it generally involves some tensile deformation. While this is a more severe condition it provides a broader base of understanding for subsequent deformation processing of ceramics. The ability to produce final shapes is also desirable in itself especially if the resultant properties cannot be obtained from sintered materials. Analysis of the plastic flow during forging and failure analysis will be utilized in order to allow interpretation of the results and correlation with the mechanical property data which will be obtained. These results will be utilized to provide modifications in forging conditions and tooling design.

A few upset forgings are planned to provide material for evaluation of the effects of forging upon subsequent properties. If particularly encouraging results are obtained from such materials, blanks may be upset prior to shape forging in order to obtain the most ductile material possible for the shaping experiments.

III. HIGH TEMPERATURE MECHANICAL BEHAVIOR

An extensive review of the literature on deformation of ceramic oxides was undertaken with the objective of identifying the deformation modes and conditions which provide the greatest amount of useful ductility and to gain as much information about high temperature fracture mechanisms as possible; a brief summary is presented here. It is the objective of this program to work with polycrystalline material so that consideration of single crystals has been limited to that necessary for an understanding of polycrystalline bodies. The refractory oxides (polycrystalline) display very limited, if any, ductility at temperatures below 1/3 to 1/2 of the melting point so that the effects of relatively rapid diffusion in terms of thermal activation, time dependence and microstructural instability must be considered with regard to basic mechanisms and resultant microstructures and properties.

The discussion is presented in terms of the various deformation mechanisms of interest; however, both deformation per se and the implications with regard to fracture mode are considered. This is followed by an enumeration of the particular areas which seem most fruitful for investigation in this program.

A. Deformation and Fracture Behavior

It seems reasonable to categorize the observed behavior in terms of three distinct mechanisms which may be dominant under appropriate conditions. The approach risks oversimplification in that a combination of or transition between these mechanisms is frequently observed and often a clear identification of the relative importance of them is not possible at the present time. These are crystallographic slip, diffusional creep and a process best identified as grain boundary sliding (GBS) which may include a range of particular variations, but is extensively observed in fine grained materials.

Deformation by slip has been observed in virtually all of the refractory oxides under appropriate conditions and in some cases at relatively low temperatures. However, most of these materials do not satisfy the Mises criteria requiring fine operative, independent slip systems for fully ductile behavior in polycrystalline bodies[11] except under rather limited conditions. If this condition is not met, stress concentrations develop, especially at grain boundaries and cause microcracks which rapidly lead to fracture. Forging under these conditions will not be fruitful and it is important, therefore, to identify and consider only those conditions under which the Mises requirement is met. The possibility of limited slip slip with the additional degrees of freedom provided by non-slip mechanisms is discussed in later sections. It should be mentioned that cracking at grain boundaries can result from a number of other mechanisms[12] and is not per se the result of failure to satisfy the Mises condition.

Extensive deformation by slip has been studied the most extensively in MgO.[8,9] The resolved critical shear stresses are low enough to allow slip on both the $\{110\}$ $\langle 1\bar{1}0\rangle$ and $\{001\}$ $\langle 1\bar{1}0\rangle$ slip systems which are necessary for five independent slip systems and also, to allow cross slip at temperatures as low as 800-1000°C.[9] However, interpenetration of oblique slip bands is difficult below 1700°C, although reduced strain rates lower this to at least 1550°C.[13] The result is fully ductile behavior in polycrystalline MgO cannot be obtained in tension below about 1700°C.[8] At least limited ductility without cracking is possible in some cases as low as 800°C in compression.[9] This difference is thought to result from a reduced tendency for crack propagation rather than from a fundamental difference in deformation mode.

At 1400°C and above some grain boundary sliding also occurs which probably does not contribute significantly to deformation in coarse grained material where slip is predominant and provides a mechanism for fracture at intermediate temperatures. At temperatures of 1700°C and above, if fracture does not result from GBS or impurities work hardening is sufficient to provide neck stability for elongations of greater than 100%. At these high temperatures fine grain sizes are not stable and relatively coarse grained materials result.

The onset of grain boundary sliding at 1400°C and above results in limited ductility as the result of nucleation of cracks and voids. The behavior is very similar to that found in many metals at intermediate temperatures.[14] Cracks develop at points of stress concentration, particularly triple points, which lead to intergranular failure.[8,9] In addition, pores develop along grain faces normal to the tensil axis which can eventually interconnect and lead to failure.[8,15] In general, it is expected that the triple point cracking will occur at higher stresses and strain rates and that cavitation along the boundaries will be predominant at lower rates.[12,14] At higher temperatures increased grain boundary migration and lower yield stresses allowing stress relaxation at triple points become sufficient to prevent cavitation and cracking at boundaries; when this occurs fully ductile behavior obtains which allows high elongation. It is under these conditions that sufficient work hardening for neck stability is necessary and quantitative information is desirable in order to analyze forging behavior.

The temperature at which fully ductile behavior results has been reported at 1700-1800°C for material prepared from recrystallized single crystals which had high purity, pore-free boundaries.[8] However, for hot pressed materials this temperature is apparently 2200°C or above.[8] This results from residual porosity and impurities. Both of these factors are expected to reduce grain boundary strength and to inhibit migration; in addition, impurities may raise the yield stress for slip making stress relaxation and conformity more difficult. The impurity effects are thought to result from gaseous species not eliminated in hot pressing,[1] from low strength or low melting point constituents such as recently reported for weakening due to retained LiF in CaO,[16] and from the segregation of solute which is known to impede boundary migration.[17] It is interesting to note that this effect of impurities on grain boundary sliding and cracking is very similar to that observed in Al alloys.[14]

Although this behavior has only been extensively studied in MgO, other cubic materials such as CaO, ZrO_2, UO_2, ThO_2 and $MgAl_2O_4$ apparently behave similarly. Extensive tensile ductility has not been reported presumably because of material limitations resulting from porosity and impurities. Compressive studies of hot pressed $MgAl_2O_4$ indicate behavior similar to that of hot pressed MgO in that multiple slip resulted but only small strains were obtained as a result of cracking which was frequently intergranular and apparently associated with some GBS.[18] The creep behavior of ThO_2 and UO_2 appears to be controlled by slip mechanisms[19] and the critical resolved shear stresses for the necessary slip systems in UO_2 are apparently low enough to be activated and correlate reasonably well with yield stresses in polycrystalline material.[20] Materials from this group have been extruded successfully in a similar manner to MgO.[1]

For the non-cubic materials extensive deformation by slip is much more difficult as a result of the limited slip systems which can be easily activated. However, in compression at 1800°C and above deformation of both Al_2O_3[2,7] and BeO[21] apparently involves extensive slip. Identification of the active non-basal slip systems operating in these polycrystalline materials is still not complete. There is no information on the behavior of these materials in tension under similar conditions; however, problems with limited ductility from slip band interaction and GBS, as found in MgO, must be anticipated.

The contribution of twinning should be mentioned at this point. There is little information on the contribution of twinning in polycrystalline oxides. By analogy with hexagonal metals where it is frequently observed, twinning may be expected to contribute somewhat to the deformation of non-cubic oxides particularly in providing an alternative to non-basal slip. Twinning has been seen in both coarse and fine-grained Al_2O_3,[2-a,22] which is not surprising in view of its frequent observation in sapphire under compression.[23]

It is unknown whether it was extensive enough to affect the macroscopic flow parameters or whether it affected ductility.

Under conditions in which slip apparently did not or could not occur the deformation of several oxides has been attributed to diffusional creep. In the case of Al_2O_3[24,25] and BeO[26], where slip is difficult, deformation has been observed to approximately fit the relation predicted by Herring[27] of

$$\dot{\epsilon} = \frac{13.3\, D \Omega \sigma}{kTG^2} \qquad (1)$$

where σ and $\dot{\epsilon}$ are stress and strain rate; D is the diffusivity, G, the grain size and Ω, the volume of the diffusing species, and kT has the usual meaning. There is, however, some uncertainty regarding the diffusing species which is limiting and in some cases calculated values of D are much higher than measured self-diffusivities.[22] Observation has been at temperatures and strain rates too low to activate slip and the mechanism is expected to be more favorable relative to slip at finer grain sizes as suggested by Eq. (1).

The observations of diffusional creep have invariably indicated concurrent GBS which is as expected in view of the need for boundary relaxation necessary for the mechanism to operate.[28] The considerable amount of sliding indicated and the deviation of the observed behavior from that predicted by Eq. (1) indicate that GBS may frequently be in excess of that necessary for accommodation of diffusional creep.[24,25,29]

These materials have invariably shown rather limited ductility with the onset of accelerated creep rates occurring after only a few percent strain. Examination has indicated extensive intergranular cracking which is thought to result from the GBS. There have been no detailed studies of this aspect of this deformation mode, but it is likely that grain boundary porosity and impurities aggrevate the problem although it was also observed in materials of high density and purity.

Under similar conditions of strain rate, temperature and grain size somewhat similar deformation has been reported for MgO,[15] UO_2,[30] and ThO_2[31]. The situation is not as clear since agreement of the results with Eq. (1) has generally not been as good as with Al_2O_3 and BeO, and some microstructural evidence of GBS and some slip is invariably observed. This is not surprising in view of the greater ease with which slip occurs in these materials. As a result, it is not certain whether pure diffusional creep will occur in these materials, but if so it will only be at very low strain rates and stresses where slip is relatively less likely.

This deviation from the behavior predicted by Eq. (1) becomes more pronounced in materials with finer grain sizes in both cubic and non-cubic oxides. Similar observations for several materials with grain sizes between 1 and 10 μ indicate that the predominant mechanism is neither slip as seen in coarser materials nor diffusional creep, but is controlled by GBS. There is not yet good agreement on the basic mechanisms involved, and there are undoubtedly some variations in different materials.

As previously discussed, GBS is frequently observed as a secondary mechanism in the deformation of the oxides. In coarse grained MgO, GBS resulted in extensive deformation in the vicinity of grain boundaries particularly at points of constraint like triple points and boundary jogs where folds in the adjacent material were found as a result of the localized shear necessary for accommodation. This was intensified as corrugations in the boundaries developed so that continued sliding resulted in extensive shear adjacent to the boundaries.[8] This was eventually relieved by boundary migration and by polygonization near the boundaries.

As the grain size is reduced the contribution of GBS to total strain generally increases as a result of the increased boundary area. However, when the grain size approaches the width of the highly deformed region associated with GBS, it is expected that the contribution of GBS should become dominant and that a change in the microscopic deformation behavior may result. A similar proposal to explain superplasticity in metals has been advanced predicting a marked increase in GBS as the grain size approaches the stable subgrain size.[32]

Sliding, of course, cannot proceed without deformation of the grains and in this context GBS is taken to imply both the boundary sliding per se and the concommittant accommodation processes.

This condition apparently exists in the various oxides at grain sizes of 5 to 10 μ and below at appropriate temperatures and strain rates. Deformation is marked by a high rate sensitivity, a strong grain size dependence and frequently by strain hardening or a region of transient creep which is much stronger than would be expected from diffusional creep and is similar to that observed in recovery creep of metals. Microstructural evidence of GBS in terms of offset scratches, displaced triple points or folded grains is common. Slip traces are usually seen in the cubic oxides; however, the contributions of dislocations is much more a matter of conjecture in Al_2O_3 and BeO.

This behavior has been studied most extensively in fine-grained Al_2O_3.[22] Materials with a 1-2 μ grain size was very ductile in the range of 1300-1550°C; the flow stress was highly strain rate sensitive with values of 0.6-0.7 determined for the strain rate sensitivity index, m, defined by the relation:

$$\sigma = K \dot{\epsilon}^{\,m} \tag{2}$$

where σ, and $\dot{\epsilon}$ have been defined and K is a material constant. The strong grain size dependence was found to approximately fit the relation:

$$\dot{\epsilon} \propto \frac{1}{G^{2.5}} \tag{3}$$

The strain rates measured were much greater than predicted by Eq. (1) using available self-diffusion data which further indicated this behavior was distinct from diffusional creep. As the grain size was increased up to 5 to 10 μ, m values increased up to about 0.8-0.9 which was taken to indicate a transition to control by diffusional creep at larger grain sizes.[22] A similar decrease in m from nearly 1 at 13 μ to 0.6 at 3 μ was seen in reviewing earlier investigations of Al_2O_3 which had been interpreted in support of diffusional creep.[25]

Limited tests of BeO of less than 10 μ grain size indicated similar non-Newtonian behavior.[33] This work also suggested that a transition from diffusional creep to GBS occurred with increasing stress. A study of 2 μ Al_2O_3 showed a transition in m from about 1 to 0.5 with increased stress suggesting a similar transition.[34] In both of these studies extended peroids of strain hardening during transient creep were observed which provides further support for the fact that the process of GBS involves a fundamentally non-Newtonian process and is not simply a result of intergranular separation.

Microstructural examination of the 1-2 μ Al_2O_3 showed evidence of GBS such as displaced triple points. In addition, electron microscopy of thin foils indicated dislocations at some of the boundaries on which sliding had occurred.[22] It was concluded that the actual boundary sliding process was probably non-Newtonian involving grain boundary dislocations and boundary migration. The accommodation process was not positively identified; it was felt to include diffusional creep and grain boundary migration. Some twinning was seen providing accommodation at points of high stress concentration such as triple points; however, it was not extensive enough to be a controlling mechanism. There was no positive evidence that dislocation slip had contributed to the necessary grain shape changes; however, the point is one of uncertainty.

Rather similar behavior has been observed in MgO, UO_2 and ThO_2 although the greater ease of slip in these materials makes a clear differentiation among the various processes more difficult. A study of MgO at low strain rates in the temperature range 1100-1500°C indicated a change in behavior for grain sizes below 5 μ which was indicated by a decrease in m from 1 to 0.67 and a marked increase in activation energy.[15] The deformation at larger grain sizes was presumably controlled by diffusional creep rather than slip as a result of the low strain rate.

Several studies of UO_2 with grain sizes below 10 μ have revealed similar behavior. For non-stoichiometric (oxygen rich) material deformation has been reported at temperatures down to 800°C with evidence of non-Newtonian behavior and extensive GBS.[35] In the range of 1000-1400°C a marked effect of stoichiometry was seen in which increase oxygen content resulted in much higher strain rates and a decline in m from 0.8 to 0.6 going from stoichiometric material to the limit of the phase field for oxygen enrichment.[30,36] Increased diffusivity with non-stoichiometry would result in higher strain rates; however, this does not per se explain the reduction of m. A similar change in stoichiometry reduces the resolved critical shear stress for slip on the $\{1\bar{1}0\}$ $\langle 110 \rangle$ system* by a factor of three or four in this temperature

* This is the more difficult to activate slip system in UO_2 and is necessary in addition to the $\{100\}$ $\langle 110 \rangle$ system to satisfy the Mises requirement.

range and thus apparently increases the ease of slip in polycrystalline materials.[20] This correlation suggests that the non-Newtonian GBS is related to the ease of slip behavior either in terms of material accommodation by slip or in terms of actual sliding by boundry dislocations.

In ThO_2 of 10 μ grain size at low strain rates a combination of GBS and diffusional creep was suggested. A reduction in m from 0.96 at 1430°C to 0.63 at 1790°C occurred along with microstructural evidence of GBS. This was interpreted as a transition in the controlling mechanism from accommodation by diffusiona creep to limitation by GBS or slip at higher temperatures.[31]

In summary, values of m between 1/2 and 2/3 indicate that the process is limited by a non-Newtonian process. Although accommodation in the grains by slip would seem a reasonable explanation for this, sliding of bicrystals of MgO was also non-Newtonian and indicated considerable strain hardening,[37] suggesting that the non-Newtonian process is intimately related to the sliding. The microstructural observation of GBS in 1-2 μ Al_2O_3 indicated that the dislocations were associated more with the boundaries than within the grains.[22] This suggests that the actual boundary sliding may be limited by movement of dislocations along it. Observations of dislocations at the grain boundary after sliding of a UO_2 bicrystal have also been reported[19] which lend further support to the view that the actual sliding involves the motion of dislocations. Neither of these studies identified the Burger's vectors of the dislocations so that the exact mechanism cannot be identified; similarly information about the sources of grain boundary dislocations and the relation with the grain accommodation processes is necessary before this type of process can be completely accepted and understood.

The mechanism of fracture for materials deforming by GBS appears to be largely by intercrystalline separation resulting from the growth of cracks and voids at the boundaries. The electron microscopy of Al_2O_3 showed the development of small voids at triple points as a result of GBS,[22] and cavitation on the boundaries normal to the tensile axis has been seen in MgO,[15] ThO_2[19,31] and UO_2[30,35]. Investigation of UO_2 indicated that intergranular cracking was more severe for the stoichiometric material[36] which would suggest that a reduced flow stress in the grains allows easier accommodation and results in less cracking. It can be expected that factors which ease the problem of accommodation and allow easier boundary migration will result in increased ductility by reducing stress concentrations and preventing the growth of crack nuclei. The presence of porosity and impurities at the boundaries can be expected to reduce ductility by restricting boundary migration and weakening the boundaries.

Although a quantitative study for the oxides at high temperature does not exist, several investigators have suggested that greater ductility and higher fracture strengths result at finer grain sizes. This seems intuitively appealing for several reasons. A fine grain size reduces the amount of sliding on each boundary for a given strain as seen from the approximate relation for the strain from boundary sliding

$$\epsilon = kn\bar{l} \qquad (4)$$

where ϵ is the strain; n, the number of boundaries per unit length, and $\bar{l}$ is the component of the mean sliding distance in the direction of interest; and k, a geometric constant near unity. If the cavitation results directly from sliding, as has been shown for Cu,[39] then the reduced sliding per boundary should result in less severe cavitation at a given strain. (If an increase in grain size results in a change in mechanism then this argument will no longer hold.)

Finer grain sizes should also reduce stress concentrations and thus reduce the tendency for cracking. If the shear stress on a boundary is relaxed by sliding, then a large stress concentration will develop at the points of constraint where sliding is restricted such as triple points or ledges. This stress concentration will be proportional to $\sqrt{c}$ where 2c is the length of relaxed boundary.[40] This will be approximately the size of the grain boundary facets, unless constraint at ledges reduces it. As a result finer grained materials should develop less severe stress concentrations at obstacles thus reducing the tendency for crack formation. Although these factors are both significant, additional factors resulting from differences in GBS mechanisms may prove to be equally important.

For a system in which there is sufficient accommodation and boundary migration to allow extensive GBS without cavitation large elongations should be obtainable. The high strain rate sensitivity which exists will provide excellent neck stability[41] eliminating the need for strain hardening for this purpose. The actual amount of strain hardening expected with this mechanism is unknown as are the possible effects upon fracture stress. However, it seems likely that the most critical problem is the elimination of grain boundation cavitation and cracking both for good ductility and to prevent degradation of subsequent properties.

B. <u>Areas for Investigation</u>

Several areas are indicated as fruitful for further investigation and forging attempts. The above review suggests two alternative approaches as most promising for initial investigation. One, it is to take advantage of the known ductility available from GBS in very fine materials; Al_2O_3 is the most appropriate material for investigation in this area. The second alternative is to forge under conditions where full ductility from slip can be obtained; for this MgO appears to be the most appropriate material. Alternatives for both of these processes utilizing $MgAl_2O_4$ also are worthy of investigation.

The work to date suggests that if sufficient understanding of GBS can be obtained to prevent boundary cavitation, then significant elongation should be obtained. This is supported by results which indicate that strains as high as 7% can be obtained in 1-2 μ Al_2O_3 without evidence of intergranular separation.[42] Investigation should include identification of the temperature and strain rate ranges in which optimum ductility results, data on flow stress dependence and some mechanistic understanding.

The Al_2O_3 + 1/4% MgO system will be utilized initially for study in this area. High quality materials of about 1 μ grain size can be prepared and the system is exceptionally stable with respect to grain growth. For MgO of high density and purity, grain growth is sufficiently rapid that grain sizes below about 5-10 μ are not stable at 1400°C even for relatively short times.[43] This approach is also desirable since the retention of fine grain sizes is desirable for subsequent properties.

The work to date has indicated the fully ductile behavior by slip does not occur until at least 1800°C and that for hot pressed materials it may be as high as 2200°C. These results were born out by the extrusion work by Rice in which greater problems resulted with hot pressed bodies than with single crystals or fused material.[1] This indicates that every effort be made to obtain high purity, high density materials and that investigation should be primarily concentrated at temperatures in excess of 2000°C.

The eventual forging investigation of $MgAl_2O_4$ is felt to be warranted for several reasons. This system apparently has sufficient slip systems to provide adequate ductility for forging, and in fact, is the only oxide in which the primary system provides five independent systems.[18] Investigation of it may provide insight into additional problems which may be posed by a mixed oxide compound.

The desire for a fine grained system which is stable at high temperatures may be provided by two phases compositions in the Al_2O_3-MgO systems. Creep studies with a series of compositions between MgO and $MgAl_2O_4$ indicated considerably higher strain rates under comparable conditions for intermediate compositions resulting in two-phase microstructures.[44] This was apparently the result of the finer grain size obtained in the two phase materials under similar conditions. This system should also provide interesting mechanistic insight since both phases are relatively ductile. Fine-grained, two phase compositions of Al_2O_3 and $MgAl_2O_4$ would also be expected to provide a stable, fine grained structure and investigation should provide insight into mechanisms involved in GBS.

IV. MECHANICAL TEST RESULTS

During the first quarter a bend testing rig was modified to allow greater displacement so that outer fiber strains of up to 5% could be obtained in 4-point bendings. A series of tests were planned of a rather exploratory nature to provide some insight into what might be expected at larger strains than had previously been studied using Al_2O_3 of 1-2 μ grain size at moderate temperatures. An initial series of tests was planned for 1450°C over a range of strain rates in which the effects of unloading and reloading, reloading after various hold times, reloading after annealing at higher temperature and reversed loading could be investigated. This was felt to be desirable in order to provide additional insight into the deformation mechanism as well as to identify areas which are worthy of additional investigation. Since the deformation mechanism has previously been tentatively identified as GBS it was desired to avoid the use of temperatures high enough to cause significant grain growth either during annealing or deformation. The test schedule called for bending the samples to the limit of the machine, 5%, outer fiber strain, and then reversing them and bending them back again so that a 10% total range was established after the first bend. The process of rebending could be continued through several cycles or until failure occurred.

The materials to be tested are hot pressed Al_2O_3 + 1/4% MgO of $> 99.7\%$ density and averages starting grain sizes of about 1-2 μ; these were similar to materials tested on a previous program which provides background information on the behavior.[22]

This series of testing are not yet complete although a number of interesting results have been obtained which have caused the series to be extended somewhat. The mechanical testing is being coupled with a rather extensive microstructural examination of the samples. Examination has been primarily with replica electron microscopy because of the small grain size. Transmission microscopy of thin foils is planned for later in the program.

Since this series is not yet complete, comprehensive coverage will not be attempted. Some typical results will be presented and the implications with respect to the GBS mechanism discussed. The combined stress-strain curve for a typical specimen is presented in Figure 1. The strain is calculated from deflection measurements taken with a sapphire probe, measured with an LVDT and continuously recorded. The outer fiber stress values presented have been calculated using the elastic equation:

$$\sigma = \frac{3\ Pa}{bh^2} \tag{5}$$

where P is the load; a, the moment arm, b the specimen width and h the specimen height; and therefore, are only approximate. A technique has been developed which will be used to analyze bend test data and reduce them to true stress values in the plastic regime.[45] This gives a value of outer fiber stress of

$$\sigma = \frac{Pa}{bh^2} \quad (2 + n_b \quad + \quad m_b) \tag{6}$$

where

$$m_b = \left.\frac{\partial \ln M}{\partial \ln \varphi}\right)_{\dot{\varphi}} \tag{7}$$

$$m_b = \left.\frac{\partial \ln M}{\partial \ln \dot{\varphi}}\right)_{\varphi} \tag{8}$$

where M is the bending moment; φ, the included angle of bending, and $\dot{\varphi}$, the rate of bending. This procedure cannot be applied until a series of tests are completed so that n_b and m_b can be determined over a range of strains and rates. Previous work established an approximate value of 0.6 for m_b in this range[22] so that the elastic calculation of stress used for preliminary purposes is seen to have a maximum error in the range of 13%.

Several interesting points can be seen from Figure 1 which merit some comment. After the first couple percent of strain a rather strong strain hardening effect starts to develop; with each successive cycle the rate of work hardening increases. In addition, a very strong Bauschinger effect (reduced yield stress on reversed strains) can also be seen which tends to diminish somewhat in magnitude with successive cycles, but does not vanish. Finally, there is an indication of some type of yield phenomena. These results

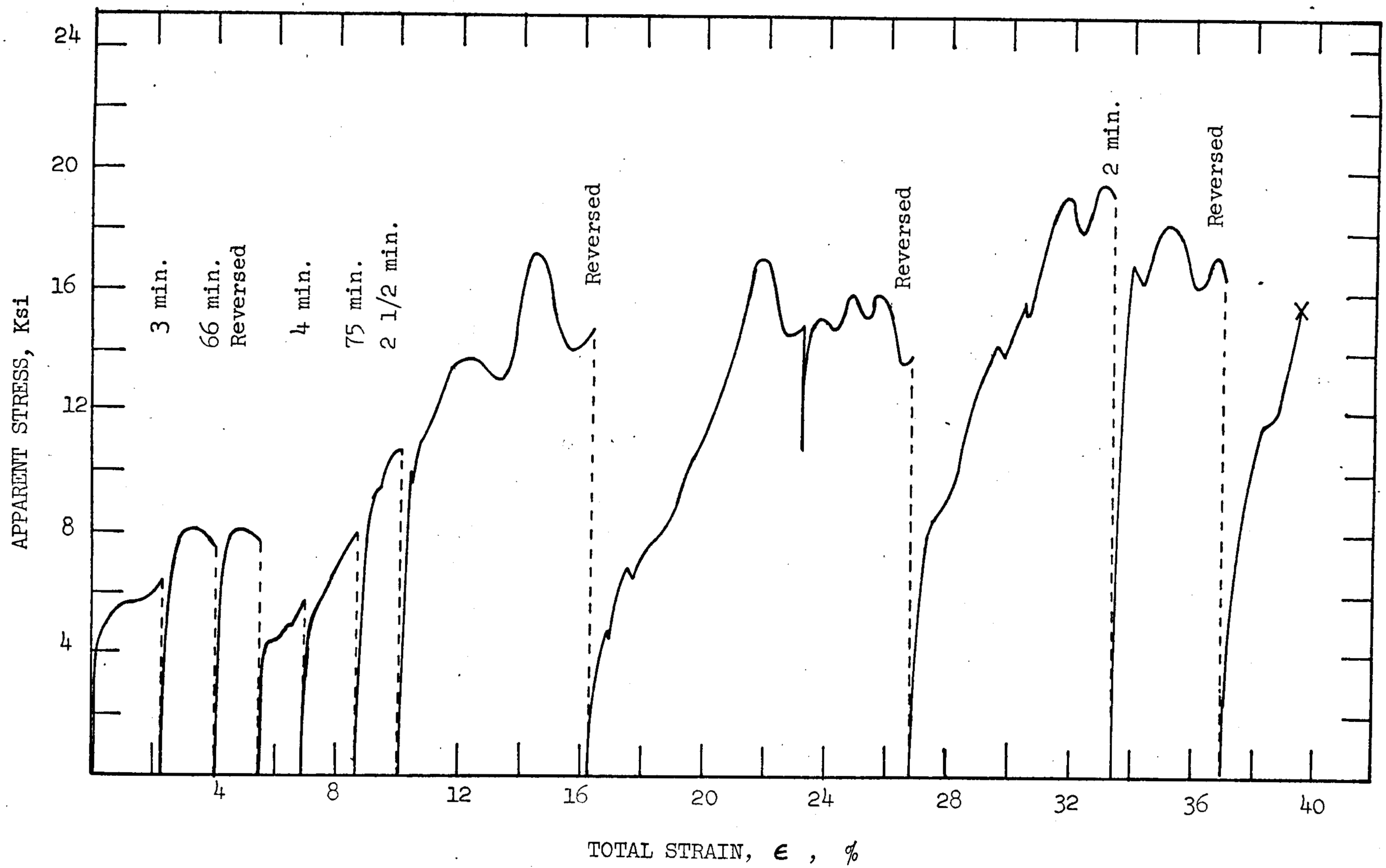


Figure 1. Apparent Stress vs. Strain Curve for Specimen FLUX-30 Tested at 1450°C Showing the Effects of Reloading and Reversed Straining.

are summarized in Table I in which the approximate yield stress, the maximum stress and the final stress are presented for each cycle; in addition, the linear rate of work hardening for the steep part of each curve is also presented.

TABLE I

FLOW STRESSES AND STRAIN HARDENING FOR TYPICAL SPECIMEN

Bend Cycle	1	2	3	4	5	
σ_{yield}	5,100	4,300	4,800	7,600	11,700	psi
σ_{max}	8,200	17,300	17,100	19,500	15,500	psi
σ_{final}	7,600	14,000	13,900	16,400	(fracture)	psi
θ	1.0×10^5	1.5×10^5	2.5×10^5	2.5×10^5	4.1×10^5	psi

Stresses are apparent stresses calculated using the elastic beam equation. θ is the linear rate of work hardening given by $\theta = \frac{d\sigma}{d\epsilon}$. Specimen FLUX-30.

This table gives a dramatic picture of the magnitude of the Bauschinger effect where the yield stress on reverse loading was generally less than half of that at the point of unloading. This behavior can be partially rationalized in terms of the relief of stresses at triple points and other obstacles to sliding; upon reversal of the sliding, this is thought to be the cause of the anelastic recovery which has been observed after creep of BeO and Al_2O_3.[46] Whether this can account for the entire effect is uncertain at the present, but seems unlikely.

It is interesting that the magnitude of the Bauschinger effect tends to be reduced with successive cycles both in terms of the magnitude of the yield stress and the amount of strain before rapid work hardening begins. This indicates that sliding back and forth does not occur in a reversible manner, but that a continual hardening process occurs.

Several of the curves suggest the occurrence of a yield phenomena of some type and one of the reloading curves in bend #1 and in bend #2 suggest a strengthening of the yield phenomena similar to that obtained in 'strain aging'. Some of the other specimens showed even more marked behavior with slight yield drops in a few instances. The cause of this variation is not understood at this time.

The cause of the irregularities in the curves is not known at present. It is possible that they are caused by sliding of the specimen along the knife edges and every effort is being made to evaluate this possibility. It is thought significant, however, that the irregularities become more pronounced at higher stresses. It is possible that they are associated with either irregular straining or cracking in the sample. Cracking was observed in this sample; however, similar irregularities have been seen for specimens in which cracks were not found.

A crack was found in the tensile surface of this specimen after the second cycle which was somewhat disappointing in terms of its early appearance and surprising in terms of the ability of the material to withstand it. The crack can be seen in Figure 2-a as it appeared after the second bend and its growth after the fourth bend is seen in Figure 2-b; the bar developed a stress of over 15,000 psi even with this crack in it. Similar cracks were not seen on the opposite surface. Failures such as this are being analyzed in an attempt to develop some understanding of their cause and an indication of how to prevent them. It is obvious that such a crack would provide a severe stress raiser at lower temperature even if it were stable at high temperature.

Microstructural examination has been done on several of the specimens using replication of the as-deformed surface. The specimens had ground surfaces initially, but thermally etched rapidly. Two micrographs are presented in Figure 3 which are from the opposite faces of a specimen which had failed in the sixth cycle and had exhibited similar behavior to that in Figure 1. Several interesting features can be seen in Figure 3-a which are suggestive of extensive GBS including corrugated boundaries, displaced triple points and wide, indistinct boundaries suggestive of extensive shear and migration. There is also a suggestion of the development of polygonization or recrystallization at one or two of the triple points.

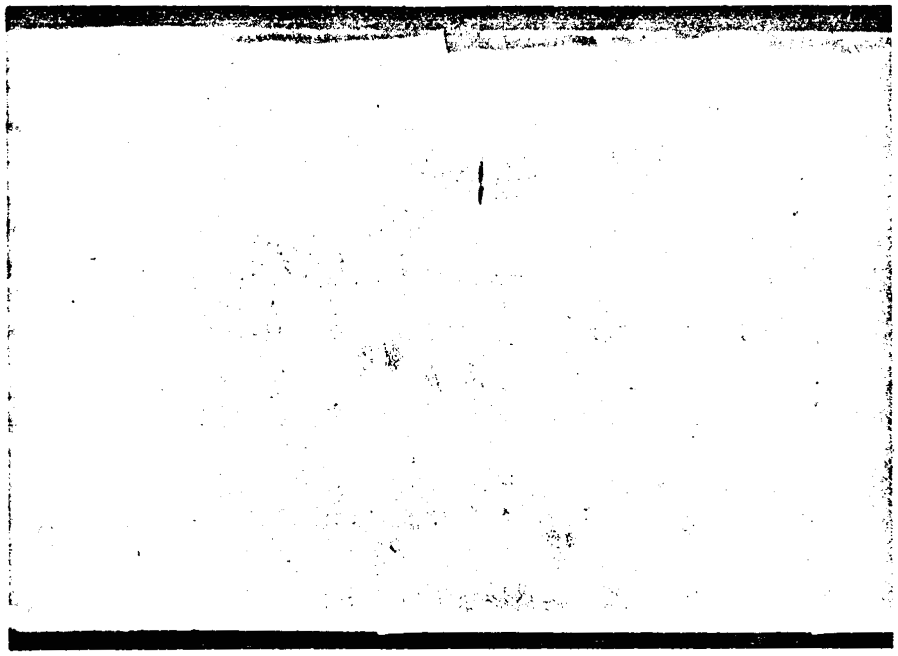
Similar features are seen in Figure 3-b with many wavy boundaries. In addition, the grain faces have a dimpled appearance which is suggestive of some type of substructure but has not yet been identified.

These microstructures indicate extensive GBS has occurred. In addition, they indicate several features which are typically associated with slip-GBS interactions in metals. The development of corrugated grain boundaries and polygonization at boundaries have been explained in terms of slip band interactions with grain boundaries.[8,14,38]

Unfortunately, the rapid thermal healing and faceting from thermal etching made the detection of folds from localized slip at triple points or of slip traces nearly impossible even if they had existed. Similarly, the deep thermal etching of the grain boundaries probably resulted from the high strain as well as the applied stress so that an indication of intergranular separation is not possible from these surface replicas.

There was an indication of strain enhanced grain growth in this specimen. Grain sizes were determined from the fracture surface near each surface where strain is a maximum and near the center of the bar where it is nearly zero. Values of 1.5 and 1.8 μ were found near the surfaces and 1.3 μ near the center. Similar measurements are being made on other specimens in order to establish the validity of these results. This type of grain growth is indicative of the amount of stress or strain enhanced grain boundary migration which occurs.

Several of the mechanical observations such as a strong rate of work hardening, an apparent yield point, a strong Bauschinger effect and 'strain aging' are typically explained by dislocation mechanisms including dislocation interactions, dislocation locking and particularly in oxide single crystals, dislocation multiplication mechanisms.[13,23,47] In addition, the



#5116 (a) 20X

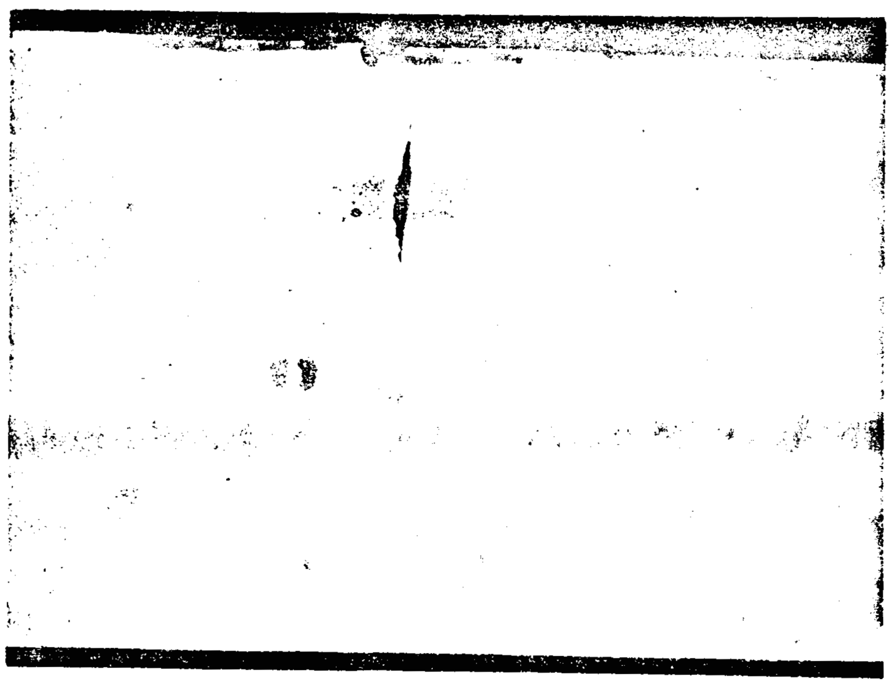


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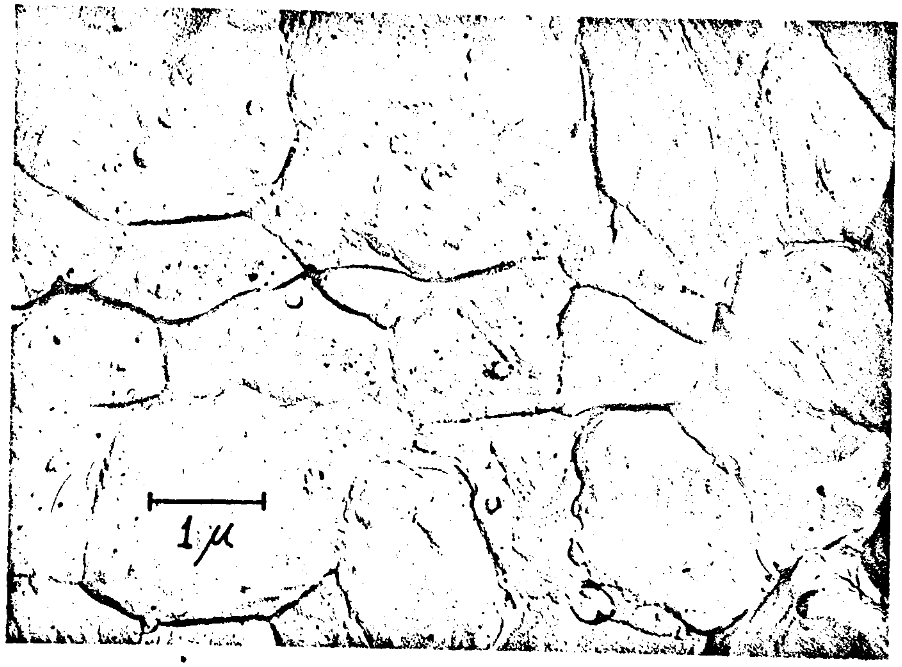
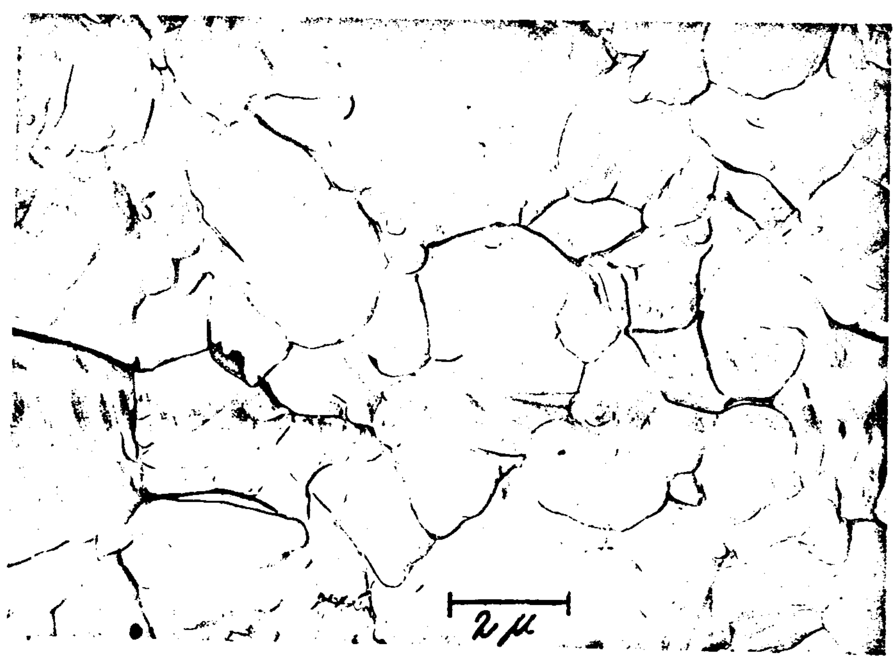
Figure 2. Crack seen in Surface of Specimen FLUX-30 during Multiple Bending, (a) after Bend No. 2, (b) after Bend No. 4.



#69849 (a) 15,000X



#69853 (b) 7500X

Figure 3. Replica Micrographs from Specimen FLUX-27 after Failure during Sixth Cycle, (a) Surface 'B', (b) Surface 'A'.

microstructural observations also are suggestive of dislocation contributions to the strain by grain shape change. This possibility is in conflict with several factors. The flow stress of these fine grained polycrystals is even lower than that of basal slip in sapphire under many conditions and its much lower than that of the non-basal slip systems in sapphire. In addition, there is no direct evidence of slip contributions from etch pit identification or transmission microscopy for polycrystalline materials except for somewhat coarser grained material upset forged at temperatures of 1800°C and above.[2] This is somewhat inconslusive, however, in view of the relative ease with which dislocations can be anihilated at grain boundaries in fine grained materials.

In order to facilitate such a comparison flexural flow stress data for several polycrystalline materials are plotted versus temperature in Figure 4 along with upper yield stress data for slip on several systems in sapphire; all data are for a tensile strain rate of 4×10^{-5} sec^{-1}. Data for tensile[48] and compressive[23] yield stress of basal slip in sapphire is shown; the stress is the tensile stress for a nominal 60° orientation. The scatter in the compressive yield at lower temperatures is due to concurrent twinning. In addition, the upper yield stress for compression of 0° sapphire which resulted in slip on what was presumed to be rhombohedral slip[49] is plotted along with a point for rhombohedral slip in a whisker.[50] Also plotted is the upper yield stress necessary to activate basal kinking in compression of 90° sapphire since this can also provide deformation normal to the basal plane.[49]

It can be seen that the flow stresses for the fine grained polycrystalline material is generally lower than the basal yield stress and more than an order of magnitude below that for rhombohedral slip. On the surface this suggests that slip in the fine grained polycrystalline material should not be significant. This conclusion cannot be finally accepted without a greater understanding of the factors controlling the yield stress in sapphire. The sharp yield stress for basal slip in sapphire is apparently the result of the dislocation multiplication process. However, it is not certain at the present whether the stress levels measured are those required to overcome the Peierls stress with the aid of thermal activation, or are determined by a dislocation climb process.[51] If they are limited by the Peierls barrier then similar stresses would have to be developed in polycrystalline materials to activate basal slip. If, however, the basal slip yield stress is determined by the stress necessary for dislocation multiplication, perhaps involving dislocation climb, then if GBS could provide an easier multiplication mechanism, basal slip would occur at lower resolved stresses than in those measured in sapphire. This is not unreasonable since the lack of cross-slip in Al_2O_3 presumably requires the creation of Frank-Read sources by a process such as climb.[23,52] However, several mechanisms have been proposed for the creation of dislocations at boundaries and recent evidence in metals indicates that the process of boundary sliding occurs by the movement grain boundary dislocations and results in the emission of dislocations into the lattice.[53,54] Presumably, such a mechanism could be equally applicable to rhombohedral as to basal slip. There is insufficient information available on either sapphire or polycrystalline Al_2O_3 to resolve this question at this time.

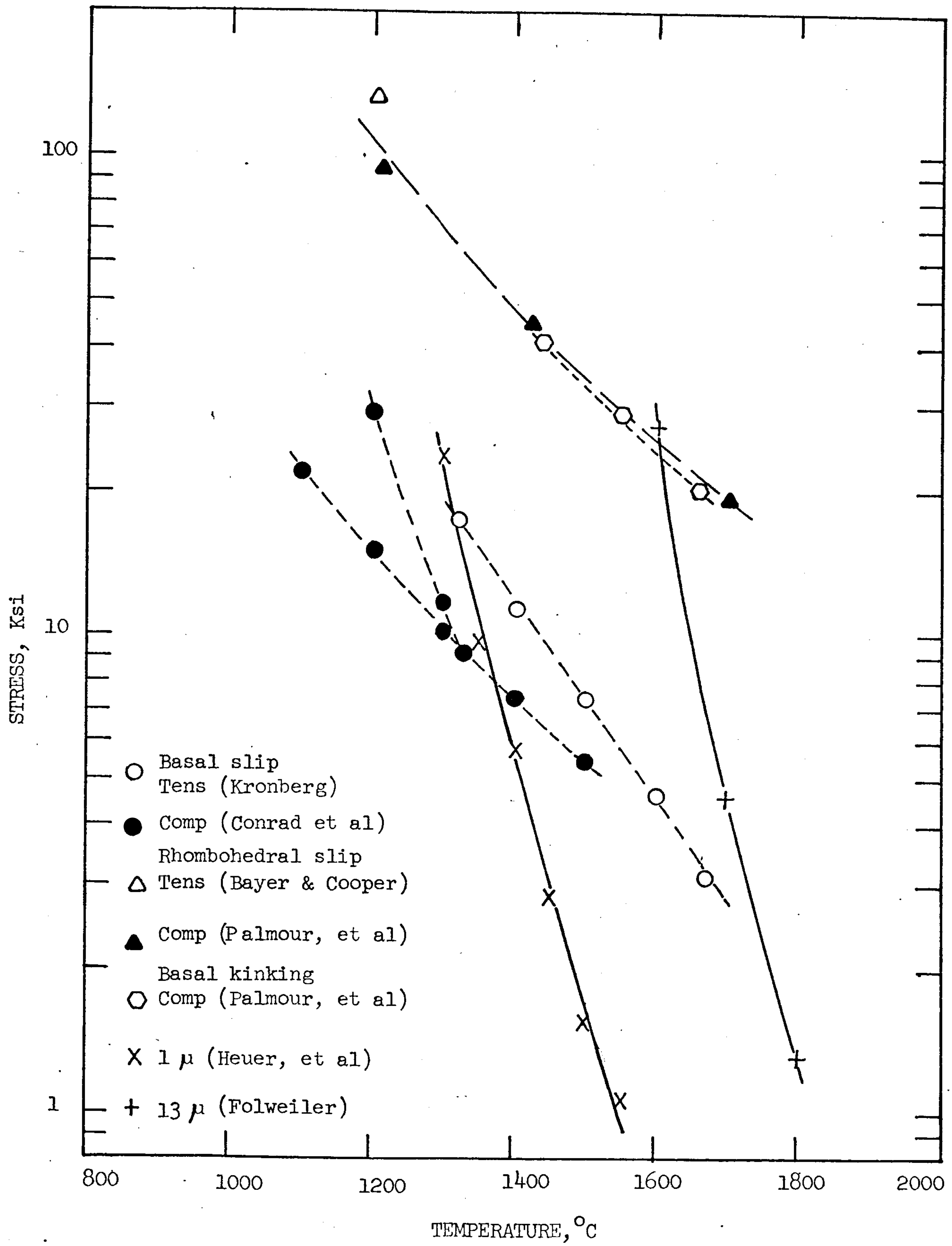


Figure 4. Yield Stress vs. Tempezature for 1 μ, and 13 μ[24] Polycrystalline Alumina and for Sapphire Oriented for Basal Slip,[23,48] Rhombohedral Slip,[49,50] and Basal Kinking.[49]

V. FUTURE WORK

The test series started during the first quarter will be finished during the next quarter and the results analyzed to provide guidance for the remainder of the program. Emphasis will continue to be upon the behavior of Al_2O_3; an additional series of tests designed to provide further information on the grain size dependence is planned. Tension and torsion testing are planned after the flexural testing is finished in order to provide continuous testing to higher strains and to failure.

The initial forgings are planned for the third quarter. Initial efforts will be the deep drawing of a hemisphere utilizing a fine-grained Al_2O_3 and a coarse grained MgO at high temperature.

VI. REFERENCES

1. a. R.W. Rice, "Hot Working Oxides," submitted for Refractory Oxides, ed. A. Alper, to be published by Academic Press.

   b. R.W. Rice, "Hot Forming of Ceramics," Proceedings of the 15th Sagamore Army Materials Research Conference, 1968, Syracuse University Press.

2. a. A.H. Heuer, W.H. Rhodes, D.J. Sellers and T. Vasilos, "Microstructure Studies of Polycrystalline Refractory Oxides," Avco Corp., Summary Report, Contract NOw-66-0506-(d), (1967).

   b. W.H. Rhodes, D.J. Sellers, T. Vasilos, A.H. Heuer, R. Duff and P. Burnett, Avco Corp., Summary Report, Contract NOw-65-0316-f (1966).

   c. L.A. Brissette, P. Burnett, R.M. Spriggs and T. Vasilos, J. Am. Ceram. Soc., 49, 165 (1966).

3. W.H. Rhodes, D.J. Sellers, R.M. Cannon, A.H. Heuer, W.R. Mitchell and P. Burnett, "Microstructure Studies in Polycrystalline Refractory Oxides," Avco Corp., Summary Report Contract N000-19-67-C-0336 (1968).

4. M.W. Benecke, "Semi-Continuous Pressure Sintering," Boeing Co., Final Report, Contract N00019-68-C-0165 (1969).

5. R.T. Dolloff and H.B. Probst, "Hot Extrusion of Carbides," presented at the 70th Annual Meeting of the Am. Ceram. Soc., April 1968. Am. Ceram. Soc. Bull., 47, (4), 441 (1968).

6. R.M. Haag, "Magnetic-Crystallographic Orientation Produced in Ferrites by Hot-Working," Avco Corp., Annual Report, Contract N00014-68-C-0364 (1969).

7. A.H. Heuer, D.J. Sellers and W.H. Rhodes, J. Am. Ceram. Soc., 52, 468 (1969).

8. R.B. Day and R.J. Stokes, J. Am. Ceram. Soc., 49, 345 (1966).

VI. REFERENCES (Cont'd)

9. S.M. Copley and J.A. Pask, J. Am. Ceram. Soc., 48, 636 (1965).

10. H. Tagai and T. Zisner, J. Am. Ceram. Soc., 51, 303 (1968).

11. G.W. Groves and A. Kelly, Phil. Mag., 8, (89), 877 (1963).

12. R.C. Gifkins, "Intergranular Creep Fracture," Tewksbury Symposium on Fracture (1963), University of Melbourne, (1965).

13. R.B. Day and R.J. Stokes, J. Am. Ceram. Soc., 47, 493 (1964).

14. A.W. Mullendore and N.J. Grant, "Grain Boundary Behavior in High Temperature Deformation," Proceedings of the 8th Sagamore Ordnance Materials Research Conference, 1961 (The Ordnance Materials Research Office).

15. E.M. Passmore, R.H. Duff and T. Vasilos, J. Am. Ceram. Soc., 49, 594 (1966).

16. R.W. Rice, J. Am. Ceram. Soc., 302, 52, 428 (1969).

17. J.W. Cahn, Acta. Met., 10, 789 (1962).

18. D.M. Choi and H. Palmour III, "Flow and Fracture of Hot Pressed Polycrystalline Spinel at Elevated Temperatures," North Carolina State U., Technical Report, Contract DA-31-124-ARO-D-207 (August 1965).

19. L.E. Poteat and C.S. Yust, "Grain Boundary Reactions During Deformation in Ceramic Microstructures," ed. R.M. Fulrath and J.A. Pask, Wiley (1968).

20. J.S. Nadeau, J. Am. Ceram. Soc., 52, 1 (1969).

21. W.L. Barmore and R.R. Vandervoort, J. Am. Ceram. Soc., 50, 316 (1967).

22. A.H. Heuer, R.M. Cannon,Jr., N.J. Tighe, "Plastic Deformation of Fine Grained Ceramics," presented at 15th Sagamore Army Materials Conference, 1968, Syracuse Univ. Press.

23. H. Conrad, G. Stone and K. Janowski, Trans. AIME, 233, 89 (1965).

24. R.C. Folweiler, J. Appl. Phys., 32, 773 (1961).

25. S.I. Warshaw and F.H. Norton, J. Am. Ceram. Soc., 45, 479 (1962).

26. W.L. Barmore and R.R. Vandervoort, J. Am. Ceram. Soc., 48 499 (1965).

27. C. Herring, J. Appl. Phys., 21, 437 (1950).

VI. REFERENCES (Cont'd)

28. I.M. Litshitz, Soviet Phys. JETP, 17, 909 (1963).

29. G.G. Bentle and R.M. Kniefel, J. Am. Ceram. Soc., 48, 570 (1965).

30. W.M. Armstrong, W.R. Irvine and R.H. Martison, J. Nucl. Matl's., 7, 133 (1962).

31. L.E. Poteat and C.S. Yust, J. Am. Ceram. Soc., 49, 410 (1966).

32. T.H. Alden, Trans. ASM, 61, 559 (1968).

33. R.E. Fryxell and B.A. Chandler, J. Am. Ceram. Soc., 47, 283 (1964).

34. E.M. Passmore and T. Vasilos, J. Am. Ceram. Soc., 49, 1966 (1966).

35. R. Scott, A.R. Hall, J. Williams, J. Nucl. Mat'ls., 1, 39 (1959).

36. W.M. Armstrong, W.R. Irvine, J. Nucl. Matl's., 9, 121 (1963).

37. a. G.T. Murray, J. Silgailis and A.J. Mountvala, J. Am. Ceram. Soc., 47, 531 (1964).

b. M.A. Adams and G.T. Murray, J. Appl. Phys., 33, 2126 (1962).

38. H. Conrad, "The Role of Grain Boundaries in Creep and Stress Rupture," in Mechanical Behavior of Materials at Elevated Temperatures, ed. J. Dorn, McGraw-Hill (1961).

39. J. Intrater and E.S. Machlin, Acta. Met., 7, 140 (1959).

40. H. Brunner and N.J. Grant, Trans. AIME, 215, 48 (1959).

41. E.W. Hart, Acta. Met., 15, 351 (1967).

42. R.M. Spriggs, J.B. Mitchell and T. Vasilos, J. Am. Ceram. Soc., 47, 323 (1964).

43. R.M. Spriggs, L.A. Brissette and T. Vasilos, J. Am. Ceram. Soc., 47, 417 (1964).

44. D.V. Poluboyarinov, R.Ya. Popil'skii, I.P. Galkina and V.S. Bakunou Izv. Akad. Nauk.SSSR, Neorg Mat'l, 2, 1115 (1966).

45. A.H. Heuer, and R.M. Cannon, Jr., "Plastic Deformation of Fine Grained Aluminum Oxide," presented at Symposium on Mechanical Testing Procedures for Brittle Materials, March 28-30, 1967, IITRI, Chicago, Ill.

46. R. Chang, "Diffusion Controlled Deformation and Shape Change in Non-Fissionable Ceramic," in Proceedings of the Conference on Nuclear Applications of Non-Fissionable Ceramics, ed. A. Boltax, and J.H. Handwerk, American Nuclear Society (1966).

VI. REFERENCES (Concl'd)

47. C.W.A. Newey and K.C. Radford, "Plastic Deformation of Magnesium Aluminate Single Crystals," Anisotropy in Single-Crystal Refractory Compounds, Vol. 2, ed., F.W. Vahldiek and S.A. Mersol, Plenum Press (1968).

48. M.L. Kronberg, J. Am. Ceram. Soc., 45, 274 (1962).

49. H. Palmour, III, et al, "Grain Boundary Sliding in Alumina Bicrystals," North Carolina State U., Progress Report No. ORO-3328-9, Contract AT-(40-1)-3328, (December 1968).

50. P.D. Bayer and R.E. Cooper, J. Mat'l. Sci., 2, 301 (1967).

51. H. Conrad, J. Am. Ceram. Soc., 48, 195 (1965).

52. J.C.M. Li, J. Appl. Phys., 32, 593 (1961).

53. C.A.P. Horton and C.J. Beevers, Acta. Met., 16, 733 (1968).

54. H. Gleiter, E. Hornbogen and G. Baro, Acta. Met., 16, 1053 (1968).