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November 1969

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## CREEP BEHAVIOR OF DOPED POLYCRYSTALLINE ALUMINUM OXIDE

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## ABSTRACT

Creep behavior of polycrystalline alumina doped with MgO and NiO, both as hot-pressed and also additionally annealed, was determined for 1300° to 1470°C and for 1000 to 15,000 psi. The deformed specimens contained intergranular separations. Creep rates were proportional to stress raised to 1.1 and 1.3, and independent of grain size changes occurring during creep. The suggested rate-controlling creep mechanism is localized plastic deformation accommodated by grain boundary separation initiated by limited grain boundary sliding.

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This study was done under the auspices of the United States Atomic Energy Commission. The senior author also received a grant from Hyogo Prefecture in Japan.

At the time this work was done the writers were, respectively, visiting professor and professor of ceramic engineering, Department of Materials Science and Engineering, University of California, Berkeley.

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## I. INTRODUCTION

In general, it has been reported that the creep of polycrystalline alumina is controlled by a lattice diffusional creep process. Folweiler<sup>1</sup> and Warshaw and Norton<sup>2</sup> determined (for fine-grained alumina, grain size 3 to 13 $\mu$ ) that the creep rates were proportional to the stress and inversely proportional to the square of the grain size as predicted by the Nabarro-Herring mechanism,<sup>3</sup> but did not obtain similar creep rates. When Folweiler's specimens, however, were tested with Warshaw and Norton's apparatus by Coble and Guerard,<sup>4</sup> better agreement in creep rates was obtained. Warshaw and Norton also observed that coarse-grained alumina (50 to 100 $\mu$ ) behaved plastically when deformed ( $\dot{\epsilon} \sim \sigma^4$ ). It is of interest that all of these investigators found evidences of grain boundary sliding, and that Coble and Guerard also observed grain boundary separation at the end of the tests. Hewson and Kingery<sup>5</sup> showed that addition of MgO reduced the creep rate of alumina, and that the lattice diffusional creep model applied. Coble and Guerard, on the other hand, found that the creep rate of alumina was enhanced by a factor of 5 to 10 times by Cr<sub>2</sub>O<sub>3</sub> addition.

Poteat and Yust<sup>6</sup> found that the microstructure of polycrystalline thoria specimens deformed in creep contained intergranular voids which were formed by the apparent growth and coalescence of pores along the grain boundaries, and that grain boundary sliding occurred during creep. They concluded that the strain rate-stress relation indicated a viscous type of creep process (stress exponents varied from 1.04 to 1.59). Passmore et al.<sup>7</sup> in creep studies on polycrystalline magnesia also found that intergranular pores formed which, with continued strain, inter-

connected to form intergranular cracks; stress exponents of 1.0 and 1.5 were determined. Bush and Hummel<sup>8</sup> have also associated room-temperature creep in beta-encryptite with crack growth and propagation.

In this paper, compressive creep behavior for fine grained alumina doped with a small amount of MgO and NiO is discussed on the basis of mechanical creep data and microstructural observations. Possible creep mechanisms are explored.

## II. EXPERIMENTAL PROCEDURES

Alumina squares, 2.5 x 2.5 x 0.5 in., were prepared by hot-pressing Al<sub>2</sub>O<sub>3</sub> powder,\* doped with 0.23 wt.% MgO and 0.22 wt.% NiO, in graphite dies at 1450°C. The hot-pressed density was 3.987 (approximately 99.5% of theoretical relative to Al<sub>2</sub>O<sub>3</sub>). Specimens were cut to dimensions of 0.225 x 0.225 x 0.5 in. and surfaces were ground smooth using a 400 grit diamond abrasive wheel. These were black because of hot-pressing in a CO gas environment. They became light green after annealing in air for a sufficient time at temperatures above 1400°C and had a density of 3.790. Traces of spinel were detected by X-ray diffraction in specimens annealed in air at 1500°C for 1 h, but no minor phases were detected in the hot-pressed specimens. In order to determine the crystalline phases more definitively, additional specimens containing 15.0 and 42.3 wt.% of NiO were prepared in a similar manner and examined by X-ray diffraction: after hot-pressing,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ni metal were present; and after annealing in air, NiAl<sub>2</sub>O<sub>4</sub> spinel and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

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\* Powder contained 0.021 wt.% SiO<sub>2</sub>, 0.00016 Na<sub>2</sub>O, 0.0011 CuO, 0.0018 Fe<sub>2</sub>O<sub>3</sub>, determined chemically.

Creep tests were performed on both the hot-pressed specimens and specimens which received an additional annealing for 168 h at 1430°C. Specimens were deformed in compression at temperatures of 1300° to 1470°C in air. Compressive strain was measured over the 0.5 in. length using a linear variable differential transformer in combination with a recording potentiometer. The stress direction was the same as the hot-pressing direction. Temperatures were measured with a Pt/Pt-10Rh thermocouple and controlled to  $\pm 2^\circ\text{C}$ . The experimental setup is described by Hulse and Copley.<sup>9</sup>

Microstructures were observed with a scanning electron microscope\* on fracture surfaces.

### III. RESULTS

#### (1) Stress and Temperature Dependence of Creep

In general, the steady-state creep rate,  $\dot{\epsilon}$ , for many metallic and ceramic materials is expressed by the equation

$$\dot{\epsilon} = A \sigma^n \exp(-\Delta H/RT) \quad (1)$$

where  $\sigma$  is the applied stress,  $\Delta H$  is the activation energy for creep,  $R$  is the gas constant,  $T$  is the temperature in degrees Kelvin,  $A$  is some function involving structure, and  $n$  is a constant. The stress exponent,  $n$ , aids in determining the rate-controlling mechanisms.

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\* The microscope was made available through Grant No. GB-6428 from the National Science Foundation and Grant No. GM 15536 from the National Institute of Health to Prof. T. E. Everhart.

To avoid experimental scatter between specimens,  $n$  was determined from a single specimen by measuring  $\dot{\epsilon}$  for a range of stresses at a constant temperature. A stress was maintained constant until steady-state creep was reached, and then instantaneously changed either up or down and maintained constant until  $\dot{\epsilon}$  was again steady.<sup>10</sup> Changes in stress were made at true strain intervals of 0.02 to 0.03.

The results of tests for both hot-pressed and annealed specimens from 1300 to 1470°C are shown in Fig. 1. The numbered points for each of the series shown represent the order in which the indicated applied stresses were changed. The legend for each line includes the grain size (GS) at the beginning and at the end of the creep experiment. As an example, for the hot-pressed specimen at 1470°C, grain size of pt. 1 at the beginning of the series was  $\sim 3\mu$  and of pt. 7 at the end of the series was  $\sim 7\mu$ . Since the scatter of points for a given series at all temperatures is random and not too excessive, it is deduced that the creep rate was independent of any grain size changes during creep within the limits covered by these experiments. For hot-pressed specimens  $n$  is about 1.1; for annealed specimens,  $n$  is about 1.3.

If  $n$  is independent of temperature and any structural changes (Fig. 1), a plot of the ratios of the strain rates vs stresses before and after the changes in stress for all experimental conditions should reduce to a single line. Such plots, seen in Fig. 2, again show lines with slopes,  $n$ , of 1.1 and 1.3, respectively.

Figure 3 shows the temperature dependencies for creep at several stress levels based on actual experimental points. The activation



energy was determined to be  $95 \pm 5$  kcal/mol for hot-pressed specimens and 126 kcal/mol for the annealed specimens. The small variation shown is a reflection of the slight scatter of points. Folweiler<sup>1</sup> and Warshaw and Norton<sup>2</sup> have reported  $\Delta H$  values of 130 kcal/mol for small grain size specimens. Hewson and Kingery<sup>5</sup> obtained a value of 110 kcal/mol for specimens doped with MgO. Passmore and Vasilos<sup>11</sup> calculated average values of  $142.5 \pm 8$  kcal/mol for dense (99.5% density), pure (99.9%) and fine grain size ( $2\mu$ ) specimens using the incremental stress and temperature method.

The creep dependence on stress can also be indicated by a plot of the temperature-compensated creep rate, called Z parameter, versus stress according to the relationship<sup>12</sup> represented by the equation

$$Z = \dot{\epsilon}_s \exp (\Delta H/RT) = f (\sigma) \quad (2)$$

where  $\dot{\epsilon}_s$  is the steady-state creep rate at a given stress. Figure 4 shows such a plot for hot-pressed specimens using the  $\Delta H$  value of 95 kcal/mol. Lines with slopes of  $n = 1.0$  and  $2.0$  are shown for comparison. The general fit to a straight line and random scatter of points also suggest that no change in the creep mechanism occurred over the test temperature range.

## (2) Microstructure Observations

The fracture surface of a hot-pressed specimen is shown in Fig. 5. The grain size is about  $3\mu$ , and it is black in appearance. In this specimen pores are visible along grain boundaries; normally, they are too small to be observed at the indicated magnification. Figure 6a

shows the microstructure of a hot-pressed specimen heated at 1400°C for about 70 h (grain size of 4 $\mu$ ); Fig. 7a is of one of these specimens annealed at 1430°C for 168 h (grain size of 6 $\mu$ ). The latter was light greenish throughout, and the former had a dark core with a light greenish outer shell as would be expected for a diffusion-controlled oxidation process. None of the specimens with a dark core, however, showed any discernible differences in microstructure in the two zones; the photographs show sections in the central portion of the specimens. In addition to grain growth, the annealed specimens showed a considerable number of intergranular voids which accounted for the lower density. The mechanisms for the void formation are unknown although they must be associated with the oxidation of the hot-pressed specimens.

The hot-pressed specimen strained at 1400°C for about 70 h is shown in Fig. 6b. Its grain size has increased to 5 $\mu$  in contrast to an increase to 4 $\mu$  in the absence of stress. A further comparison with Fig. 6a indicates that many intergranular voids and grain boundary separations perpendicular to the generated tensile stresses have occurred as a result of creeping. The annealed specimen deformed at 1400°C for 70 h is shown in Fig. 7b. A comparison with Fig. 7a indicates that during creep grain boundary migration occurred as evidenced by larger voids. The average grain size, however, remained essentially the same.

The appearance of a surface after creep at 1300°C for 200 h under a stress of 5000 psi is shown in Fig. 8. Some grain rotations caused by grain boundary sliding are indicated by the small black arrows. Several grains, marked A and B, were actually ejected from the matrix on the

surface. This phenomenon was also mentioned by Folweiler.<sup>1</sup>

Greater grain growth and grain boundary separation were observed in the strained hot-pressed specimens with increase of the creep temperature above 1300°C. Figure 9a shows a fractured surface of a specimen deformed at 1470°C for about 70 h (grain size about 7 $\mu$ ). Large internal cracks are visible. Figure 9b is an enlarged sketch of the outlined area in Fig. 9a. Grain boundary separation is indicated by corresponding lettered points. The boundaries that separated were essentially perpendicular to the tensile stresses caused by the uniaxial compression.

#### IV. DISCUSSION

##### (1) Grain Boundary Sliding and Separation Mechanism

One of the characteristic features of all of the creep specimens was the occurrence of grain boundary separations. Figure 10 shows a schematic sketch of a possible model for such a mechanism along grain boundaries defined by grains A, B, C and D; the upper part of the separation with closure is not shown. An intergranular crack could be generated initially as a wedge-shaped void by grain boundary sliding (shearing) at the triple point (line on a three-dimensional basis) formed by grains A, B, and C.<sup>13</sup> The void or crack is gradually extended until it is blocked by a barrier such as another properly oriented triple point which thus acts as a stress concentration point. Stresses developed at such points are relieved by localized plastic deformation as well as sliding and adjustment of grain boundaries which results in three-dimensional grain rotations and grain boundary migrations.

(2) Evaluation of Rate Controlling Creep Mechanism

Diffusional or viscous creep requires the stress exponent,  $n$ , of Eq. (1) to be 1.<sup>3</sup> The exponent has been reported to vary from 3 to 5.5 for mechanisms based on some type of dislocation interaction in the lattice,<sup>14</sup> and a value as high as 6.6 has been observed for creep of polycrystalline LiF.<sup>10</sup> The latter mechanisms show no grain size dependence. The diffusional creep mechanisms, however, have an inverse grain size relationship and can be expressed by a modification of Eq. (1) at a constant temperature in the form

$$\dot{\epsilon} = \frac{K}{(G.S.)^m} \quad (3)$$

where  $K$  is a constant,  $(G.S.)$  is the grain size, and  $m$  is a constant. The value of  $m$  is associated with the mechanism of diffusional creep:  $m = 2$  represents bulk or lattice diffusional creep (Nabarro-Herring<sup>3</sup>);  $m = 3$ , grain boundary creep with grain elongation (Coble<sup>15</sup>) or grain boundary sliding with no grain elongation (Gifkins<sup>16</sup>); and  $m = 1$ , accommodated grain boundary sliding with some grain elongation (Gifkins<sup>16</sup>). It is evident from Eq. (3) that any grain growth during creep would lead to a time decay in the strain rate. Consequently, the data obtained at a given temperature with the described incremental stress technique would be expected to show a larger scatter of points than observed experimentally if the specimen was exhibiting diffusional creep, e.g., pt. 6 for the hot-pressed material at 1470°C should have a  $\dot{\epsilon}$  of  $2.1 \times 10^{-6} \text{ sec}^{-1}$  if  $m$  in Eq. (3) is taken to be 1 instead of a value equal to that for pt. 1 at which time the grain size was about half

that at pt. 6. Specimens with varying starting grain size were not available to verify the non-existence of grain size dependence more definitively.

It is possible to calculate creep rates using the equations proposed by Nabarro-Herring, Coble, and Gifkins but the values would be meaningless considering the apparent lack of experimental grain size dependence. This type of procedure is tempting in comparing the hot-pressed and annealed specimens whose starting grain sizes are 3 and 6 $\mu$  since the creep rate for the former was found to be faster by a factor of about 2 for equivalent test conditions. This approach, however, also is not valid because of the differences in the character of the grain boundaries and the different values of  $\Delta H$  for creep for the two types of specimens.

The dominant rate-controlling mechanism for creep in these polycrystalline specimens appears to be some deformation mechanism which has been accommodated by grain boundary separation initiated by a limited amount of grain boundary sliding. If grain boundary integrity were maintained during creep, then some dislocation climb and interaction mechanism would have to operate because of the lack of capability of polycrystalline alumina to deform only by glide within the grains,<sup>17</sup> and the stress exponent  $n$  would be expected to have some value above 3. The strength of the grain boundaries appears to be sufficiently low to allow their separation under localized stress concentrations. This accommodation mechanism is non-diffusional in nature and thus not dependent on the grain size (at least within the indicated experimental conditions); also, the lack of interaction between the separations themselves does not

contribute to an increase in the stress exponent. The experimental values of about 1.1 and 1.3 thus suggest localized plastic deformation within the grains at the stress concentration points (the increase in exponent for the annealed specimens can be attributed to stronger grain boundaries) with a considerable contribution to the accommodation process within the specimens by grain boundary separations. The grain boundary migration associated with the accelerated grain growth and/or growth of void size during creep also must be a further means of accommodation of some of the stress concentrations within the system.

#### V. SUMMARY

Creep characteristics of polycrystalline alumina containing 0.23 wt/o of MgO and 0.22 wt/o of NiO, both as hot-pressed and as annealed, were determined from 1300° to 1470°C under stresses of 1000 to 15,000 psi.

1. The creep rates were proportional to stress raised to the 1.1 and 1.3 power. No grain size dependence, as a result of grain size changes during creep, was observed.
2. The activation energies for creep were determined as 95±5 kcal/mol for hot-pressed specimens and 126 kcal/mol for annealed specimens.
3. The rate-controlling creep mechanism for these specimens appears to be some localized deformation mechanism which has been accommodated by grain boundary separation that has been initiated by limited grain boundary sliding. Grain boundary migration contributes to the accommodation of stress concentrations arising within the system.

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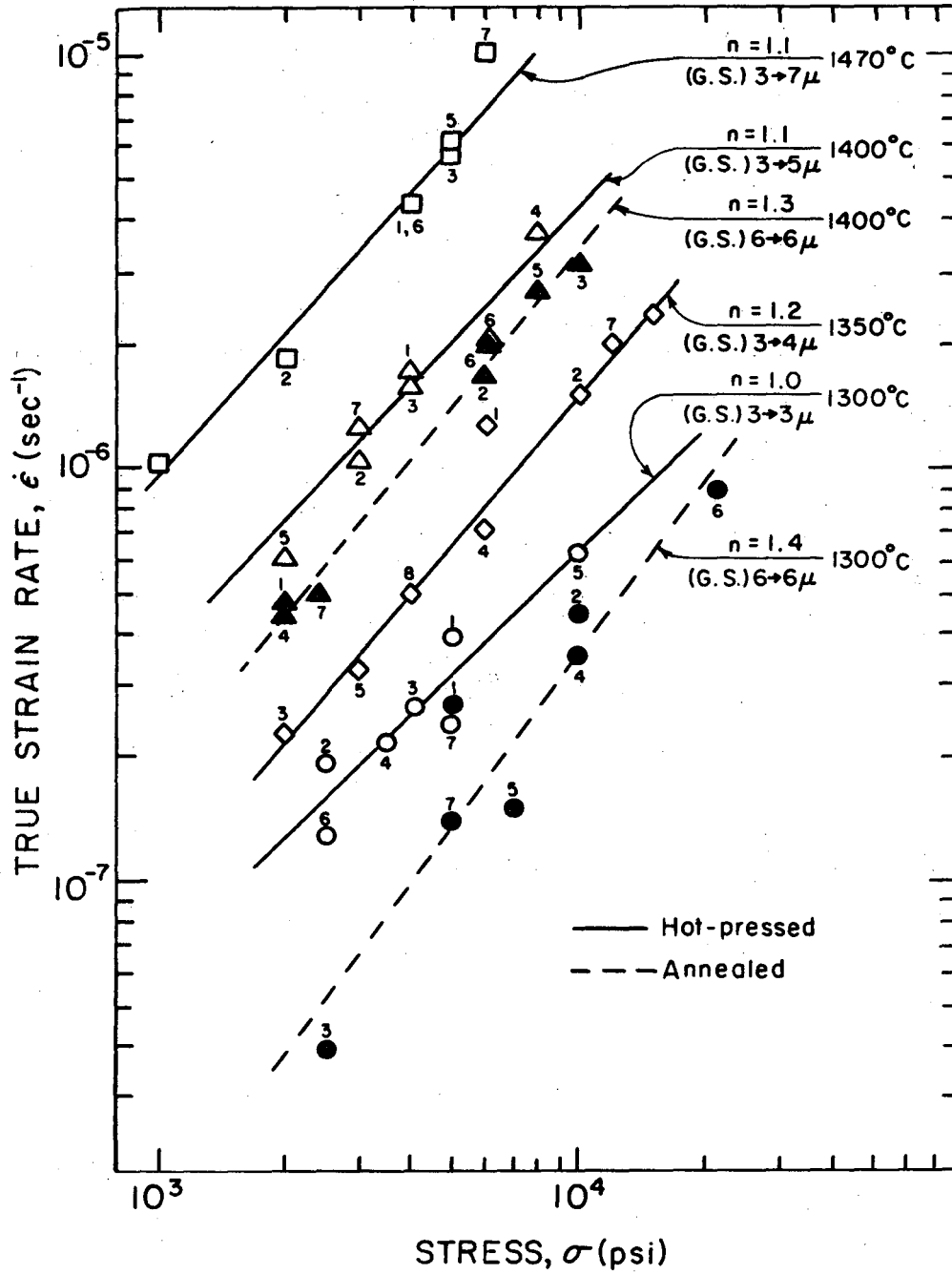


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FIGURE CAPTIONS

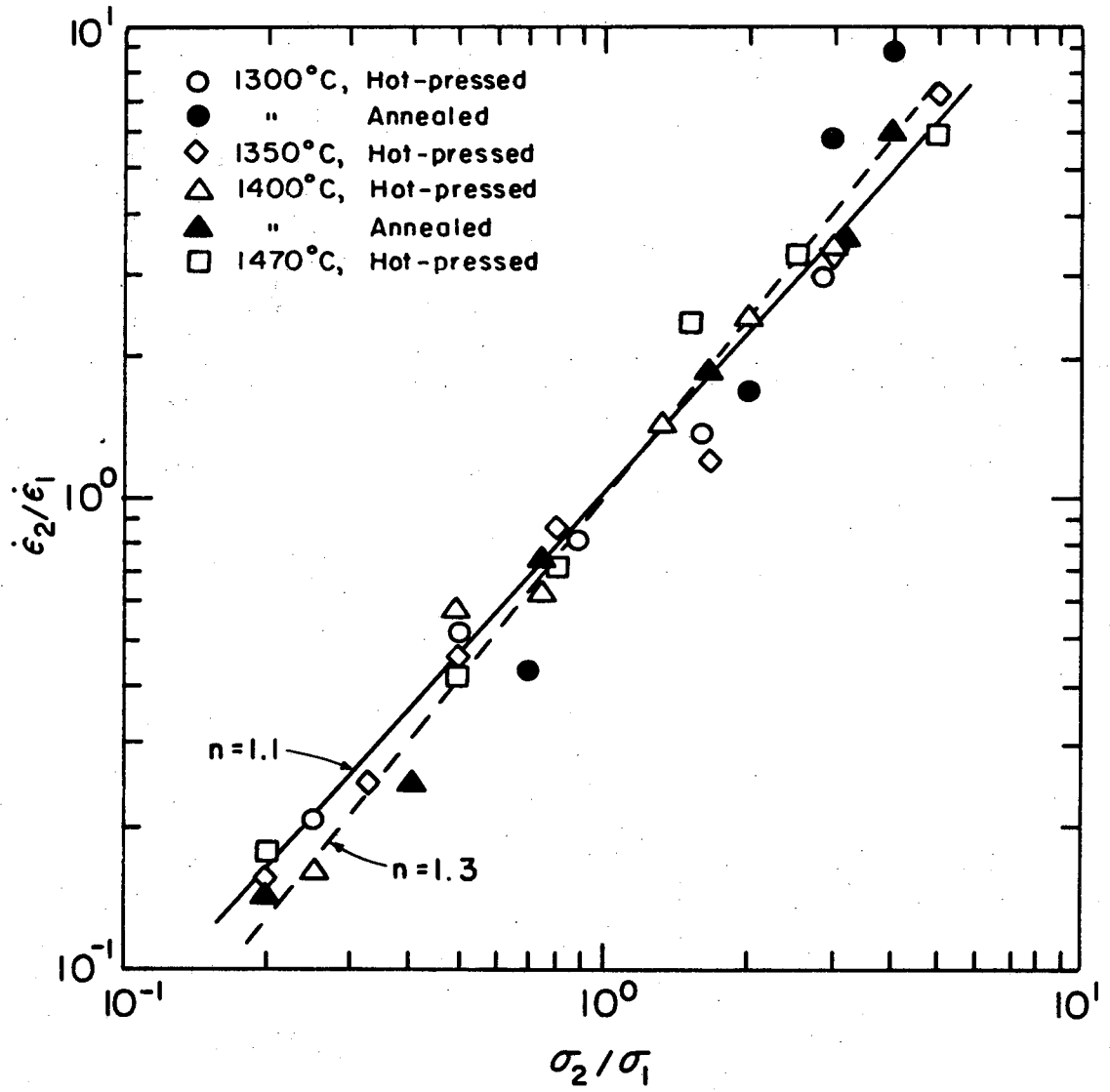
- Figure 1. Creep rate versus stress for specimens of two different heat treatments and grain sizes.
- Figure 2. Creep rate ratios versus stress ratios obtained by instantaneous changes in the stress at constant temperature.
- Figure 3. Temperature dependence of creep rate for specimens of two different heat treatments.
- Figure 4. Temperature-compensated creep rate plotted as a function of the stress for hot-pressed specimens.
- Figure 5. Fracture surface of hot-pressed specimen before creep testing.
- Figure 6. Fracture surfaces of hot-pressed specimens after being heated together at 1400°C for about 70 hours: (a) with no loading, and (b) after creeping. Arrows indicate stress direction.
- Figure 7. Fracture surfaces of (a) specimen annealed at 1430°C for 168 h and (b) annealed specimen after creep at 1400°C for about 70 h. Arrows indicate stress direction.
- Figure 8. Appearance of polished surface after creep. Creep test was performed at 1300°C for 200 h under a stress of 5000 psi. White arrows indicate stress direction and small black arrows indicate grain rotations by grain boundary sliding.
- Figure 9. An example of grain boundary separation in hot-pressed specimen after creep, and (b) enlarged sketch of indicated section in (a) with intergranular separation indicated by corresponding points. Arrows indicate stress direction.

Figure 10. A model of void formation due to grain boundary sliding and separation with a vertically applied compressive stress: in figure, (a) represents distance of separation, and (b) distance of sliding with grain boundary shearing.



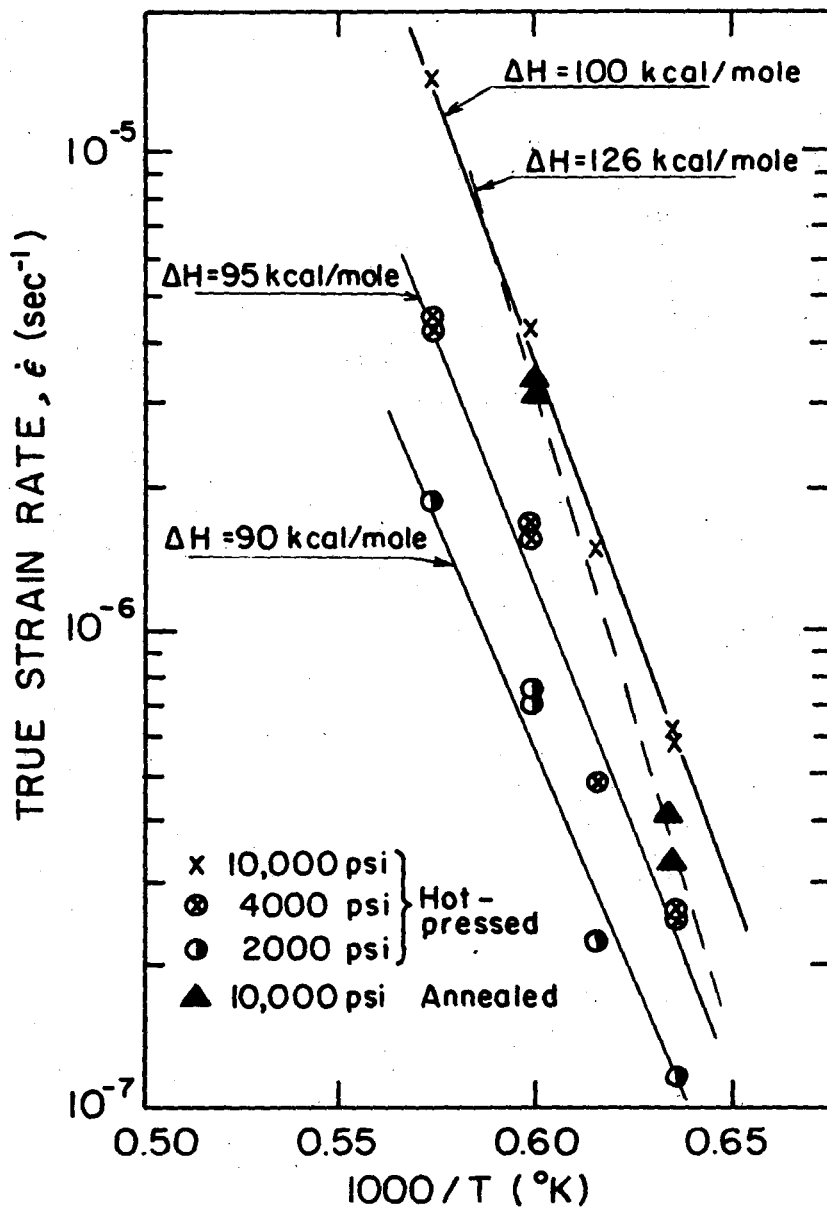
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Fig. 1



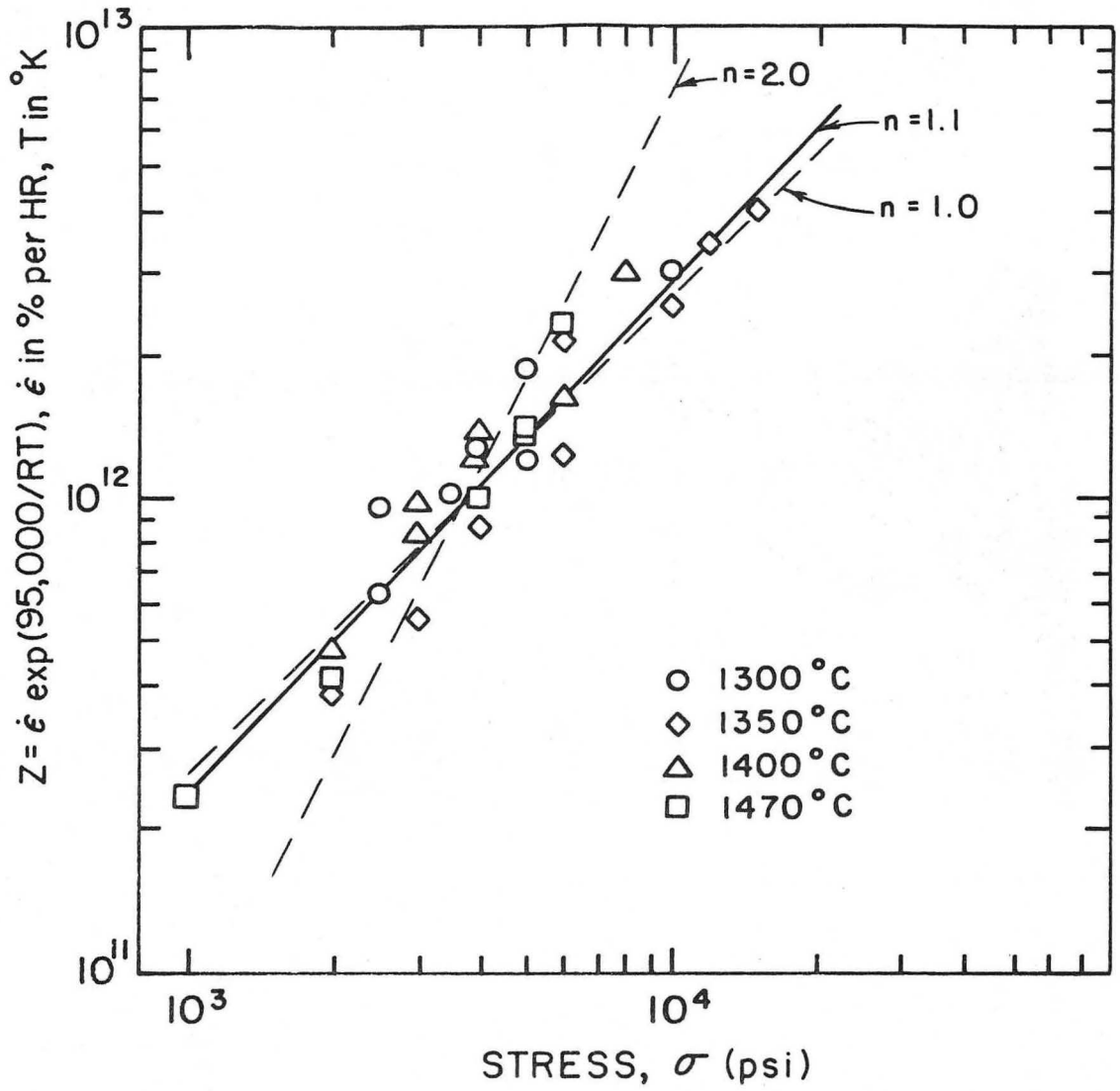
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Fig. 2



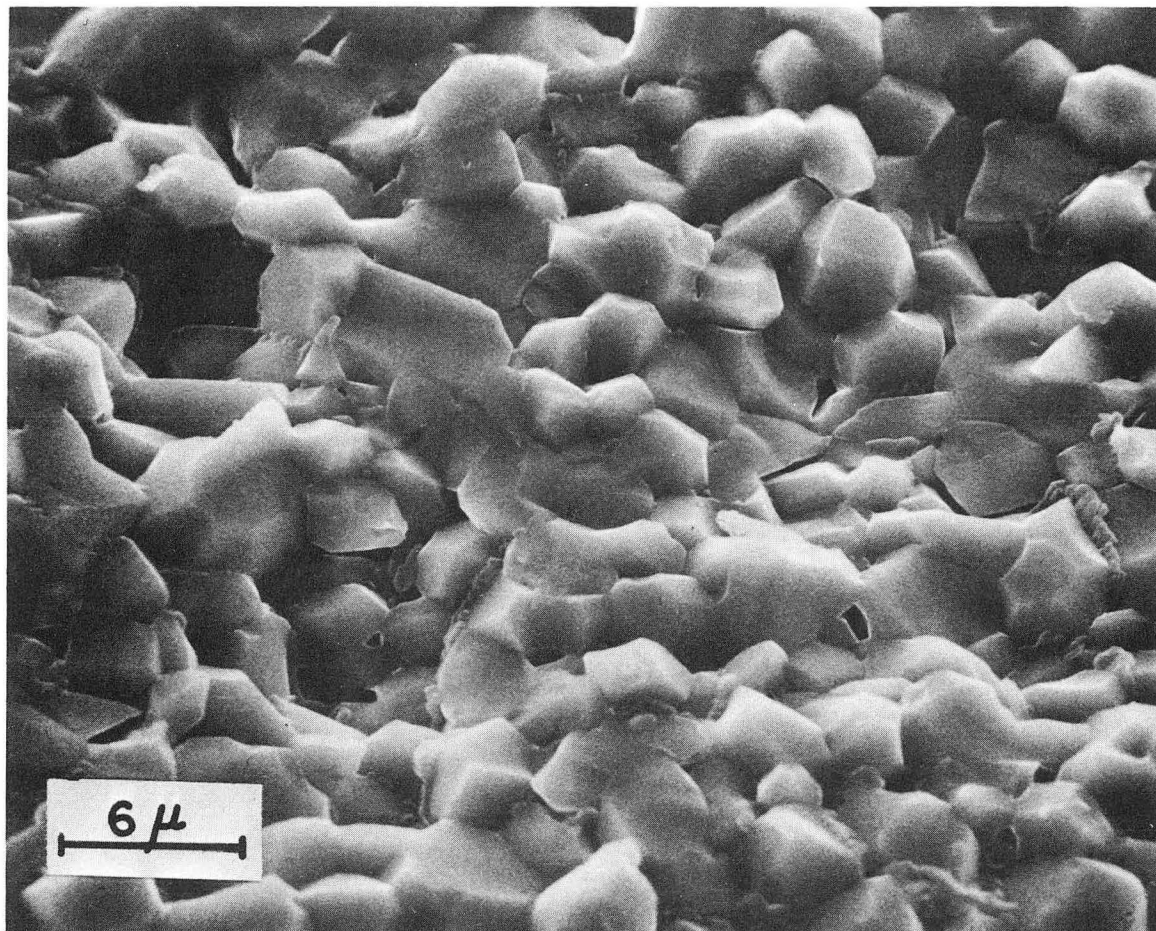
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Fig. 3



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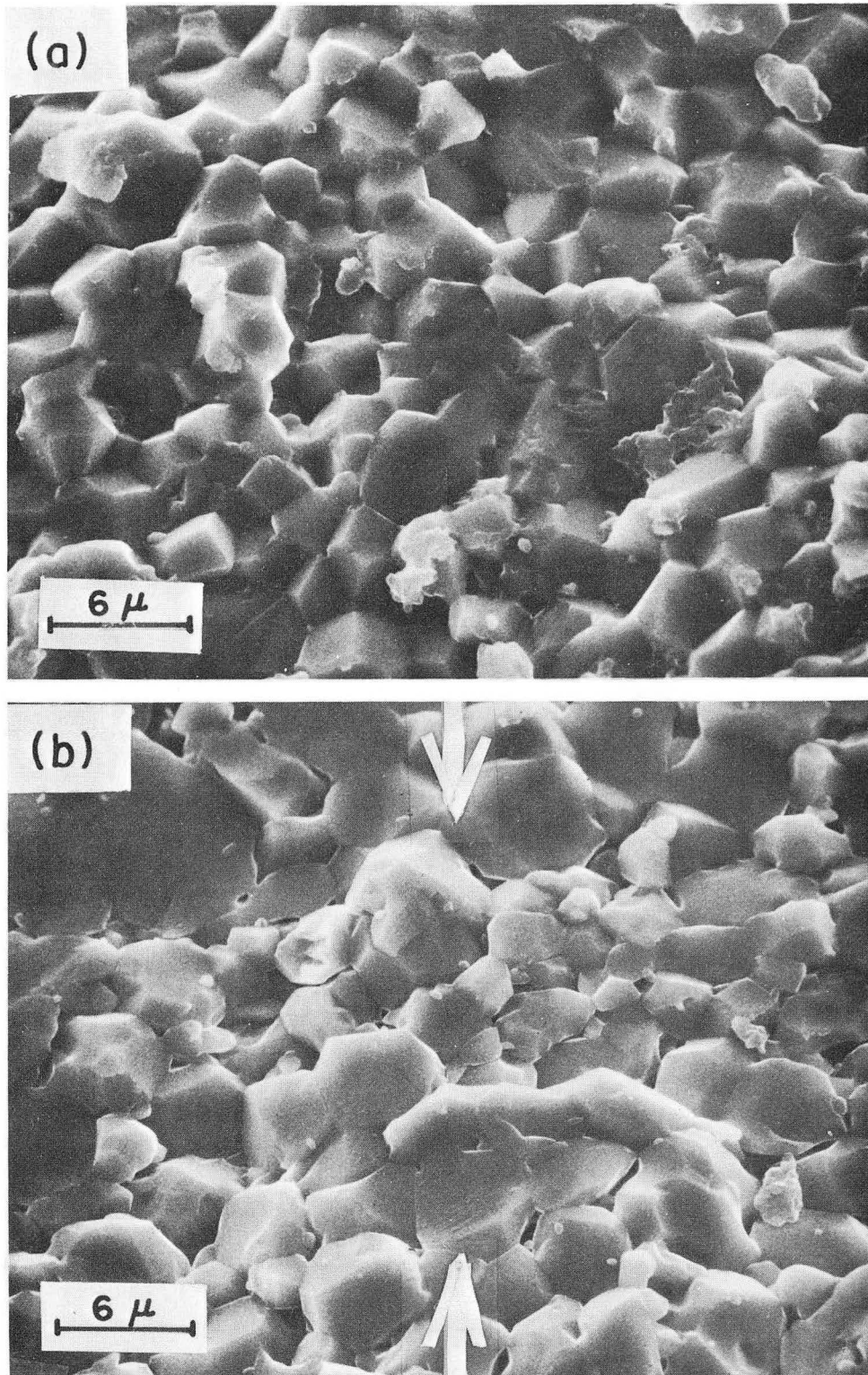
Fig. 4



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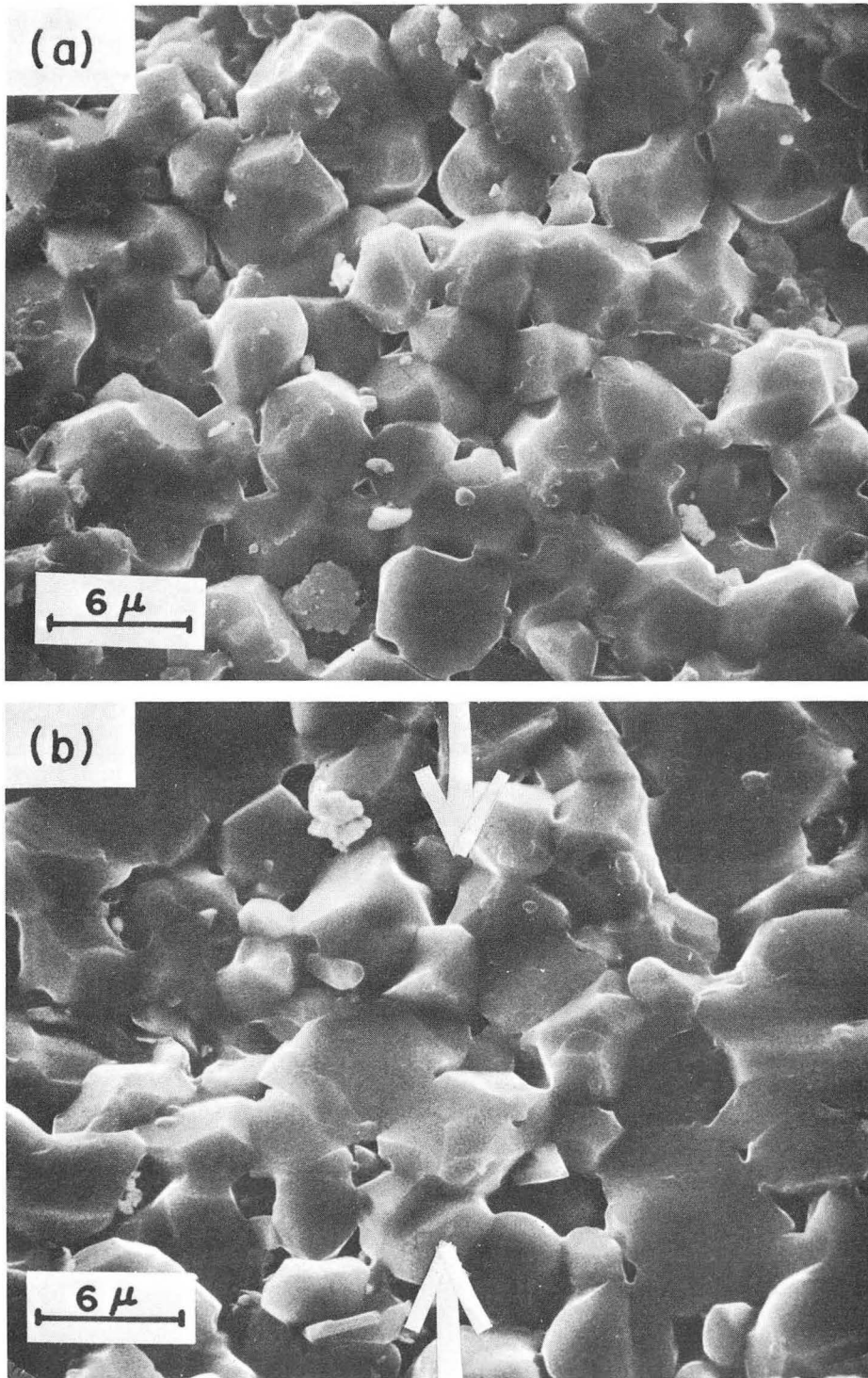
Fig. 5





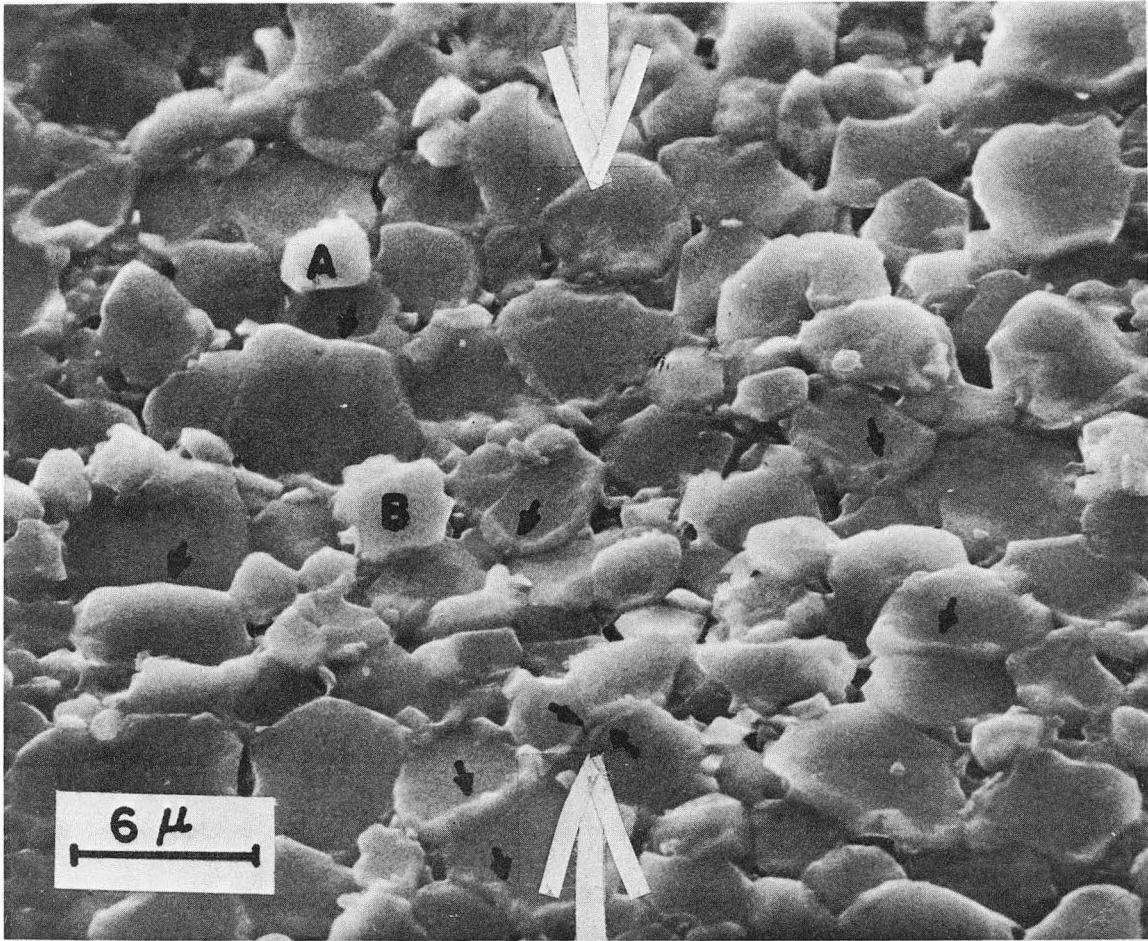
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Fig. 6



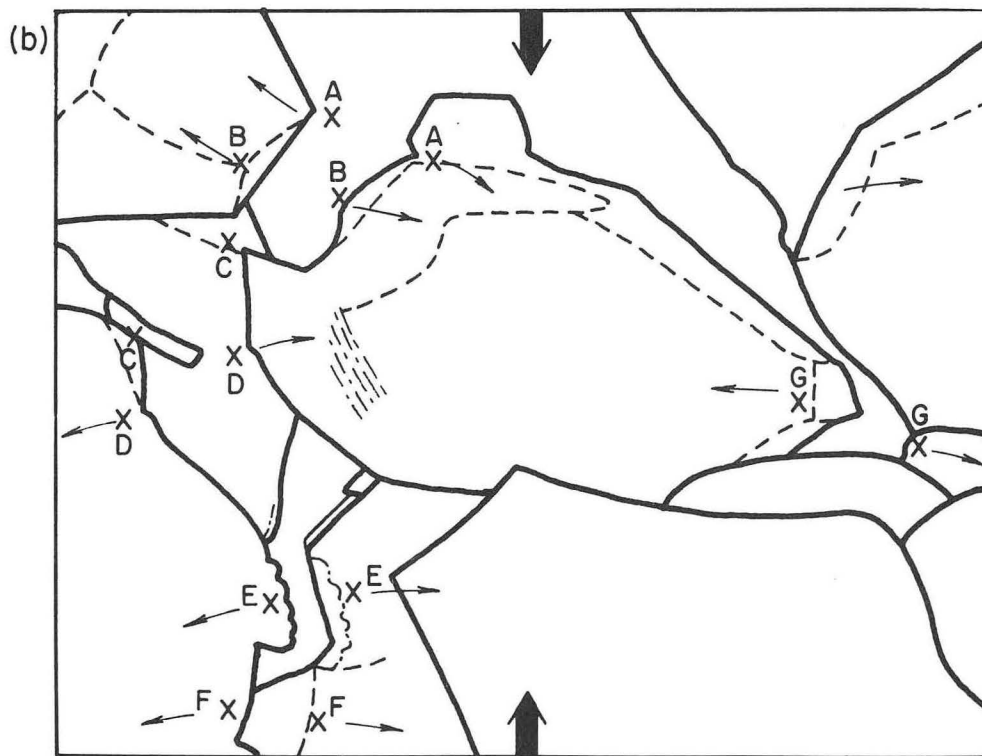
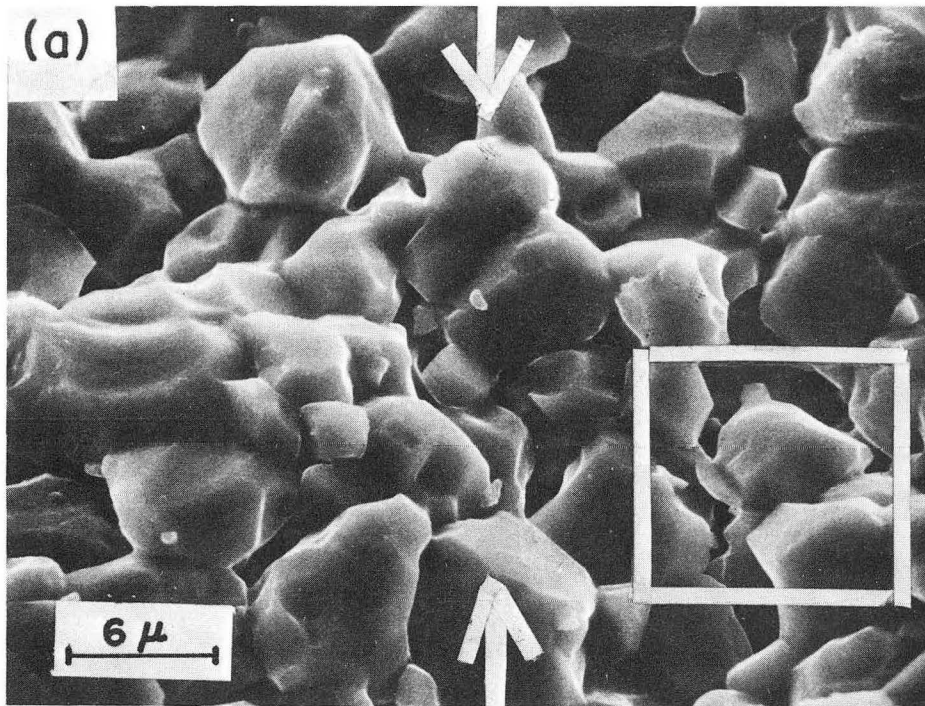
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Fig. 7



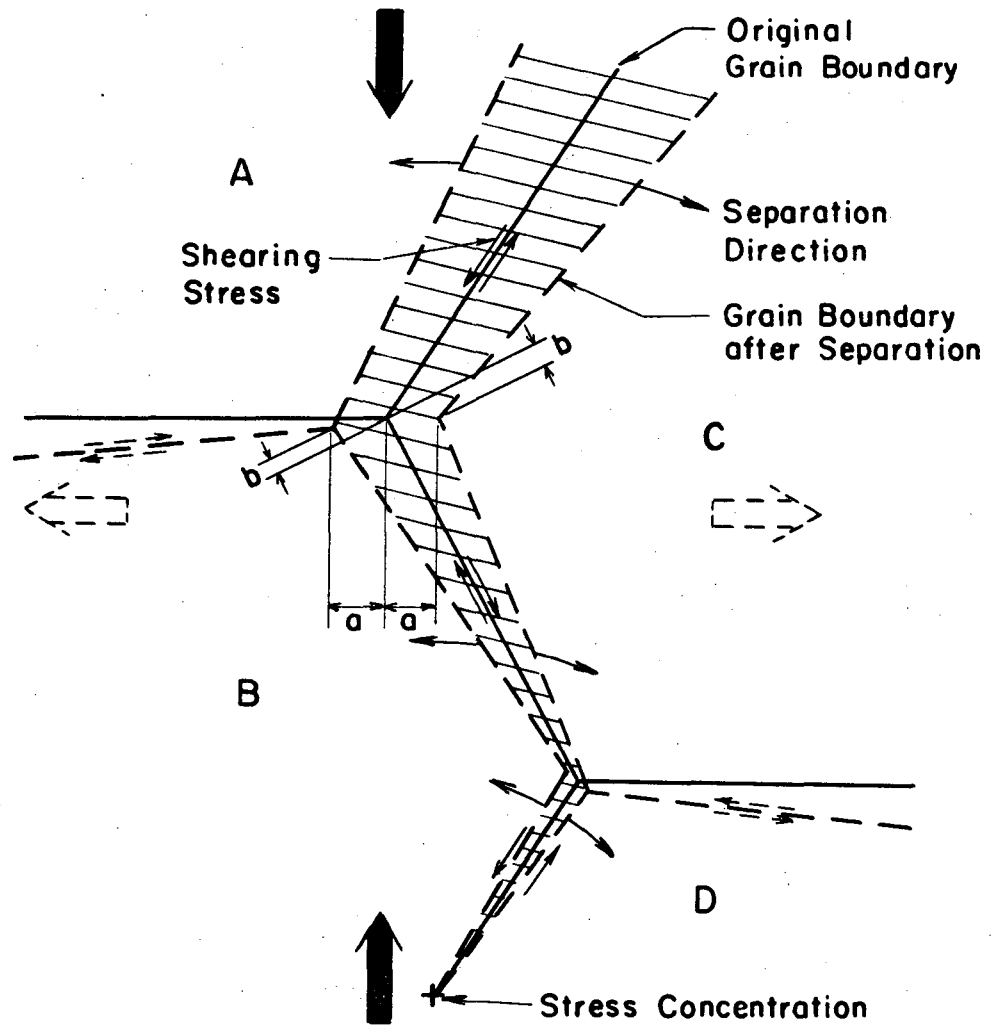
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Fig. 8



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Fig. 9



XBL 696-805

Fig. 10

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