Title

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Publication Date

1975-09-01

Submitted to Journal of
American Ceramic Society

LBL 3700 Rev.
Preprint C.1

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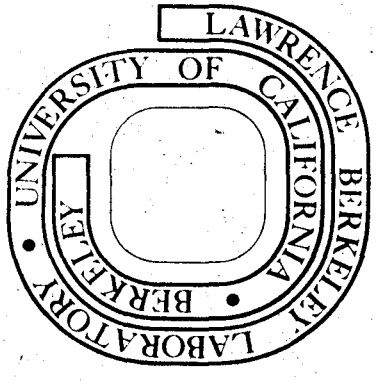

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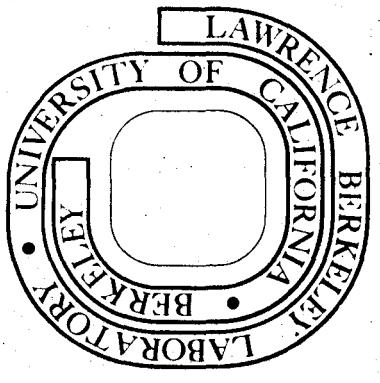

LBL-3700 Rev.

DISCLAIMER

EFFECT OF PROCESSING ON MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF MAGNESIUM OXIDE

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ABSTRACT

Specimens of polycrystalline MgO were fabricated from two powders by hot pressing in graphite or alumina dies, followed by annealing in air, vacuum, or within the graphite die in vacuum. Character parameters affected were density, grain size, and visual appearance which was considered to be dependent on grain boundary structure. The formation of a liquid phase with one type of powder tended to eliminate the effect of processing variables. Correlations of the microstructures of the specimens were made with their mechanical behavior in compression at a constant strain rate at 1200°C.

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*Based on a thesis submitted by T. B. Sweeting for the M.S. degree in ceramic engineering.

I. INTRODUCTION

Properties of materials are dependent on their character (microstructure, in a broad sense) which in turn are dependent on the processing parameters. Extensive studies have been reported correlating density, and grain and pore characteristics as critical character parameters with the mechanical behavior of materials. The nature of the grain boundary was shown to play a role in determining the mechanical behavior of polycrystalline MgO at elevated temperatures in tension,[1] bending,[2] and compression.[3-5]

The objective of this study is to emphasize the significance of the nature of the grain boundary in affecting the compressive stress-strain behavior of polycrystalline MgO at elevated temperatures. The specimens were formed by a three-step process: powder preparation, hot pressing, and annealing. The character parameters examined are density, grain size, and visual appearance. The annealing step, which affects the grain boundary, is correlated with the stress-strain behavior. A preliminary study was made to determine the powder preparation procedure to be followed in making the specimens for the mechanical study.

II. EXPERIMENTAL PROCEDURE

(1) MgO Powders

Two MgO powders were used in this study, and will hereafter be referred to as Type I and Type II. Their characteristics are listed in Table I. The major difference in the analyses is the higher Si, Ca and sulfate contents in Type II. Also, Type II has five times the surface area and is twice as reactive as Type I. The surface area was measured by adsorption from an iodine solution. The reactivity was a function of

time for solution of powder in citric acid. The higher reactivity of Type II was also indicated by the smaller crystallite size, which was one-third that of Type I.

(2) Powder Preparation

A powder preparation step was necessary since the starting powders had agglomerates which caused undesirable microstructural inhomogeneities. The procedure followed, as discussed later, consisted of dispersing the powder in isopropanol, drying at 90°C, and dry milling in a rubber-lined mill with alumina balls.

(3) Specimen Preparation for Mechanical Testing

Disks, 2 in. dia., were prepared by hot pressing in a graphite die. A thin (.005") graphite foil was used between the powder and the die and plunger. The powder was cold pressed at 2000 psi within the die which was then placed in the hot press, and evacuated to 10^{-4} torr before heating. The heating cycle consisted of heating at 8°C/min to 1250°C with arrests at 500°C for 15 min and 1000°C for 1 h to allow gas from decompositions to escape, and finally at 1250°C for 30 min. Pressure of 3000 psi was applied at 1200°C and maintained constant through the hold at 1250°C. Pressure was then released and the specimen was furnace-cooled. All of the disks were cut into specimens approximately .6 in. x .25 in. x .25 in., using a diamond blade.

Hot-pressing characteristics in the graphite die are shown in Fig. 1 by a plot of density obtained from the measurements of ram travel on hot pressing versus temperature. Some densificaton, greater for Type II powder, occurred between 800 and 1000°C. Type I then showed little change in density until pressure was applied at 1200°C;

densification continued until near the end of the 30 min hold period at 1250°C. Type II, on the other hand, started to further densify with increase of temperature after 1000°C and reached its final density only a few minutes after pressure was applied at 1200°C.

All of the specimens formed through the hot-pressing step were the same within experimental error. The atmosphere was the processing variable during annealing at 1550°C for 2 h: air, vacuum, and vacuum within the graphite die. These atmospheres had decreasing partial pressures of oxygen. A specimen was also annealed in air for 24 h.

Specimens were also hot pressed in an alumina die in vacuum. Annealing at 1500°C for 2 h was done in air.

Approximately .15 in. was cut from the end of each test specimen. The internal surface of the end piece was used for microscopic examination. All samples were etched using .5M $AlCl_3$ at 50°C for about 1 min. Grain size determinations were made by counting the number of grains in a known area, converting to equivalent spherical diameter, and multiplying by a statistical factor of 1.28 or $4/\pi$.[6] Over 500 grains were counted in each case.

Density measurements were made using a displacement technique in mercury. A value of 3.58 was taken as theoretical density of MgO to compute relative densities.

(4) Mechanical Testing

Specimens for mechanical testing were prepared by metallurgical polishing and then chemically polishing in 85% orthophosphoric acid at 110°C for 2 min. The final dimensions were approximately .36 in. x .18 in. x .18 in.

All stress-strain data were obtained in compression at 1200°C at a constant strain rate of .025/min based on original sample height. All stresses reported are based on original cross-sectional area, and all strains are true strains calculated from the recorded engineering strain. The amount of plastic strain was taken as the difference between the strain at .2% offset yield stress and the strain at the maximum stress recorded.

III. RESULTS AND DISCUSSION

(1) Effect of Powder Preparation on Microstructure

Experiments were performed to determine the powder preparation procedure to be followed to form specimens for the mechanical behavior study. Type I powder was prepared according to the following processing procedures:

(1) Dry milled 2 h -- alumina balls.

(2) Dispersion in isopropanol, dried, dry milled 2 h -- alumina balls.

(3) Dry milled 2 h -- teflon balls.

(4) Wet milled 1 h in isopropanol, dried, dry milled 2 h -- teflon balls.

The ball milling in all cases was done in a rubber-lined mill. Specimens were then formed by hot pressing these powders and an untreated powder in a graphite die.

The visual appearance of specimens after hot pressing varied: procedure (1), light gray and slightly translucent core covering approximately four-fifths of the cross-sectional area with the areas adjacent to the surfaces white; (2), similar but slightly lighter gray core; (3)

and unmilled powder, uniform white cross-sections; (4), very dark gray throughout. All specimens were white after annealing in air. The resulting density and grain size data are summarized in Table II.

Evaluation of the data in Table II and the visual appearances after hot pressing indicates that contamination of the powder by organics from the rubber occurred from abrasion by Al_2O_3 balls and from solution by isopropanol during the wet milling stage (procedures (1) and (2), and (4)). The rubber contamination alone did not significantly affect the densification process since the hot-pressed and annealed densities and grain size of (1) and (2) were essentially the same as the specimen prepared from the unmilled powder. In (3) and (4), however, the contamination introduced by milling with teflon balls, which are softer than MgO, reduced their hot-pressed and annealed densities and retarded grain growth. In all cases, milling increased the green density of the specimens and improved their homogeneity.

Procedure (2) was selected for the processing of the MgO powders in the fabrication of all of the specimens for mechanical testing. The selection was based on improved homogeneity and maximum green, hot-pressed and air annealed densities.

(2) Mechanical Behavior

(A) Characterization of Test Specimens

(a) Type I MgO: Table III includes data on density and grain size for the Type I MgO specimens hot pressed in a graphite die and annealed in air, vacuum, or graphite die vacuum, and hot pressed in an alumina die and annealed in air. A description of the visual appearance follows.

The specimens formed in the graphite die had a grayish slightly translucent core as described previously under procedure (2). Those formed in the alumina die were white, which was attributed to the higher partial pressure of oxygen.

The appearance of the specimens, formed in graphite die, after annealing was dependent upon the annealing atmosphere: in air, white; in vacuum, a retained faint gray core of about the same proportions as that after hot pressing but with no translucency; in die vacuum, gray throughout. The specimen formed in an alumina die and annealed in air remained white; some clouding was present in the center region, similar to that reported by Rice.[7]

The average grain size in the graphite die specimens annealed in different ambient atmospheres at 1550°C for 2 h was essentially constant (∿29 μm). Annealing in air for 24 h increased the grain size to about 60 μm. The number and size of pores varied although they were predominantly on grain boundaries.

Specimens from the alumina die annealed for 2 h have considerably greater grain sizes, ∿40 μm, indicating that the hot-pressing ambient atmosphere affects subsequent grain growth during annealing. Thus, it can be noted that in general the graphite environment during hot pressing has a retardation effect on grain growth during annealing. These observations are in general agreement with reported results of MgO grain growth retardation by a fine dispersion of carbon.[8]

The variations in visual appearance of the MgO specimens are concluded to be due to variations in structure and composition of the grain boundary regions. An analytical analysis, however, is not possible at

the present time.

(b) Type II MgO: Density and grain size data for Type II MgO specimens fabricated in both dies and then annealed in various ambient atmospheres are listed in Table III. A description of the visual appearances follows.

The disks hot pressed in the graphite die were gray and translucent throughout their entire cross-section; in the alumina die, white and translucent. After annealing in air both types were white and showed considerable clouding in their centers. Similar but a lesser amount of clouding was observed in the vacuum annealed specimen. The graphite die annealed specimens were uniformly gray throughout.

Porosity was present mainly within the grains for all cases. A second phase film was present along grain boundaries as shown in Fig. 2. This phase was attributed to the relatively higher CaO and SiO_2 content of the Type II powder which leads to the formation of a calcium-magnesium-silicate liquid phase during annealing at 1550°C. Leipold[9] found segregation of Al, Si and Ca at grain boundaries during hot pressing even when present in average amounts as low as 30 ppm. The large increase in grain size, ∿90 μm vs ∿29 μm for Type I MgO specimens formed under the same conditions, was concluded to be due to the presence of the liquid phase. Initial grain growth rates are also fast, as indicated by a grain size of 74 μm with no holding time at 1550°C compared with 84 μm after an annealing time of 2 h.

The liquid phase has also eliminated any grain boundary differences due to atmospheric effects introduced during hot pressing since the grain size was similar for all annealed specimens of Type II MgO. For

Type I MgO, the grain size was larger for the specimens formed by hot pressing in the alumina die.

(B) Evaluation of Mechanical Behavior. Stress-strain curves for the specimens formed in the graphite die and annealed in different atmospheres, and the curves for the air annealed specimens formed in the alumina die, are shown in Fig. 3. The yield stress, maximum stress and plastic strain at maximum stress values are summarized in Table III.

Data for the Type I specimens from the graphite die with 2 h anneals show that the yield stresses were similar but that the plastic strain was reduced with decrease of P_{O_2} during annealing; the air annealed specimen had nearly three times as much strain as the die annealed specimen. Since the microstructure, with respect to grain size and the amount and distribution of pores, was similar in each case, the significant variable must have been the nature of the grain boundary after annealing, e.g. the grain boundary of the air annealed specimen which was white would be expected to be closer to an ideal structure than the grain boundary of the die annealed specimen which was gray and thus behaved differently.

Even though the air annealed specimen had ∿23% plastic deformation, its fractured surface showed considerable cracking and boundary separation, as seen in Fig. 4 by SEM. These cracks, however, must not have propagated readily because of accommodation by some localized plastic deformation and material grain boundary separation akin to crack branching. The die annealed specimen, on the other hand, with ∿9% plastic strain could not accommodate the initial cracks as easily because of less perfect grain boundaries; the cracks were thus fewer in number, as

seen in Fig. 5.

According to von Mises[10] plastic deformation of a polycrystalline specimen by dislocation glide requires movement on five independent slip systems. For MgO, this requirement is fulfilled by two {110} <1$\bar{1}$0> and three {100} <1$\bar{1}$0> slip systems. At 1200°C with uniaxial loading at a stress rate of 20 psi/sec, the yield stress for a single crystal with <100> orientation is ∿3000 psi and with <111> orientation, ∿18000 psi.[11] Plastic deformation without or with limited grain boundary separation has shown yield stresses intermediate between these values because of localized stress concentrations sufficiently large to activate secondary slip systems in adjoining grains due to dislocation motion on the primary slip systems.[3-5] The high yield stresses for the Type I specimens relative to the single crystal values indicate the presence of grain boundaries that offer resistance to nucleation and transmission of slip. This condition is also indicated by the extensive grain boundary separation as an accommodation mechanism in the deformed air annealed specimens. Further resistance is indicated by the die-annealed specimen on the basis of more limited grain boundary separations and failure at a smaller strain.

The Type I air annealed specimen from the alumina die showed reduced plasticity and yield stress in comparison with the air annealed specimen formed in the graphite die (Fig. 3). The grain size, however, is about 33% larger, 44 μm compared to 28 μm. A specimen from the graphite die annealed in air for 24 h showed even lesser plasticity, lower yield stress, and a larger grain size, 60 μm. This correlation with grain size is similar to that of Vasilos et al.[12] who reported a

decrease in strength with increase of grain size, and of Evans et al.[2] who showed a decrease in the stress to initiate cracks by grain boundary dislocation pile-up with increasing grain size.

The stress-strain curves for all of the Type II specimens were markedly different from those of Type I but similar to each other showing comparable low yield stresses and plastic strains (Fig. 3). This relationship was attributed to two factors: the presence of the second phase, and the large grain size. The Type II specimens were the only ones that had a second phase (Fig. 2) and that showed debris on the fractured surfaces created at room temperature after deformation (Figs. 6 and 7).

The brittle second phase along grain boundaries hinders the transmission of any generated dislocation motion within a grain across grain boundaries.[13] The resulting high stress concentrations can be accommodated by the formation of cracks, which can be large in a large grain material. The brittle second phase plays this significant role as indicated by the fact that the yield stress and plastic strain values are lower than expected on the basis of extrapolating data for air-annealed Type I specimens to the average grain size of 82 μm of the Type II specimens. Another significant effect of the second phase was to eliminate the dependence of amount of plastic strain on the annealing atmosphere that was observed for Type I MgO, in accordance with the similar visual appearance of all the Type II specimens after annealing.

Macroscopic examination of the specimens after testing revealed that all Type I specimens contained visible vertical cracks near the center on one or more faces, whereas Type II specimens had cracks at the

edges extending along the vertical length of the specimen. In compression testing, frictional forces develop between the specimen and the ram faces; these constraining forces lead to a barreling type of deformation which results in tensile stresses perpendicular to the loading direction and regions of high strain on the faces. The Type II specimens, which showed little ductility, could not accommodate this high strain on the edges and fractured as indicated. In contrast, Type I specimens, which exhibited much more ductility, accommodated the strain at the edges by yielding in shear and eventually failed in the center, the region of maximum tensile stress.

IV. SUMMARY AND CONCLUSION

MgO powders required preparatory treatment in order to reduce agglomerates and realize more homogeneous and uniform microstructures. Variations in the preparation of Type I MgO powder and keeping the subsequent processing parameters of hot pressing and air annealing constant resulted in variations in the densities and grain size. Use of teflon milling balls reduced the hot-pressed and air-annealed densities, and retarded grain growth. The procedure selected for subsequent preparation of powders consisted of dispersing in isopropanol, drying, and milling in a rubber-lined mill with alumina balls.

Specimens for mechanical behavior studies were made by keeping the powder preparation and hot-pressing steps constant and varying the annealing atmosphere: air, vacuum, and within graphite die in vacuum (i.e., decreasing P_{O_2}). Type I MgO specimens indicated a corresponding visual appearance from white to gray, which was considered to be due to differences of the structure in the grain boundary regions. Type II MgO

specimens were white for all annealing atmospheres, which was considered to be due to the presence of a second phase along grain boundaries resulting from the presence of a small amount of CaO and SiO_2 impurities.

Type I specimens showed a decrease in plastic strain with decrease of P_{O_2} in the annealing atmosphere. Type II specimens prepared in all annealing atmospheres showed a considerably smaller plastic strain and essentially no variation.

Impurities in the powder, and the nature of the ambient atmosphere during the processing steps affect the visual appearance and the mechanical behavior of MgO polycrystalline specimens without a second phase that can only be interpreted in terms of resulting differences in the structure of the grain boundaries, which are unknown in detail.

ACKNOWLEDGMENTS

Helpful discussions with William S. Snowden are gratefully acknowledged. Thanks are extended to Leonard Lee of Merck and Co. and Robert B. Langston of this laboratory for assistance in providing analytical data on the MgO powders.

This work was partially supported by the U. S. Energy Research and Development Administration and partially with the aid of a research grant from Kaiser Refractories Division of the Kaiser Aluminum and Chemical Co.

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Table I. Characterization of MgO powders

	Type I	Type II
Chemical		
†Al_2O_3	.13%	.04%
††CaO	.21	.46
†FeO	.09	.06
†Na_2O	.014	.007
††SiO_2	.06	.31
Cl^-	.005	.021
$SO_4^=$	.01	.22
CO_2	.71	.82
H_2O	2.64	2.48
*Free moisture	.37	.28
*Loss on ignition	3.74	3.82
*$MgCO_3$, calculated	1.35	1.57
*$Mg(OH)_2$, calculated	8.6	8.8
Physical		
**Surface area, M^2/g	11.5	56.5
**Reactivity, sec.	87	44
X-ray crystallite size, Å	360	120

†Based on spectrographic analysis of elements, Lawrence Berkeley Lab., Univ. of Calif., Berkeley, Calif.
*Based on chemical analysis, Merck and Co., South San Francisco, Calif.
††Based on chemical analysis, Robert B. Langston, Inorganic Materials Research Div., Univ. of Calif., Berkeley, Calif.
**Performed by Merck and Co., South San Francisco, Calif.

Table II. Densities and grain sizes of Type I MgO Specimens produced by different processing procedures

Procedure	Green Density	Hot Pressed Density	Air Annealed Density	Average Grain Size
Unmilled	34	98.0	97.8	32
(1) Dry milled - alumina balls	39	98.0	97.8	30
(2) Dispersed, dry milled - alumina balls	46	98.5	98.2	28
(3) Dry milled - teflon balls	39	96.5	96.2	21
(4) Wet milled, dry milled - teflon balls	41	95.5	95.1	19

Table III. Data for Type I and Type II MgO specimens

Die Used	Annealing Environment†	Density %	Grain Size μm	Yield Stress	Maximum Stress	Plastic Strain*
Type I						
Graphite		98.5	<3			
	Air	98.3	28	24,000	37,200	23.4
	Air, 24 h		60	16,000	31,600	8.8
	Vacuum	98.1	28	24,600	36,400	14.0
	Die	98.3	30	22,800	32,300	8.6
Alumina		99.0	<5			
	Air	98.6	44	20,000	34,900	10.6
Type II						
Graphite		99.1	<3			
	Air	98.0	84	5,300	9,050	2.4
	Air, 0 h		74	6,500	9,100	2.3
	Vacuum	98.0	90	6,000	9,900	2.4
	Die	98.5	101	6,000	10,050	2.9
Alumina		99.0	<5			
	Air	98.0	87	4,540	6,850	2.1

†All annealing times 2 h except as noted.
*At maximum stress.

FIGURE CAPTIONS

Fig. 1. Typical curves of density versus temperature and time during hot pressing in a graphite die.

Fig. 2. Photomicrograph of Type II polycrystalline MgO specimen.

Fig. 3. Stress-strain curves in compression at a constant strain rate of 0.025/min. at 1200°C for specimens annealed in air, vacuum, and vacuum within a graphite die after hot pressing in graphite and alumina dies.

Fig. 4. Fracture surface after deformation of Type MgO hot pressed in graphite die and (a) annealed in air, and (b) annealed in vacuum within the graphite die.

Fig. 5. Fracture surface after deformation of Type II MgO hot pressed in graphite die and (a) annealed in air, and (b) annealed in vacuum within the graphite die.

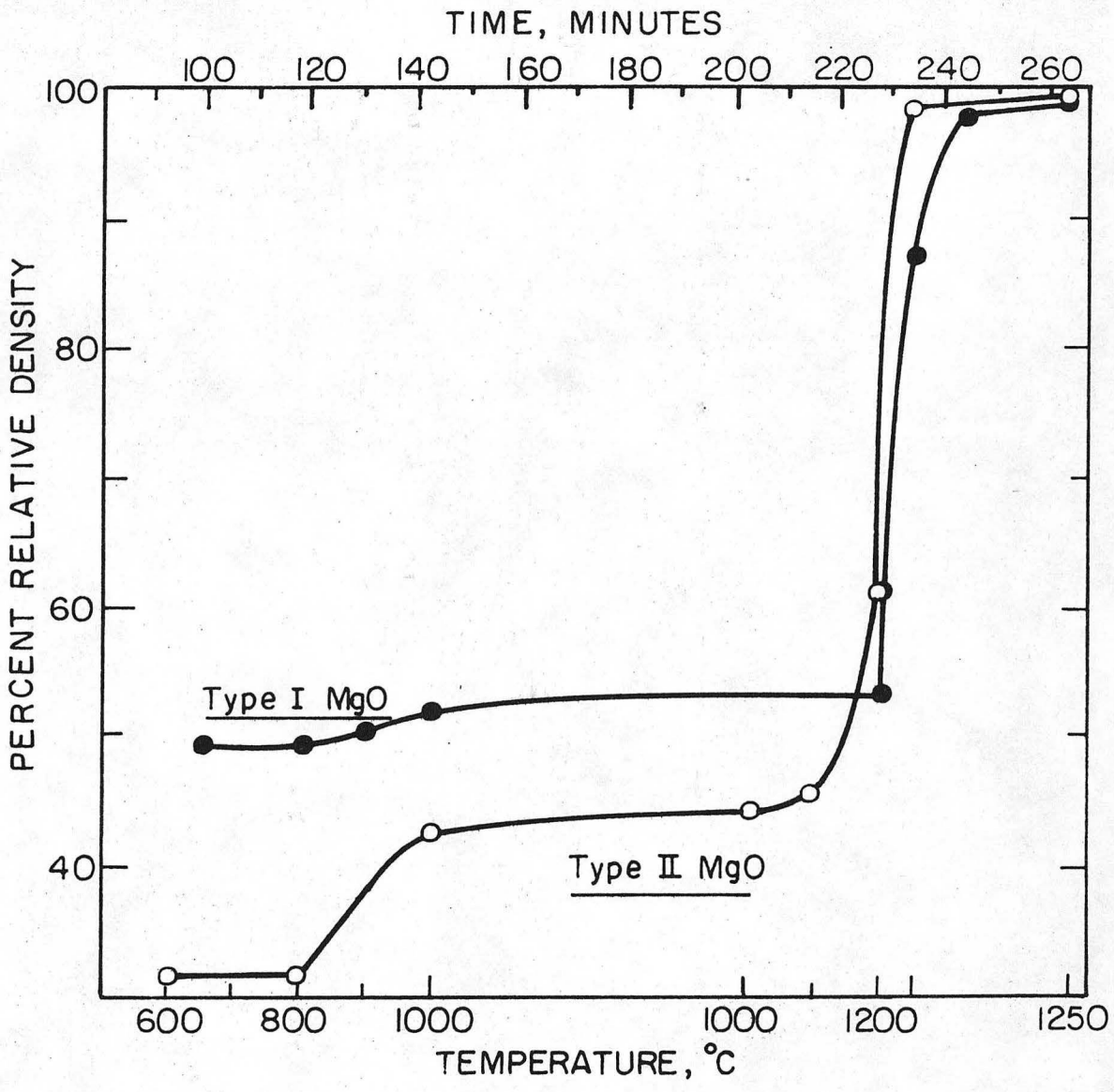
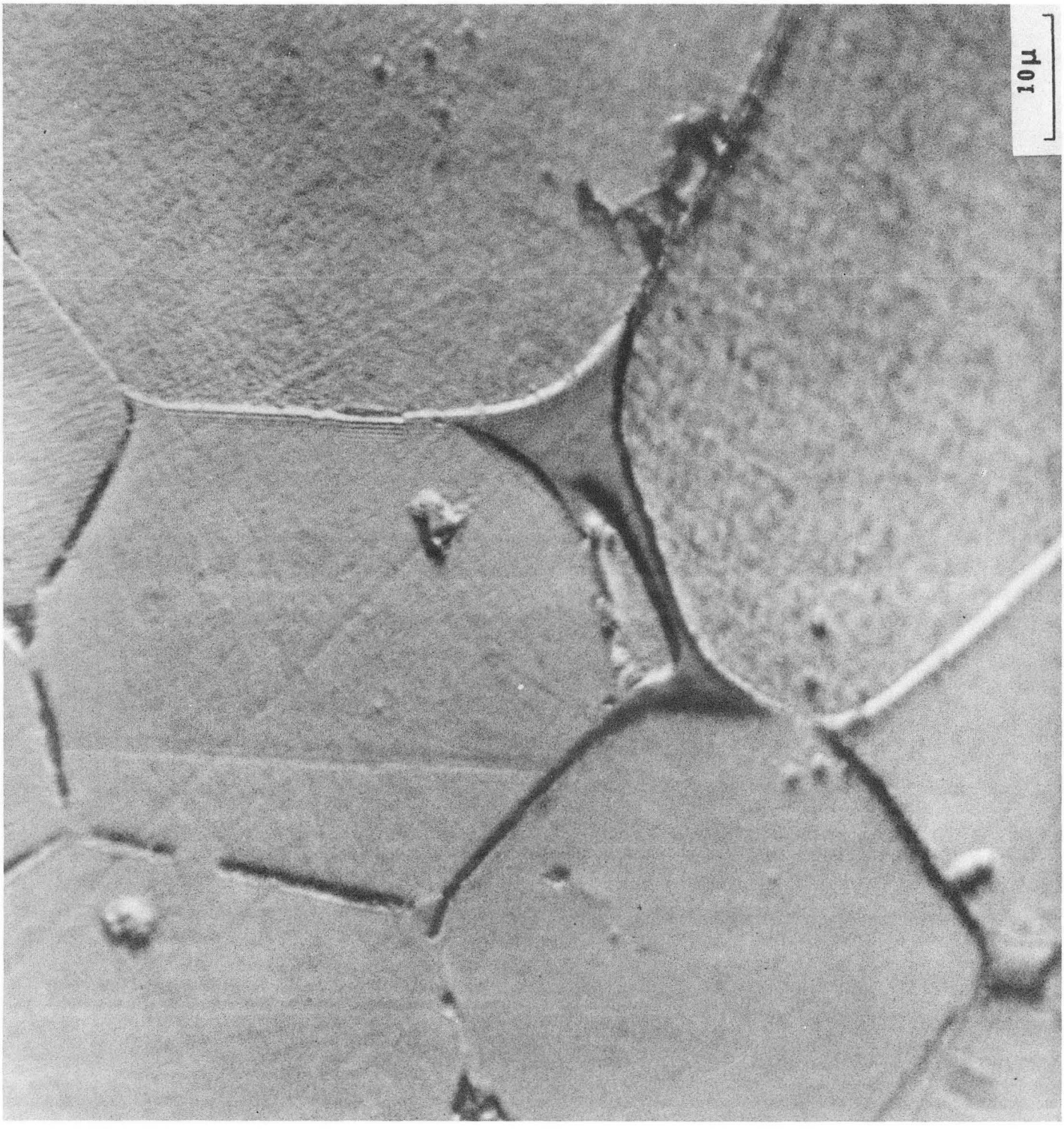


Fig. 1



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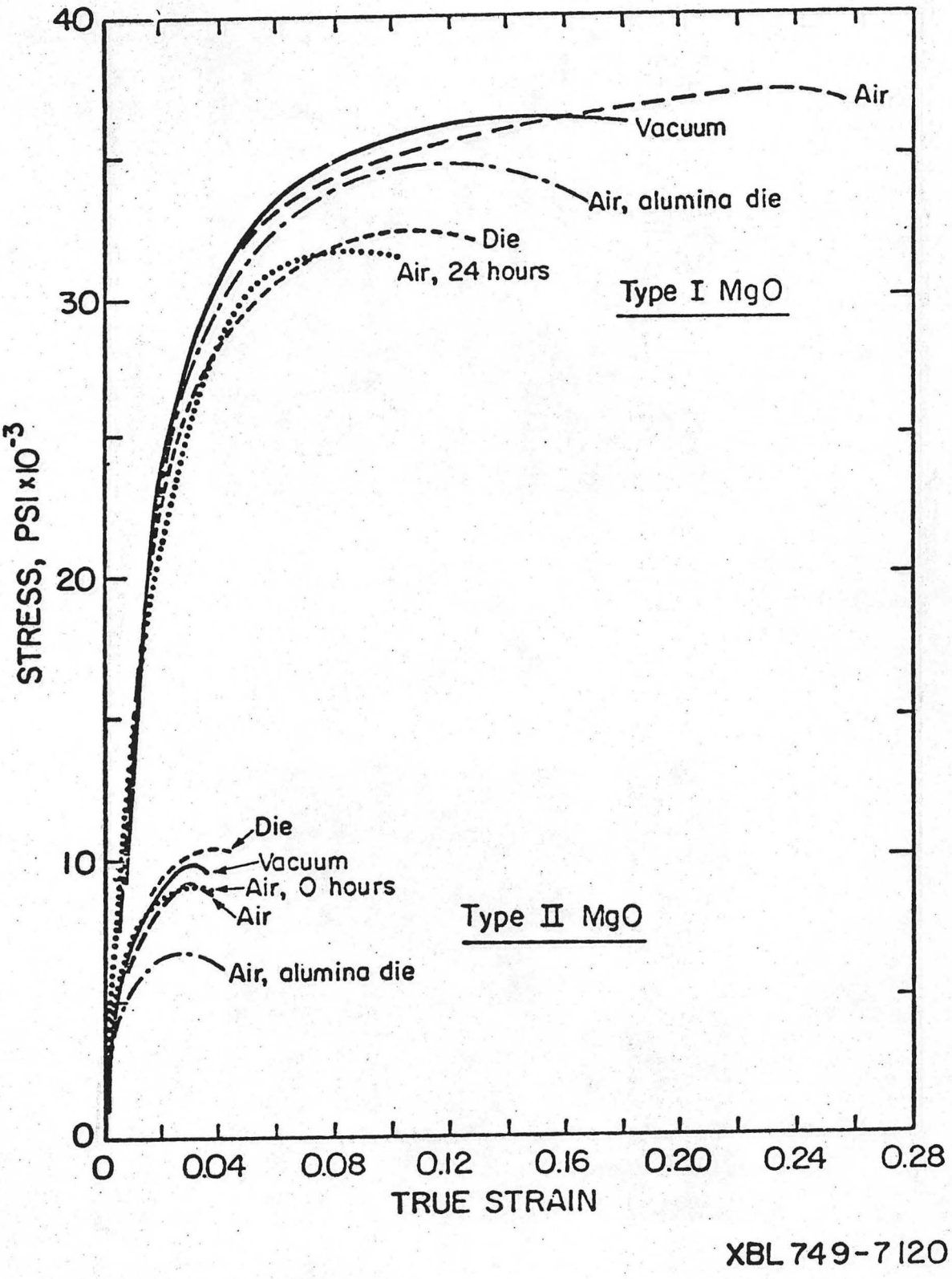
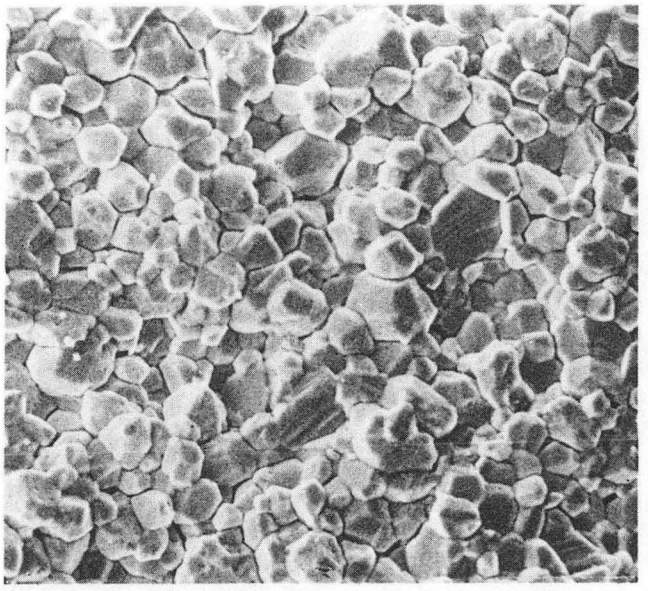


Fig. 3

a



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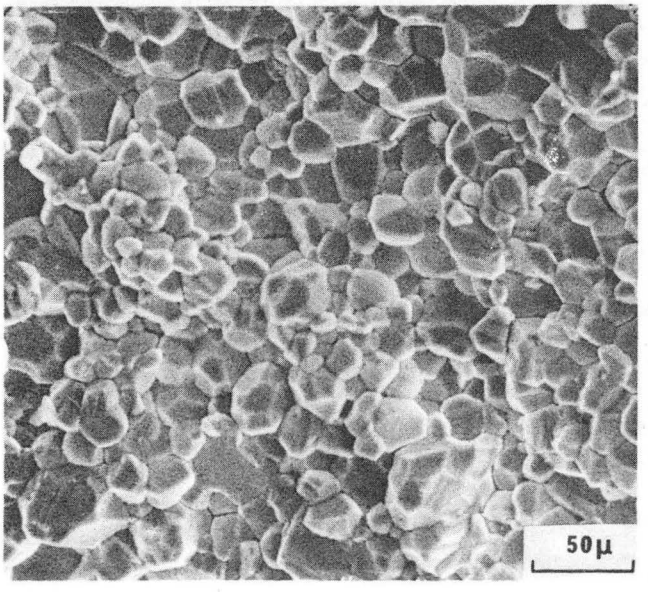

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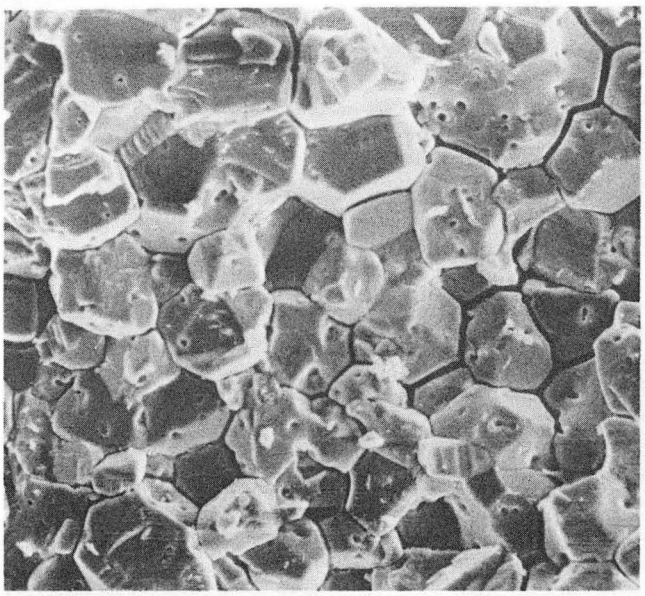
Fig. 4

b



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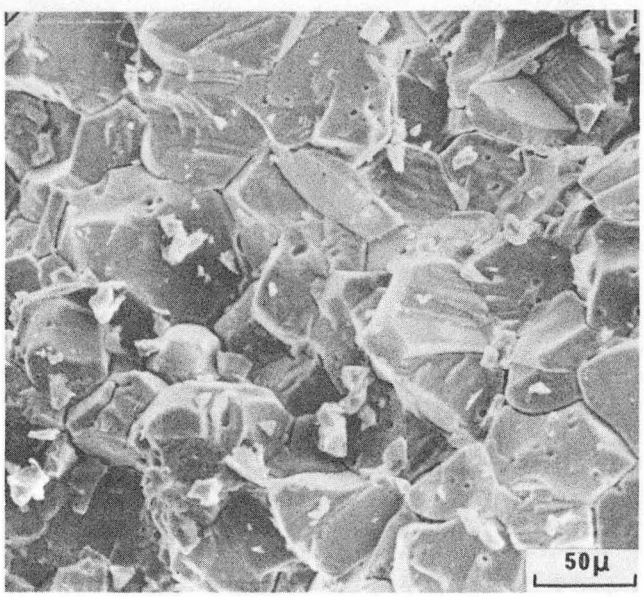

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Fig. 5

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