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Submitted to the Journal of the
American Ceramic Society

UCRL-16368

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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August 11, 1966

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ABSTRACT

Transparent polycrystalline specimens can be fabricated by hot-pressing fine MgO powder with a small LiF addition, and a subsequent heat treatment. The LiF addition allows MgO to be hot-pressed to near theoretical density at reduced temperatures and stresses. The stress-temperature-time conditions must be designed to attain a hot-pressed density of at least 99.5% of the theoretical density of MgO to obtain a transparent specimen during the subsequent heat treatment employed in this study. Two possible densification mechanisms are proposed: a plastic deformation process, and/or an enhanced diffusional grain boundary creep process.

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Footnotes:

Presented at the 18th Pacific Coast Regional Meeting, The American Ceramic Society, Los Angeles, California, October 29, 1965.

This work is based on a thesis submitted by Mark W. Benecke in partial fulfillment of the requirements for the degree of Master of Science in ceramic engineering, University of California at Berkeley, January, 1965.

This work was done under the auspices of the United States Atomic Energy Commission.

At the time this work was done, the writers were, respectively, graduate research assistant, junior engineer, and professor of ceramic engineering.

temperature measurements was estimated to be within ±5°C. A vacuum of about 10^{-1} torr was used to protect the graphite dies from oxidation.

Pressure was applied by a manually operated hydraulic jack which moved against the water-cooled copper ram. Compaction of the powders was recorded continuously with a linear variable differential transformer which measured translation of the hydraulic ram with respect to the furnace top.

B. Sample Preparation

In this study, specimens were prepared from Baker and Adamson reagent grade MgO, Lot No. Y011, and J. T. Baker reagent grade LiF, Lot No. 26452. (Using the electron microscope, the smallest magnesium oxide particles were determined to be approximately 0.1μ in diam.) Only certain sources of MgO powder, determined by testing, produced transparent specimens.

Thirty gram batches of magnesium oxide with 2 wt. % of lithium fluoride were mixed by tumbling the powders in isopropyl alcohol. The slurries were then dried in an oven. The resultant cakes were broken, hand-stirred with a spatula, and placed in a dessicator under vacuum for several hours before hot-pressing.

C. Procedure

For most experimental runs a constant pressure in the range of 570 to 4000 psi was applied at room temperature and maintained during the heating and soak times. This pressure was released before the temperature was lowered from the soak temperature. The specimens were heated at a rate of 5.5°C per min. until the desired final temperature in the range of 775 to 975° was reached. They were then held there from

zero to 5 hrs.

The hot-pressed samples in all cases were slowly heated overnight to 1300°C and held for 3 hrs. Then, they were allowed to cool in the furnace. This heat treatment was done in air in a small Kanthal-wound vertical tube furnace with the specimens standing freely on a pedestal.

III. RESULTS AND DISCUSSION

A. Phenomenological Aspects

An example of the favorable effect of LiF on the densification of MgO powder is shown in Fig. 2. When 1705 psi is applied at room temperature and the heating rate is 5.5°C per min., densification (based on the linear change in the specimen length) begins at about 570°C and is essentially complete by the time the melting point of LiF is reached (846°C).[5] The degree of densification attained without LiF up to 1050°C was negligible. The importance of the nature of the powder is indicated by the third curve in Fig. 2 which shows that densification was delayed for mixtures of LiF and MgO powder presintered at 1400°C for 5 hrs. Rice also made the same observation.[3] Also, single crystal MgO ground in a mortar to -200+325 mesh and hot-pressed with 20 wt. % LiF showed no densification of the MgO at 950°C and 2000 psi.

Figure 3 shows how densification is affected by varying the applied pressure. Increasing or decreasing the pressure reduces or increases the time, and thus the temperature, required to complete densification during hot-pressing. It should be noted that complete densification was not achieved at 580 psi within the temperature limit of the experiment and that no discontinuity occurred in the

densification curve at 846°C, the melting point of LiF.

The dependence of the final heat-treated appearance on the hot-pressing conditions is indicated in Table I. From data in Fig. 3 and Table I it is evident that this is a kinetic process and that there is a proper combination of temperature, pressure, and time required to produce a satisfactory specimen. In addition, the data in Table I indicate that a relative density of 99.5% or greater, based on the theoretical density of MgO, must be achieved during hot-pressing in order to develop transparency during the subsequent heat treatment employed in this study. It is expected that the critical hot-pressed density would vary as the parameters of the subsequent heat treatment are varied. It was also observed that a certain degree of translucency in the hot-pressed specimens was a necessary but not sufficient condition for eventual transparency.

Grain growth occurred during processing. Several examples of hot-pressing conditions and resulting grain size are: 2840 psi applied at 850°C and held 10 min. - 0.3μ; 2275 psi applied at room temperature, heated to 850°C, and held 3 hrs. - 1.2μ (Fig. 4); and 2275 psi applied at room temperature, heated to 900°C, and held 3 hrs. - 1.9μ (Fig. 5). Specimens that became transparent during the subsequent specified heat treatment had a final grain size of approximately 20μ.

In this study most of the batches were made with 2 wt. % of LiF, but some were prepared with up to 4 wt. % additions. In all cases, however, as indicated by the density values relative to MgO and

subsequent analyses,* practically all of the LiF was removed during hot-pressing. Observations indicated that the lost LiF was removed by being squeezed out of the compact and by vaporization. If it is assumed that the remaining LiF in a compact of 99.5% theoretical density of MgO is uniformly distributed as a film along the grain boundaries and the grains have a uniform diameter of 1.2μ (Fig. 4), the calculated thickness of the film becomes about 60 Å. Approximately this amount or less apparently lends itself to further removal during the final heat treatment without development of porosity, resulting in a transparent specimen.

If too much LiF remains as a result of inadequate hot-pressing conditions, its distribution apparently is not uniform. Porosity then develops as additional additive is removed during the subsequent heat treatment, which is not eliminated by sintering. This final porosity results in a translucent specimen.

B. Densification Mechanisms

The principal mechanisms of interest are the distribution of LiF throughout the compact at temperatures as low as about 575°C when densification starts, and the function of LiF in the operating densification process or processes. Densification processes to be considered are solution-precipitation commonly referred to as liquid phase sintering,[6] Nabarro-Herring based on a stress-enhanced volume diffusion,[7] enhanced diffusional grain boundary creep process, and plastic deformation.[8]

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* A hot-pressed specimen with an initial 4 wt. % of LiF showed only 0.1 wt. % of Li as determined by the American Spectrographic Laboratories Inc., San Francisco, California.

The effectiveness of LiF indicates that it must become evenly distributed on all the MgO surfaces in the compact at about 575°C. Because 2% of relatively coarse particles is insufficient to provide such distribution, distribution must be achieved by means of liquid or vapor phase. Since LiF melts at 846°C, liquid phase distribution would require the formation of a eutectic liquid. DTA studies of a number of mixtures, however, detected no liquid formation other than the melting of LiF. Also, there was no evidence of any liquid formation or reaction between single crystals of the two materials in contact at 840°C for one-half hour. Therefore, if a eutectic does exist, its composition and temperature must be very close to that of LiF and its melting point.

At temperatures below its melting point, LiF must then be distributed throughout the powder compact through its vapor phase. Its equilibrium vapor pressure at 575°C is 3×10^{-8} atm which is sufficient for distribution throughout a system such as a powder compact.[9] Vapor coming in contact with the surface would be expected to interact with the surface because sessile drop experiments of molten LiF on MgO single crystals indicated a contact angle of about 20°.

A liquid phase sintering mechanism does not appear to be operative because complete densification can be achieved at temperatures where no liquid was observed. Furthermore, the sintering process did not seem to be affected in experiments whose temperature range passed through the LiF melting point where a liquid actually appeared.

In hot-pressing, stress-enhanced bulk diffusion is often considered to be the densification mechanism following the initial rearrangement both of which, in this case, could be favorably influenced by the

presence of LiF. There is evidence that some mass transport process does occur because of the observed grain growth. Using the Nabarro-Herring relation with data from density-vs-time curves shown in Fig. 6, the calculated values of the diffusion coefficient were found to be many orders of magnitude larger than the apparent diffusion coefficients calculated by Vasilos and Spriggs from hot-pressing data for MgO without any additives.[10] These values, particularly at the low test temperatures employed, are not realistic; the application of the equation in this case is thus doubtful.

If abnormally large diffusion coefficients should exist, however,, they may result if Li^+ and/or F^- should diffuse into MgO thus creating vacancies. The previously mentioned compact of single-crystal MgO powder and 20 wt. % LiF was examined with an electron beam microprobe. The microprobe was set to analyze Mg-K_α radiation to determine if there was any inter-diffusion of Mg^{++} and Li^+, particularly in the LiF phase. Although inconclusive because of experimental difficulties, no diffusion was detected by the microprobe examination. The final low content of LiF in the hot-pressed specimen and the further decrease in amount after heat treatment also argue against such a bulk diffusion enhancement mechanism.

Grain boundary or surface diffusion in the chemisorbed layer or film of LiF, or some complex composition, resulting from a surface reaction, is a possible mechanism that would also account for the observed grain growth. This mechanism would generally correspond to the "activated surface" layer hypothesis proposed by Tacvorian.[2] Further enhancement of diffusivity could be realized by the applied pressure, the overall effect being an increase in densification rates comparable

to the experimental results. Unfortunately, the analysis of the composition of such thin layers is presently not possible with the microprobe.

The rapid densification which occurs at relatively low temperatures and stresses suggests that some type of deformation process may be the operating mechanism but that it is dependent upon the presence of LiF and the fine particle size. The stress levels, calculated on the basis of the bulk specimen, however, appear to be too low in the temperature range where densification is observed to begin. General bulk plastic deformation of MgO particles constrained in some way and randomly oriented, would require dislocation motion on both the $\{110\}$ $\langle 1\bar{1}0 \rangle$ and $\{001\}$ $\langle 1\bar{1}0 \rangle$ slip systems. Yield stresses measured in compression for MgO single crystals at 600°C are about 8000 psi for the $\{110\}$ $\langle 1\bar{1}0 \rangle$ slip systems[11] and nearly 40,000 psi for the $\{001\}$ $\langle 1\bar{1}0 \rangle$ slip systems.[12] Nevertheless, some plastic deformation may be possible before compaction of the particles reaches some stage due to stress concentrations at point of contact. Constraints during this early period would be at a minimum and lubrication of the particles by LiF could also allow some favorable rearrangement of particles for flow. An example of the development of high shear stresses in a complex system was provided in an investigation on the mechanical behavior of polycrystalline LiF where dislocation movement was observed near grain boundaries on slip systems which required nearly ten times the calculated shear stresses developed by the applied load.[13] But, these stress concentrations should exist whether LiF is present or not, whereas LiF was found to be necessary for densification. LiF thus may

play the role of removing or displacing an absorbed surface layer which prevents dislocations from forming or from passing out of the MgO particles. This possible function of LiF, however, if it does exist, is not sufficient since no densification occurred when the coarse powder ground from single-crystal MgO was used with LiF.

There should be no problem of squeezing the excess LiF out of the compact during hot-pressing. The maximum resolved yield shear stresses for single crystals of LiF in compression were found to be only about 200 psi at 500°C and 100 psi at 700°C.[14]

IV. CONCLUSIONS

Transparent polycrystalline MgO can be fabricated by hot-pressing a specific powder with a small LiF addition, and a subsequent heat treatment. The hot-pressed density must be at least 99.5% of the theoretical density of MgO for the final heat treatment used in this investigation to yield a transparent specimen. The parameters of temperature, pressure, and time must be designed to yield this critical density. As an example, transparent specimens can be obtained by hot-pressing MgO powder with 2 wt. % LiF at temperatures as low as 825°C with 4000 psi and subsequently heat treating at 1300°C.

This study has shown that the process is dependent upon the presence of LiF and upon the fine particle size of MgO powder. Two densification processes appear to be possible: a plastic deformation process, and/or an enhanced diffusional grain boundary creep process.

In the former case the small size of the particles in the powder would allow some favorable orientation and deformation of the particles

at reduced temperatures and stresses, particularly in the early stages of densification. In the latter case, the LiF film, or a film of complex composition formed by reaction, on the fine particles, which have a high surface/volume ratio, would provide an "activated layer" through which an enhanced grain boundary or surface diffusivity could occur. With pressure the deformation along grain boundaries could be creep-like in nature but enhanced in the regions of higher stress.

Studies on this problem are continuing in this laboratory. Particular objectives are a more definitive kinetic and quantitative analysis of the densification process, and a specific evaluation of the operating mechanisms. Another objective is an evaluation of the powder characteristics that play a part and are critical in the densification mechanisms. This point is of special concern since the process with the steps as outlined does not produce transparent polycrystalline specimens with all MgO powders.

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Table I. Hot-pressing conditions and density after hot-pressing, and heat-treated appearance.

Hot-pressing conditions	Relative density (%)*	Heat-treated appearance+
4000 psi to 875°C, held 3 hrs	99.6	trsp
4000 psi to 850°C, held 3 hrs	99.6	trsp
4000 psi to 825°C, held 3 hrs	99.6	trsp
4000 psi to 800°C, held 3 hrs	99.5	trsl
2275 psi to 900°C, held 3 hrs	99.6	trsp
2275 psi to 850°C, held 3 hrs	99.5	trsp
2275 psi to 800°C, held 3 hrs	99.1	op
1000 psi to 925°C, held 3 hrs	99.3	trsl
1000 psi to 875°C, held 3 hrs	99.3	op
1000 psi to 825°C, held 3 hrs	98.9	op
1705 psi to 875°C, held 5 hrs	99.6	trsp
1705 psi to 875°C, held 1 hr	99.4	trsl
1705 psi to 825°C, held 5 hrs	99.2	op
2275 psi at 900°C, held 1 hr	99.5	trsp
2275 psi at 850°C, held 1 hr	99.0	op
2275 psi at 800°C, held 4.6 hrs	98.9	op

*Based on theoretical density of MgO of 3.581 gm/cm^3. Densities were measured by displacement in ethanol using an automatic analytical balance. The accuracy and reproducibility of these measurements was ±0.1%.

+ trsp = transparent; op = opaque or poor translucency; trsl = good translucency. Specimens were approximately 0.280 in. thick.

FIGURE CAPTIONS

Fig. 1. Vacuum hot-press arrangement used for preparation of specimens.

Fig. 2. Relative density vs temperature curves obtained at a stress of 1705 psi and a heating rate of 5.5°C. (A = MgO powder, B = MgO powder plus 2 wt % LiF, and C = MgO powder presintered at 1400°C for 5 hrs plus 2 wt % LiF).

Fig. 3. Relative density vs temperature curves obtained at a heating rate of 5.5°C for 3 stresses.

Fig. 4. Microstructure of specimen formed by application of 2275 psi, heating to 850°C and holding for 3 hrs. Average grain size is 1.2μ.

Fig. 5. Microstructure of specimen formed by application of 2275 psi, heating to 900°C and holding for 3 hrs. Average grain size is 1.9μ.

Fig. 6. Relative density vs time curves obtained at 2275 psi at 4 temperatures.

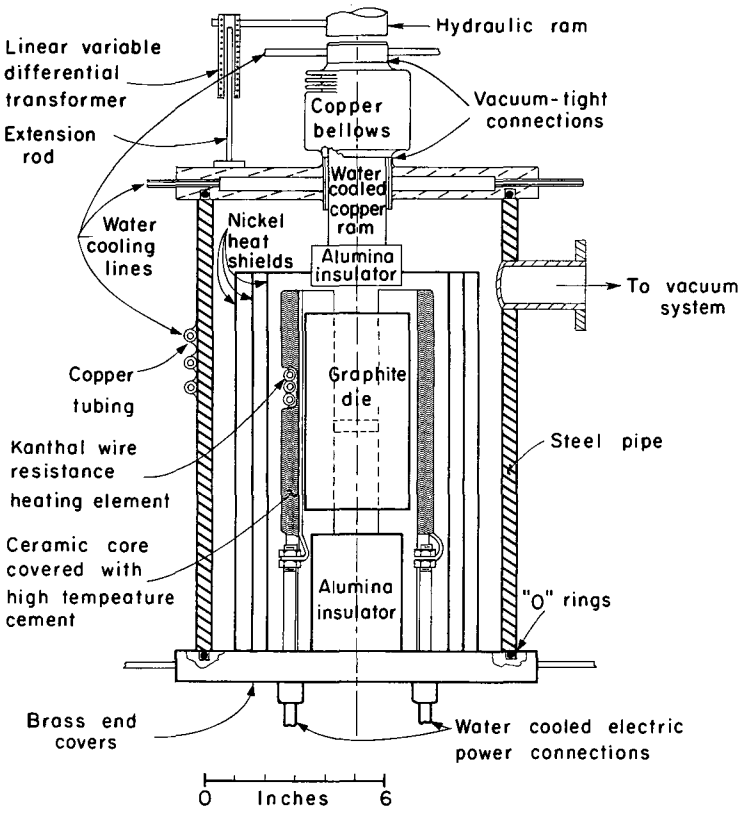

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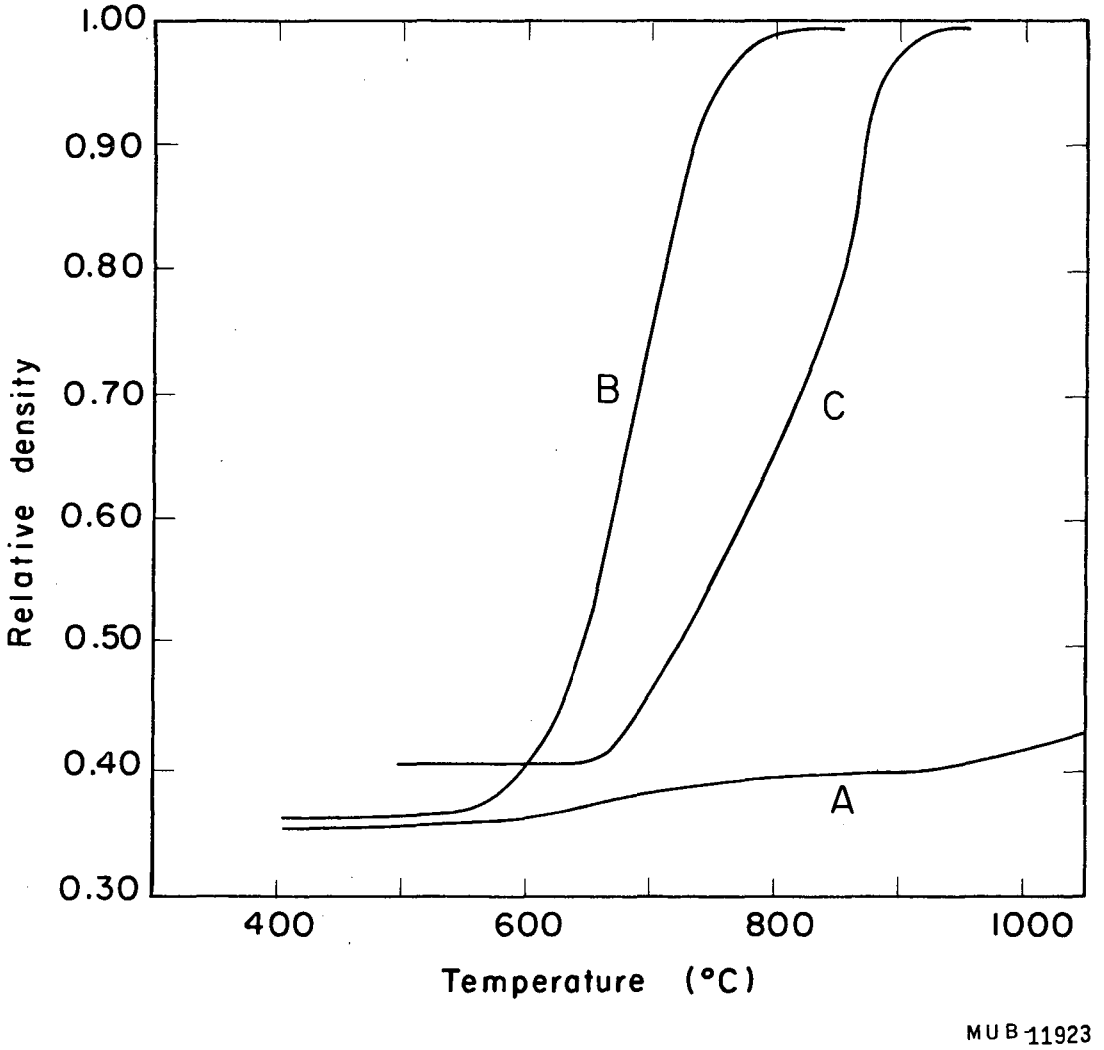
Fig. 1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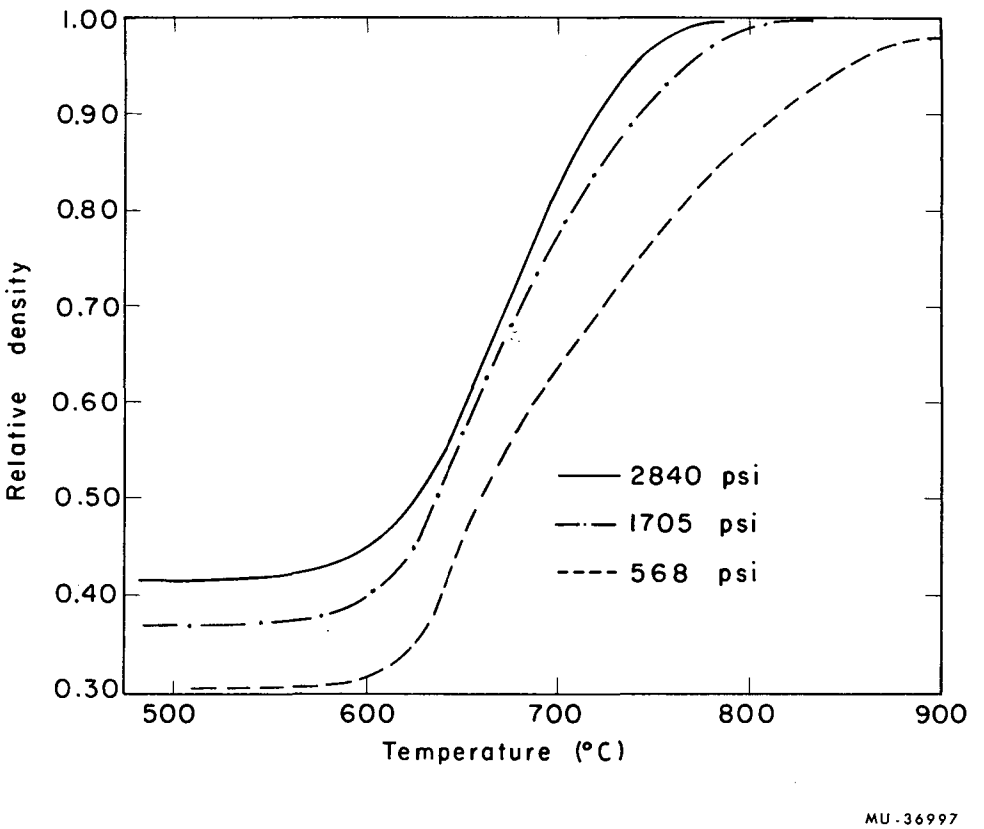
0.80
0.70
0.60
0.50
0.40
0.30
Relative density
B
C
A
400
600
800
1000
Temperature (°C)
MUB-11923

Fig. 2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0.40
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MU-36997

Fig. 3

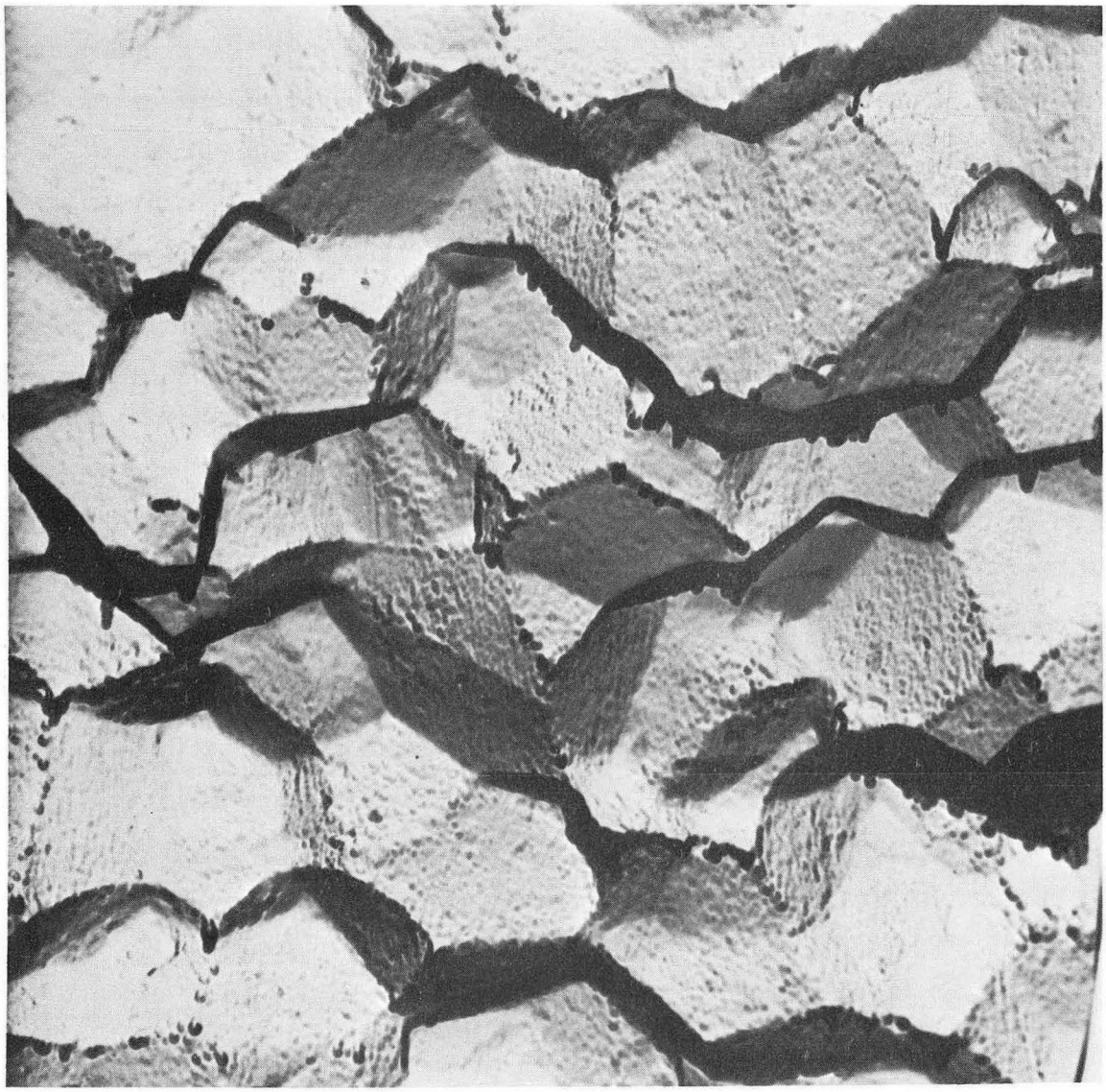

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Fig. 4

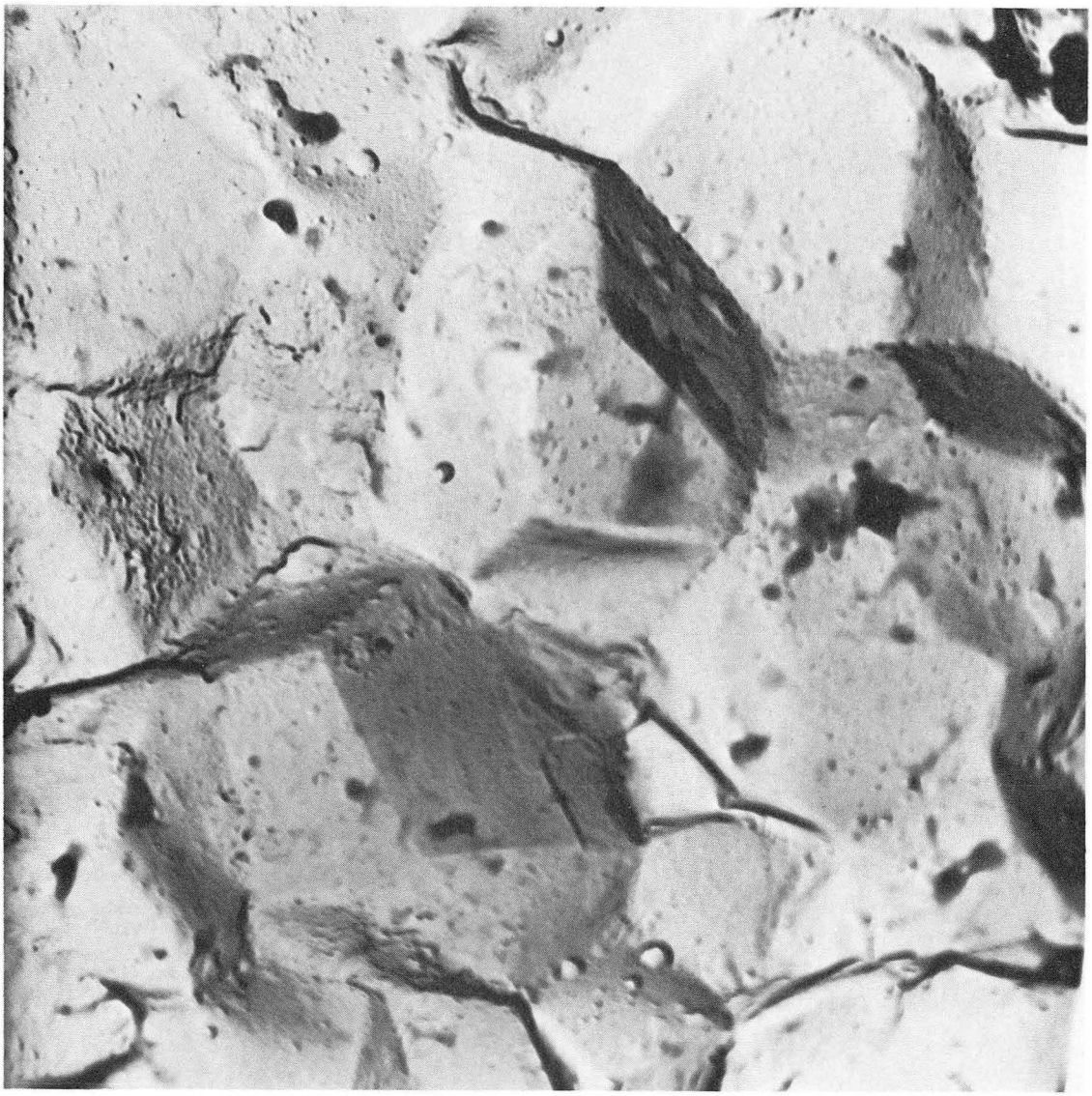

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Fig. 5

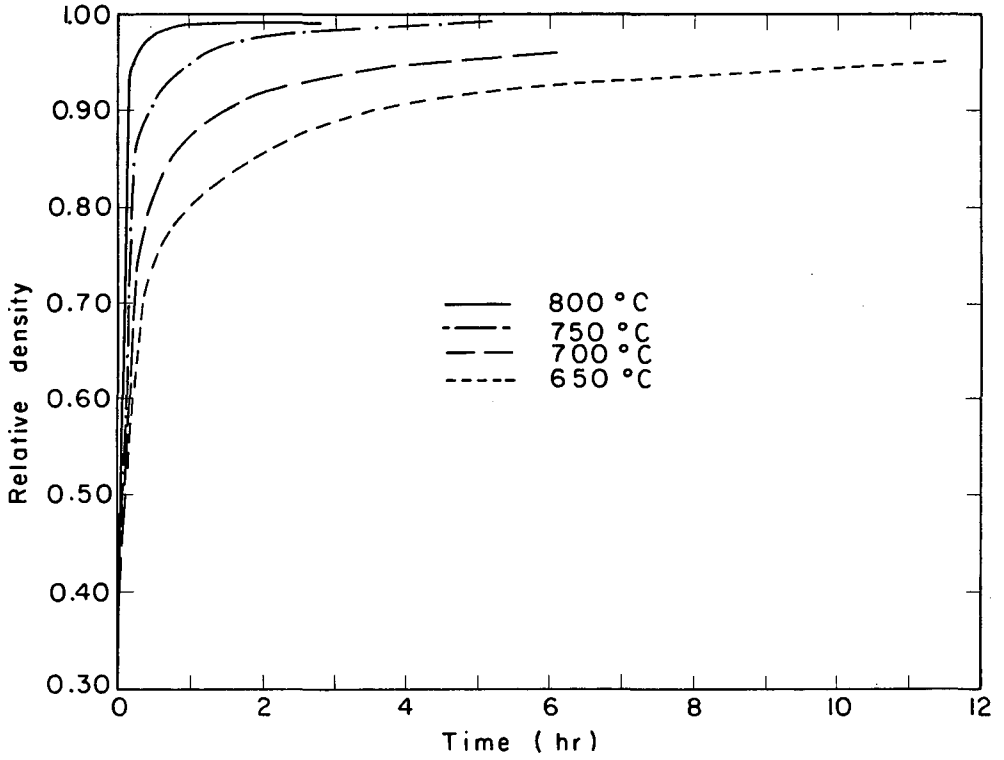

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Fig. 6

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