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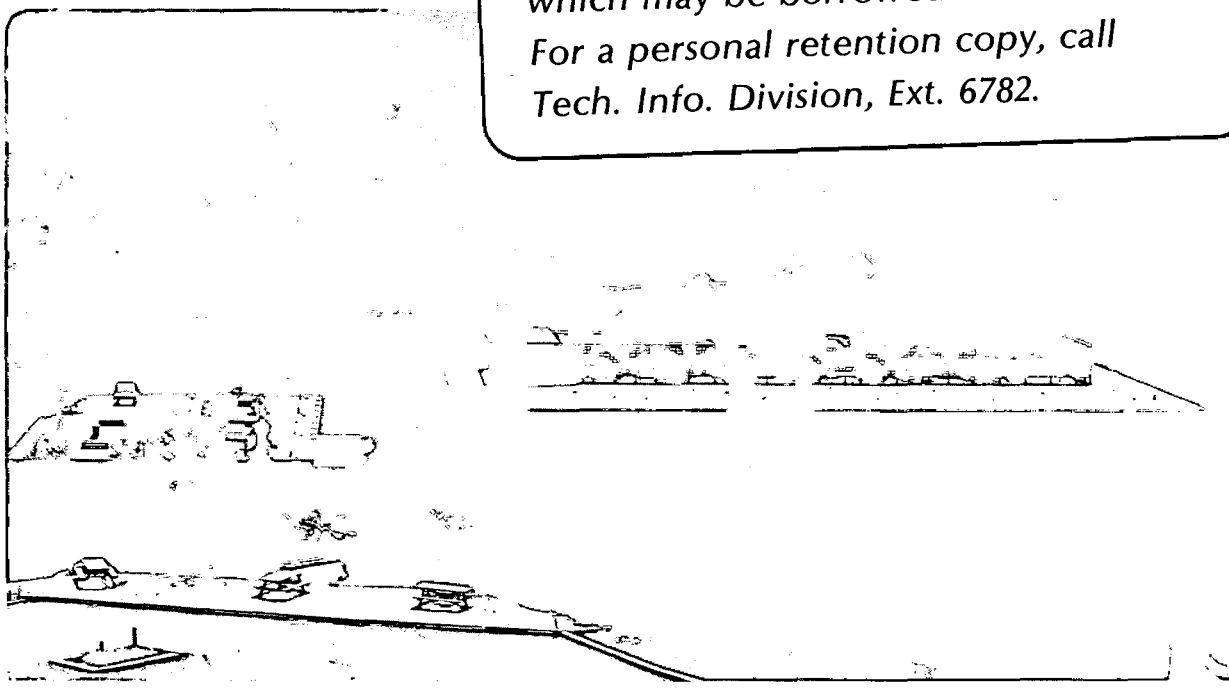

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ABSTRACT

Increased densification rates were found as much as 200°C below the eutectic temperature (980°C) for MgF_2 containing small amounts of CaF_2. Constant heating rate and constant temperature sintering data, as well as microstructural developments indicated that solid state grain boundary transport rates had been enhanced by the eutectic forming additive. The effect saturated at about 1 wt% CaF_2. The results suggest that densification of ceramic powders could be favorably affected without a substantial increase in the grain growth rate, by the addition of small amounts of eutectic forming additives, and sintering below the eutectic temperature.

INTRODUCTION

Many densification processes of ceramic powders involve some form of liquid phase sintering. While these liquids enhance the densification rate very significantly, they tend to lead to strongly enhanced grain growth. The process of liquid phase sintering is usually explained by invoking rapid material transport through a continuous, liquid grainboundary film, assisted by capillary forces arising from voids in the liquid that resides in interparticle interstices (Ref. 1). In a study of the transient liquid phase densification of

sodium-beta alumina by an arrested zone sintering method (Ref. 2) it was, however, observed that significant densification occurred well below the temperature that liquid phases could be present. To clarify the nature of this effect, possibly occurring near the eutectic temperature of many eutectic forming powder mixtures, the model system magnesium fluoride-calcium fluoride was examined. In this system the eutectic temperature is 980°C, while the melting points of calcium fluoride and magnesium fluoride are 1410°C and 1252°C respectively. The mutual solubilities are less than 1 wt%, but have not been determined accurately (Ref. 3).

EXPERIMENTAL METHODS

MgF_2 powder* was sized with an Acucut** air classifier to obtain a uniform agglomerate fraction with a size of 2.5 μm and a primary particle size of about 0.5 μm. Measured amounts of CaF_2 were added to this powder, and were mixed with anhydrous ethanol. The slurry was stirdried at 80°C. Both pure and mixed powders were subjected to the same procedures. The powders were die pressed at 3500 kg cm^{-2} to a green density of 55% theoretical. Vacuum drying was carried out under a total pressure of less than 10^{-3} torr, at 350°C. for 1 hour. This removed the water, while minimizing oxidation, hydrolysis, and sintering of the fluorides. A thermobalance experiment showed that no

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*Materials Research Corporation, Orangeburg, New York 10962, USA (99.8% pure).

**Majac-Donaldson, P.O. Box 43217, St. Paul, Minnesota 55164 (USA). Orion Chemical Company, Hunt Beach, California 92646, USA (99.999 pure).

further weight changes occurred in this environment to within the detection limit (~ 10^{-3} wt%).

Since it might be argued that some pre-eutectic liquid might form as a consequence of undetected oxidation or hydrolysis during densification, CaF_2-MgF_2 eutectic mixtures were prepared containing 5 wt% MgO and CaO. A thermal analysis was performed under conditions identical to those in the dilatomater. No evidence of pre-eutectic liquid formation could be detected.

Dilatometry was carried out at a constant heating rate (CHR) of 4.5°C/min in flowing helium from which the oxygen had been removed by a hot zirconium getter. Constant temperature (CT) sintering was also carried out between 650°C and 850°C in the dilatometer, using a rapid heat up rate. In that case, the specimen reached the sintering temperature in about five minutes.

The microstructures of specimens quenched from particular temperatures during CHR sintering was observed on fracture surfaces of highly porous specimens or on polished and etched surfaces of the denser specimens. The etchant consisted of 100 g boric acid in 200 cm^3 of sulfuric acid (Ref. 4) used at 150°C for about 7 min. This removed CaF_2 completely, but only etched grain boundaries in MgF_2.

Data for CaF_2-MgF_2 interdiffusion were not available, so an interdiffusion experiment was performed on an MgF_2 single crystal embedded in CaF_2 powder. The couple was annealed in vacuum, at 950°C, for 96 hours. Afterwards, the MgF_2 crystal was briefly polished, sufficient to remove the CaF_2 particles that stuck to its

surface but removing only a few hundred Ångstrom of the crystal itself. A composition versus depth profile was obtained by measuring the relative Ca content as a function of sputtering time in an Auger system equipped with a secondary ion mass spectrometer. The sputtering gas was Ar and the sputtering rate was 400 Å/min. The results permitted a fair estimate of the cation interdiffusion rates at 950°C.

Auger analysis was also performed on intergranular fracture surfaces of partly sintered compacts in conjunction with Ar-ion sputtering to determine the Ca distribution during the pre-eutectuc sintering.

RESULTS AND DISCUSSION

Some dilatometry data, converted to % shrinkage (= 100 $\Delta L/L_0$; where ΔL is the length change and L_0 is the initial sample length) are shown in Fig. 1 for CHR sintering of samples containing up to 5 wt% CaF_2. It is evident that enhanced densification rates are observed as much as 200°C below the eutectic temperature. The enhancing effect of the CaF_2 appears already noticeable when as little as 0.1 wt% is added to the MgF_2, and saturates above 1 wt% of CaF_2. This behavior is difficult to bring in agreement with, at present, the only quantitative treatment of liquid phase sintering (Ref. 1), and argues for a different mechanism of pre-eutectic densification.

Grain growth rates are increased as a result of the CaF_2 addition, but at 900°C, Figure 1 shows that they are still relatively modest.

The microstructures of samples quenched from 900°C and 1000°C are compared in Figures 2 and 3, while the grain sizes at other temperatures are listed in Table 1. The grain size of the pure MgF_2 at 1000°C is about four times that of the 1 or 5 wt% CaF_2 containing MgF_2 at 900°C, while their densities are about equal (89% theoretical). Thus, the grain growth rates have not been increased sufficiently to overcompensate for the faster densification kinetics. This behavior may be qualitatively understood by considering the isothermal shrinkage and grain growth of a porous powder compact. The isothermal densification of a porous compact may be empirically described, to a good approximation, as:

$$\Delta L = L - L_o = -K_L D_L t^m \tag{1}$$

where L = sample length at time t, L_o is the initial sample length, K_L and m are constants, and D_L is the effective diffusion coefficient for densification. Equation (1) covers a very large part of the densification process, and only excludes the later stages. Other functional forms may also describe the densification adequately in the same densification regime but, as discussed by Exner (Ref. 5), there are presently no compelling arguments supporting one expression over another. The exponent m in Eq. (1) is usually found to be between 0.3 and 0.5. In the same densification regime grain growth may be described by

$$G = K_G(D_G t)^n + G_0 \tag{2}$$

where G is the average grain diameter and G_0 is the initial average grain diameter, K_L and n are constants, and D_G is the effective diffusion coefficient for grain growth. n in Eq. (2) is usually in the neighborhood of 0.3 (Refs 6-8). If $G >> G_0$, then combination of Eq. (1) and (2) gives:

$$G^{m/n} = (-\Delta L)(K_G{}^{m/n}/K_L)(D_G{}^m/D_L) \tag{3}$$

or

$$G = K(-\Delta L)^{n/m} \tag{4}$$

Expressions such as Eq. (4) have been derived theoretically by Kuczinski (Ref. 9), and have been observed experimentally, e.g., by Uskoković et al. (Ref. 10).

A comparison of grain sizes in the intermediate stage of "pure" and "doped" powders can be made at constant sintered density, i.e., ΔL = constant. Then, from Eq. (3) it follows that $G^* < G$ if

$$(D_G{}^*)^m/D_L{}^* < (D_G)^m/D_L \tag{5}$$

The quantities within asterisk refer to the "doped" powders, while those without one refer to the "pure" powders. Since n in Eq. (5) and (1) is less than 1, one might expect Eq. (5) to be usually satisfied if the impurity enhances the transport rate constants, D_L and D_G,

about equally. Particularly if such an impurity is below the solubility limit, segregating strongly to the grain boundaries, and densification is dominated by grain boundary transport while grain growth is controlled by impurity drag, should a decrease in grain size at constant density be expected in the intermediate stage. Above the solubility limit, grain boundary precipitates would tend to depress grain growth, leading to a further lowering of the apparent transport parameter D_G*. Densification rates will be slowed as well (Ref. 11-13). Particularly if diffusion along the particle/matrix is slow compared to the matrix/matrix grain boundary diffusion, may the effective D_L* be decreased significantly. Then densification becomes controlled by volume diffusion around the inclusion, and if this is also slow, significant back stresses can arise opposing or even arresting densification. Thus, at constant ΔL, G* is expected to be lower than G if the interface transport along the particle/matrix interface and the grain boundary diffusion is fast. If this is not the case, the opposite might result. Above the eutectic temperature, when an intergranular liquid phase increases the grainboundary mobility dramatically, a larger grain size should be expected at constant density. Significant enhancement of the grain growth rate can also be found above the eutectic temperature of the MgF_2-CaF_2 system, as can be seen in Fig. 2 and 3, and in Table 1.

The experiments on CaO-MgO-MgF_2-CaF_2 mixtures showed that no liquid forms below the eutectic temperature. At the same time, densification and grain growth behavior below 980°C is not in

agreement with what would be expected if a liquid phase sintering mechanism were active. It is therefore concluded that the enhanced pre-eutectic densification kinetics are due to a solid state transport mechanism with a rate increased by the eutectic additive. While the CHR experiments permit a convenient and rapid evaluation of the sintering behavior of different powder mixtures, a detailed analysis of the kinetics (Ref. 14) is not reliable due to possible interference from non-densifying mechanisms (Ref. 15). A possible indication of the sintering mechanism may come from a comparison of diffusion rates derived from CT experiments, assuming a single rate controlling mechanism, with those obtained from the diffusion couple experiment.

TABLE 1. Grain sizes in μm of specimens quenched after CHR sintering at 4.5°C/min.

Temperature(°C)	CaF_2 content in wt%			
	0	0.1	1	5
800	0.4	0.5	0.5	0.5
900	0.6	1.0	2.2	2.4
1000	10	10	20	50

Some CT densification data are shown in Fig. 4. A time correction, δt, was necessary to take into account the densification that took place in the heat-up cycle, by forcing the data to obey a

relationship of the type $\log (\Delta L/L_0) = m \log (t + \delta t) + B$, where B is a constant. This is a relationship similar to Eq. (1).

To determine which transport mechanism is dominant during sintering, diffusion coefficients calculated from the densification data should be compared to those obtained from an interdiffusion measurement. Diffusion data obtained from sintering experiments are subject to significant uncertainties, mainly because the sintering models involved in the calculations are still inadequately developed. Large discrepancies are therefore necessary between the two diffusion coefficients before conclusions can be drawn about mechanisms. From the data obtained here, such large descrepancies were indeed found, as discussed below.

The expected transport mechanisms are either grain boundary or volume diffusion. Assuming that volume diffusion only is operating, the effective volume diffusion may be estimated from the data with an expression developed by Johnson (Ref. 16)

$$- \ln (1 - P) = 378\gamma\Omega\bar{D}(t_f - t)/G^3 kT \qquad (6)$$

For t = 10 min, with $t_f \approx 100$ min estimated from extrapolation of the data shown in Fig. 4 to full density, the porosity P = 0.33 at t = 10 min, $\gamma \approx 500$ erg cm^{-2} (Ref. 17), the measured grain size G 10 micron, T = 1125K, and the molecular volume of MgF_2; $\Omega \approx 33 \times 10^{-24}$ cm^3, one finds the diffusion coefficient $D \simeq 2 \times 10^{-11}$ cm^2/sec at 850°C. This value is to be compared with the interdiffusion coefficient determined from the MgF_2 - CaF_2 couple. The relative Ca

concentration versus the squate root of the sputtering time is shown in Fig. 5. The sputtering rate was about 400 Å min^{-1} giving a mean penetrative distance of about $1x10^{-4}$ cm after 96 hrs, making D ≈ $1.4x10^{-14}$ cm^2/sec at 950°C. The activation energy was not determined in the present work, but was estimated to be at least 90 kcal $mole^{-1}$ from diffusion data of Sr and Ca in CaF_2 (Ref. 18,19). This makes the estimated diffusion coefficient at 850°C about $6x10^{-16}$ cm^2 sec^{-1}. It can then be concluded that the volume diffusion rates necessary to account for the observed pre-eutectic densification rates are 4 to 5 orders of magnitude higher than those obtained from the interdiffusion experiment.

Additionally, the Auger analysis of intergranularly fractured specimens indicates that the grainboundaries are significantly enriched in Ca to a depth of less than 100 Å, as shown in Fig. 6.

All the obtained results thus strongly indicate that enhanced pre-eutectic densification rates can be attributed to increased solid state grain boundary transport rates caused by the presence of an additive that can form a eutectic liquid at a higher temperature. This phenomenon might be understood if one considers that diffusion rates scale approximately as the absolute temperature of the melting point of a solid (Ref. 10). If the grain boundaries are rich in the eutectic forming additive then their relative melting points should be considerably below that of the matrix, and their transport rates should be accordingly enhanced.

The results, therefore, suggest that densification of ceramic powders could be favorably affected, without an undue increase in the

grain growth rate, by the addition of small amounts of eutectic forming additives, and sintering below the eutectic temperature.

ACKNOWLEDGMENTS

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Fig. 1. Shrinkage and grain size vs temperature for pure MgF_2, 0.1 wt%, 1 wt%, and 5 wt% CaF_2 containing MgF_2. The heating rates are 4.5°C/min. The eutectic temperature is 980°C. Theoretical density corresponds to 20.1% shrinkage. XBL 814-5598

Fig. 2. Scanning electron micrographs of powder compacts quenched from 900°C, after CHR sintering at 4.5°C/min. The calcium fluoride contents are indicated in wt% in the lower left corners. XBB 815-3802

Fig. 3. Scanning electron micrographs of powder compacts quenched from 1000°C, after CHR sintering at 4.5°C/min. The calcium fluoride contents are indicated in wt in the lower left corners. XBB 815-3804

Fig. 4. Log $(\Delta L/L_o)$ versus log $(t + \delta t)$ for MgF_2 containing 1 wt% CaF_2 additive, sintered at the indicated temperatures. The heatup time was about 5 min leading to a small amount of densification before temperature equilibrium was reached; this was corrected for by the time correction, δt. XBL 815-3785

Fig. 5. Relative Ca concentration as a function of sputtering time in the Auger analysis of the MgF_2-CaF_2 interdiffusion couple. The sample was annealed for 96 hours at 950°C. The mean Ca penetration depth is about 1 μm. XBL 831-7668

Fig. 6. Auger electron depth profile on intergranular fracture surface of a CHR sintered specimen with an average CaF_2 content of 1 wt%. The specimen was sintered at 4.5°C/min to 900°C. The eutectic composition has a Ca/F ratio of about 0.25. XBL 815-5836

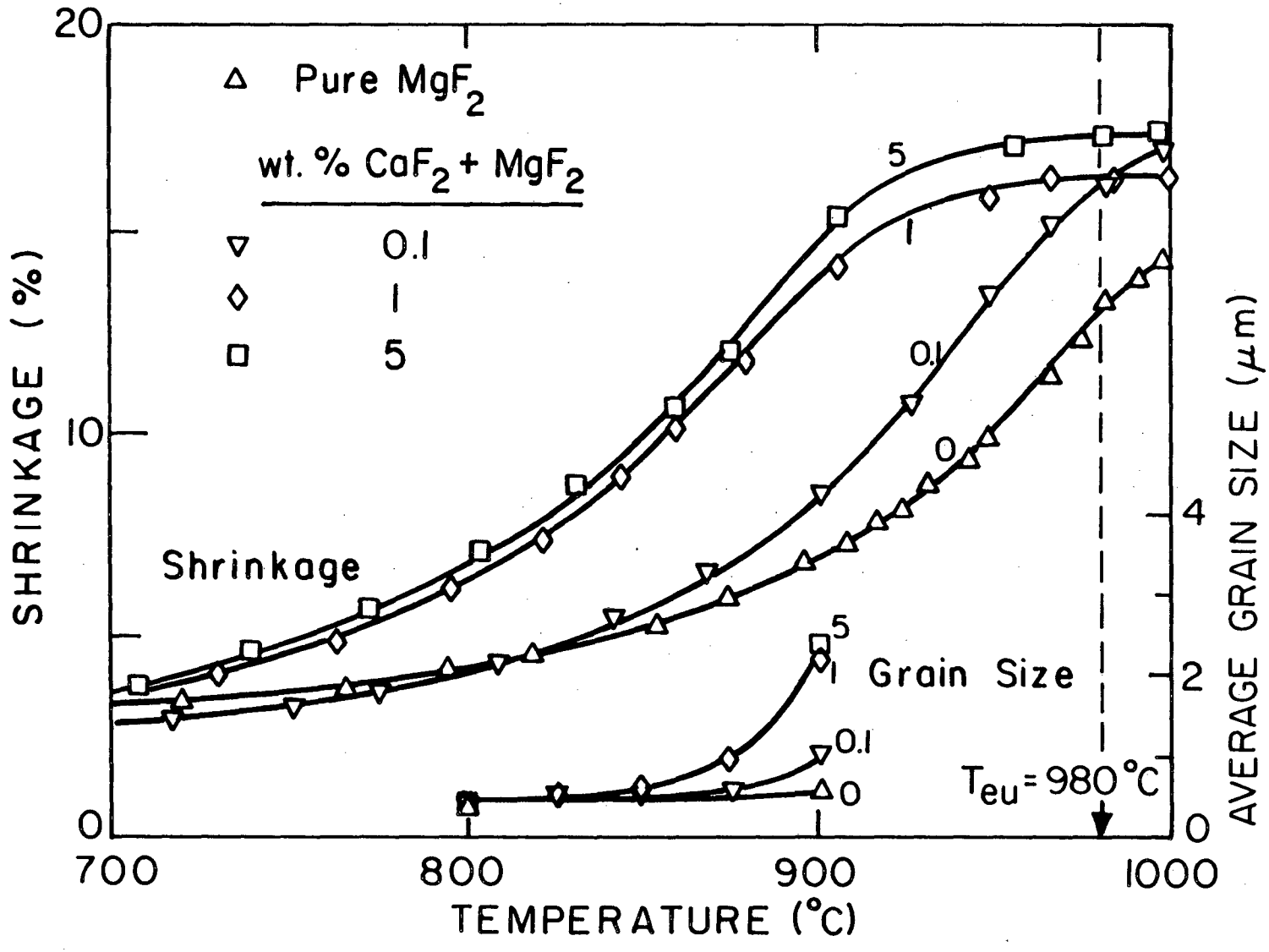

Figure 1

XBL 814-5598

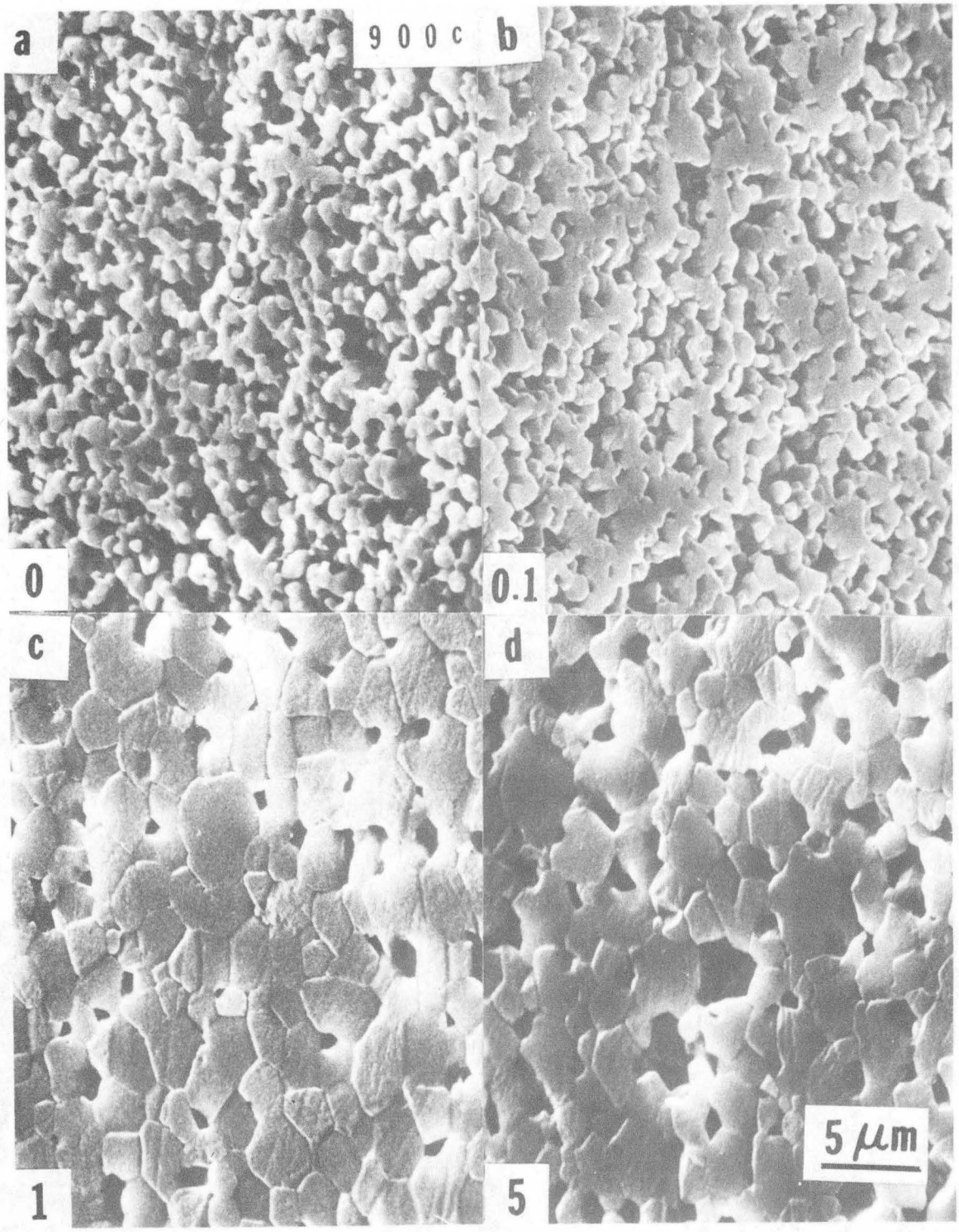

Figure 2 XBB 815-3802

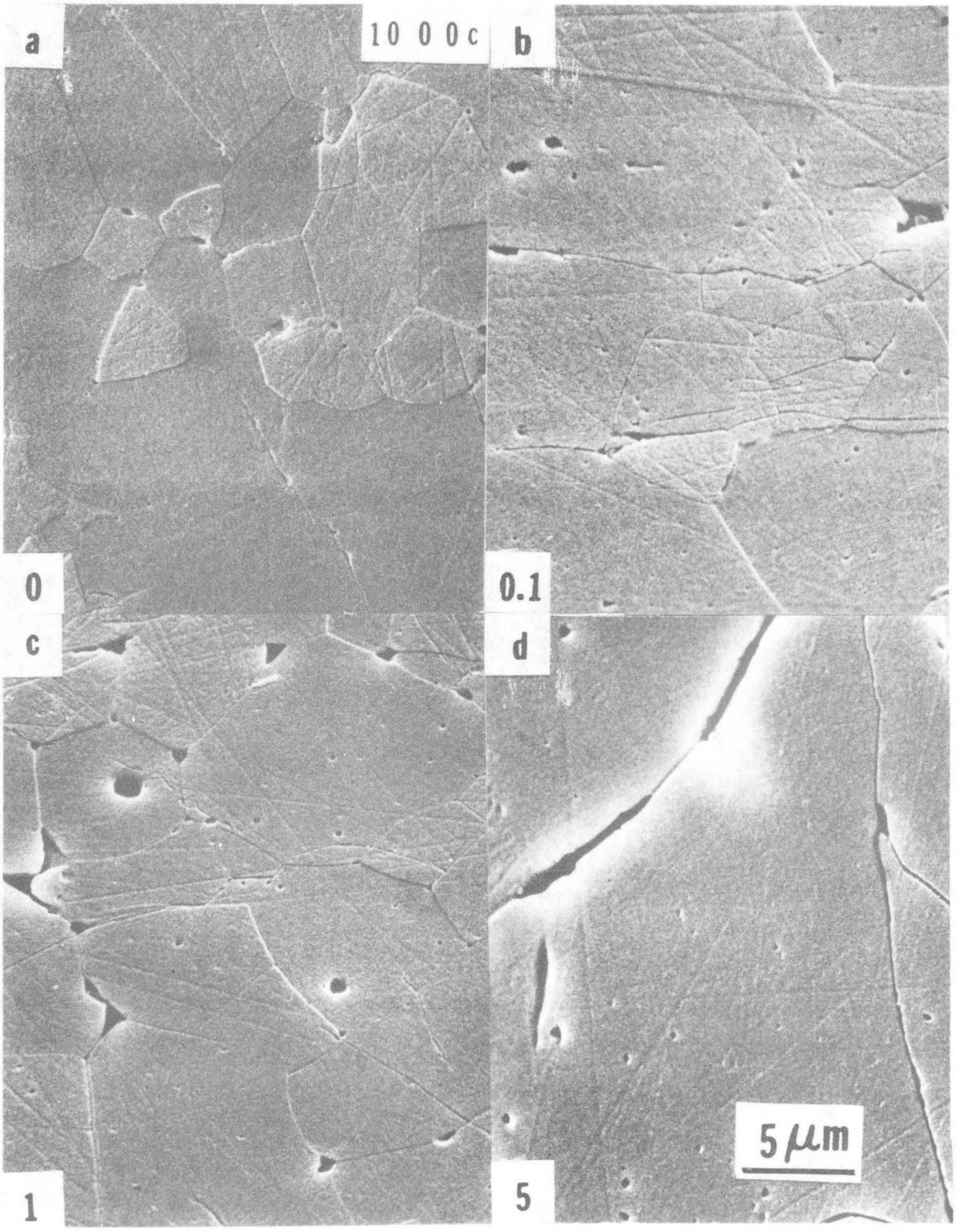

Figure 3

XBB 815-3804

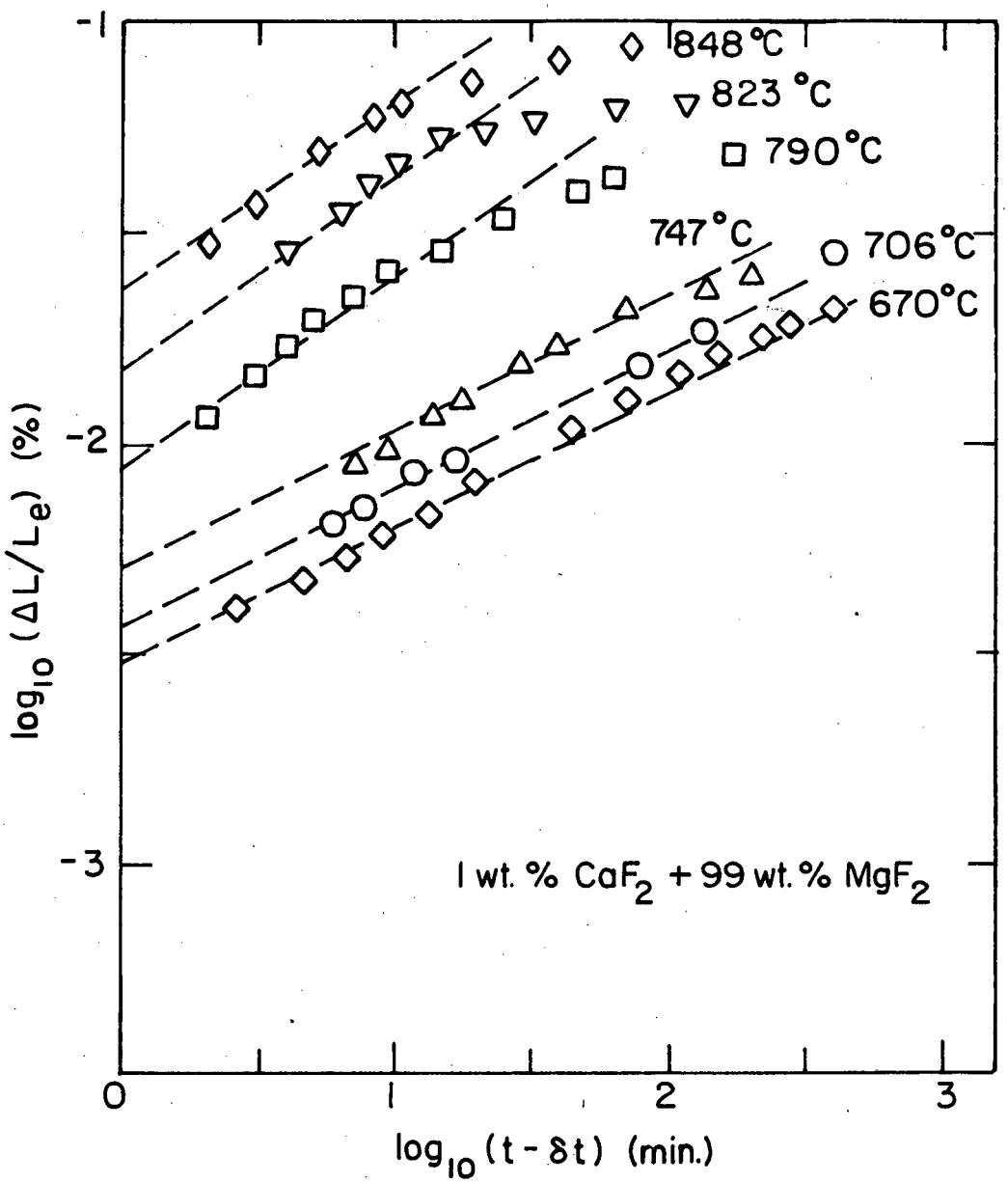

Figure 4

XBL 815-5785

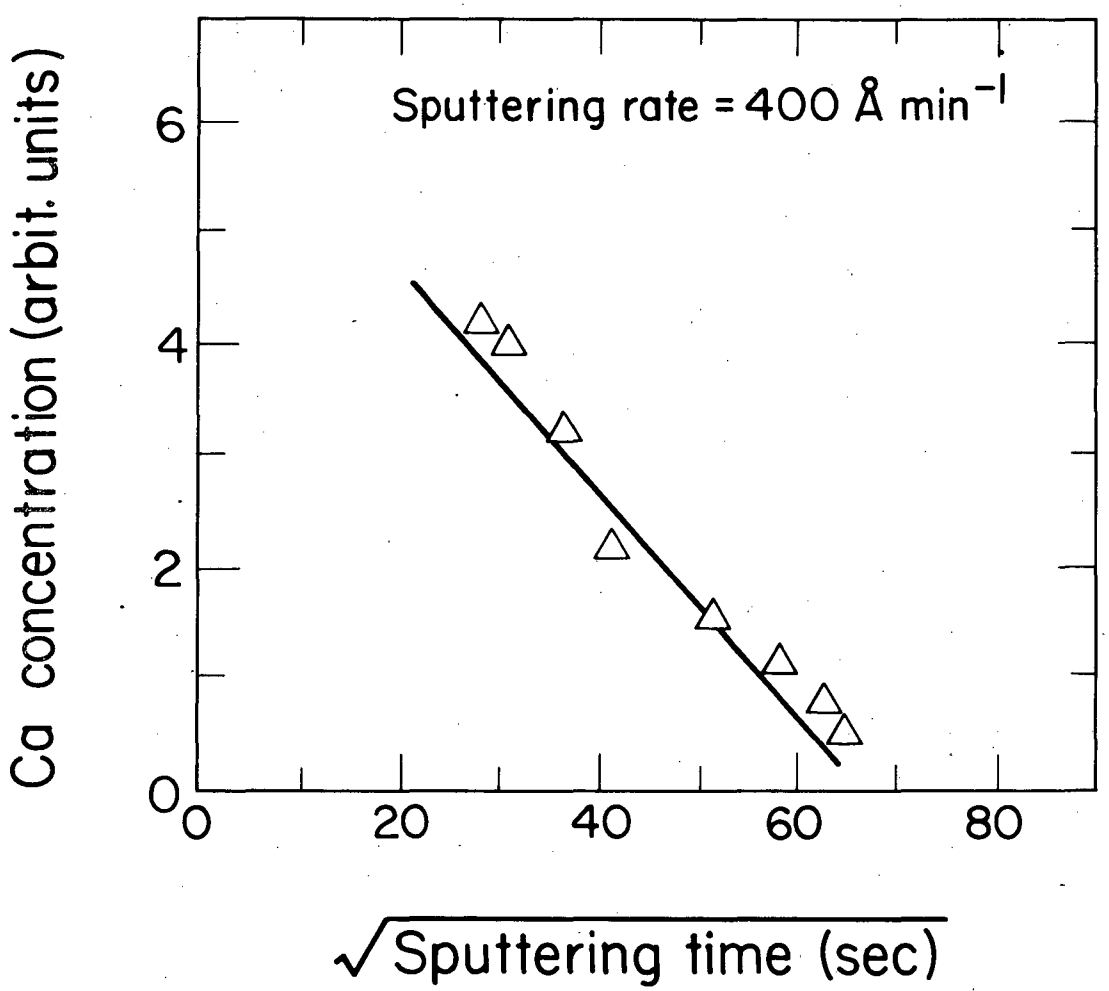

Figure 5

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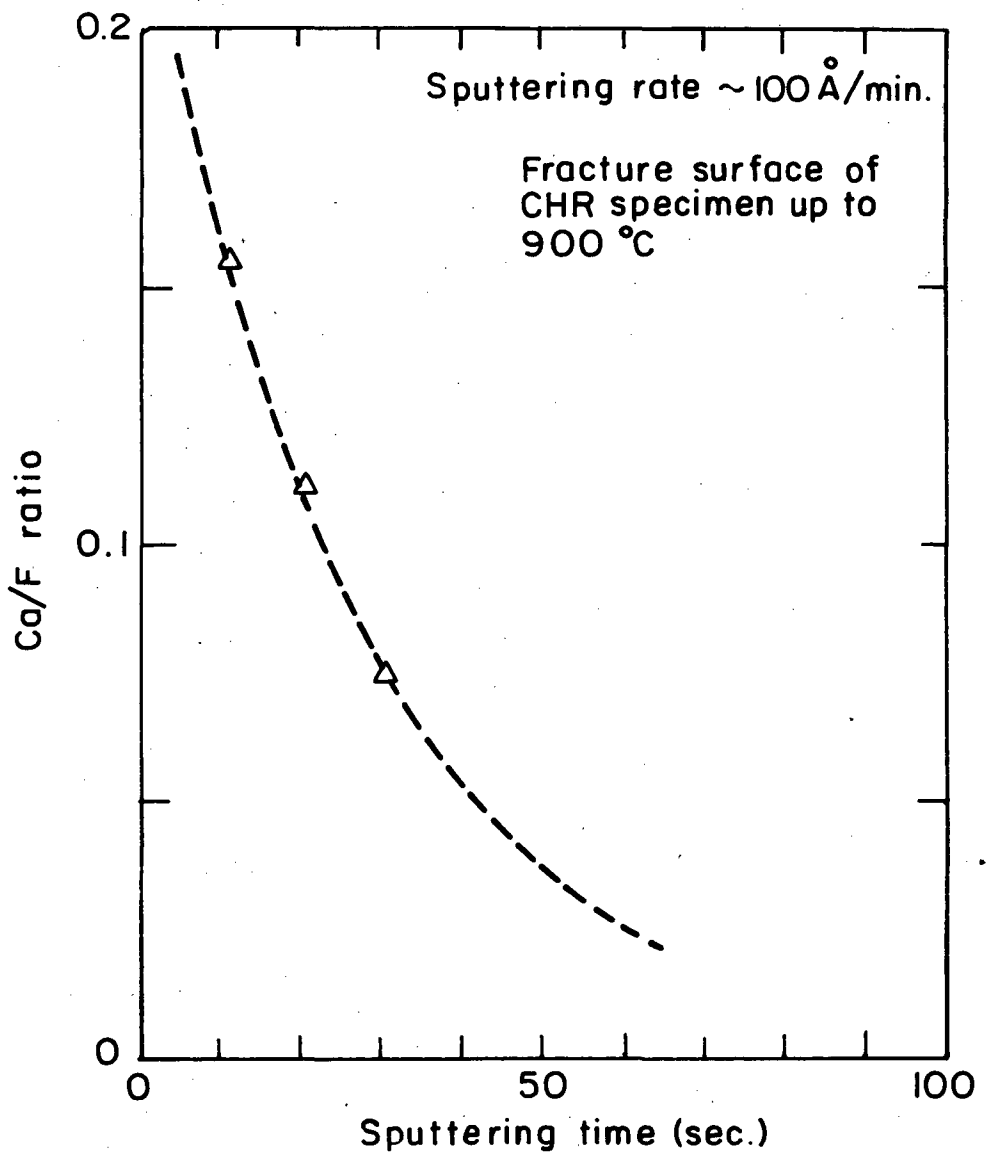

Figure 6

XBL 815-5836

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