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MICROSTRUCTURE ANALYSIS AND STRESS-STRAIN BEHAVIOR OF A MODEL REFRACTORY SYSTEM MgO-CaMgSiO<sub>4</sub>

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### Publication Date

1975-02-01

0 0 0 0 4 2 0 0 7 1 5  
Submitted to Journal of American  
Ceramic Society

LBL-3507 Rev.

c.1

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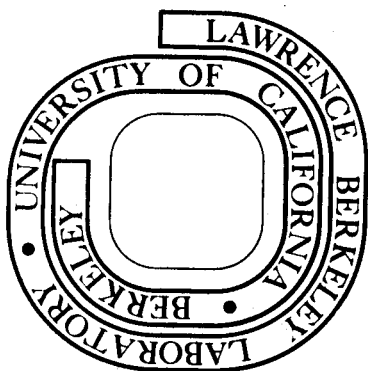
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February 1975

Prepared for the U. S. Atomic Energy Commission  
under Contract W-7405-ENG-48

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MICROSTRUCTURE ANALYSIS AND STRESS-STRAIN BEHAVIOR  
OF A MODEL REFRACTORY SYSTEM  $\text{MgO-CaMgSiO}_4$

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ABSTRACT

The effects of the presence of a silicate boundary phase on the high-temperature stress-strain behavior of MgO materials has been studied using a model system  $\text{MgO-CaMgSiO}_4$  (monticellite, CMS). Specimens for testing were fabricated by hot pressing, or by hot pressing and annealing, and contained up to 15% silicate phase. The boundary phase consisted primarily of CMS. The stress-strain behavior of these specimens in the range 1200-1400°C was found to be strongly dependent on the degree of continuity of the grain boundary phase, and on the temperature.

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## I. Introduction

The suitability and durability of various magnesia refractories for use in severe environments at high temperatures are well known, and the mechanical behavior of specific compositions is frequently discussed in the literature.<sup>1-3</sup> Little work of a fundamental nature, however, has been directed toward establishing basic relationships between microstructural features of multiphase systems and behavior under load. While this situation is no doubt due in large part to the extreme complexity of practical refractory systems, the mechanical behavior of both single crystal and polycrystalline MgO seems sufficiently well understood to provide a starting point for a more detailed investigation of these systems than has been reported to date.

In a recent paper, Snowden and Pask<sup>4</sup> reported on the significance of grain boundary character in influencing the high temperature mechanical behavior of polycrystalline MgO. Marked differences in both stress-strain and creep results for two types of MgO were attributed to differences in the structure of the grain boundary region. The importance of the nature of the grain boundaries in MgO has been recognized by many other investigators as well.<sup>5-8</sup> Porosity, microscopic and sub-microscopic impurities, and the presence of a silicate film along grain boundaries can all significantly alter the mechanical behavior at elevated temperatures. Thus, to study the relationship between microstructure and mechanical properties of practical refractory systems, it is necessary to first evaluate the effect of a well-characterized grain boundary phase on high temperature behavior.

The principal purpose of this work was to develop a model system consisting of MgO and  $\text{CaMgSiO}_4$  (monticellite, subsequently referred to as CMS), and to study the effects of the amount and nature of distribution of the second phase on the high temperature mechanical behavior of MgO materials. The selection of this particular system as a model was due in part to the nature of the liquid-solid phase equilibrium at high temperatures, and to specific applicability to practical refractory systems.

## II. Experimental Procedure

### (1) Specimen Preparation and Characterization

Mixtures of reagent grade MgO,  $\text{CaCO}_3$ , and  $\text{SiO}_2$  were prepared to yield final compositions containing MgO with an equivalent of 0%, 5%, 10%, and 15% CMS by weight. Powders were dried in a vacuum oven and dry mixed for 24 h. The mixtures were placed in a vacuum hot press, heated at  $1000^\circ\text{C}$  for 2 h, and then pressed at  $1250^\circ\text{C}$  with a load of 3000 psi for 30 min. The compacts were subsequently annealed in air at  $1550^\circ\text{C}$  for 2 h. These specimens were designated as Type HPA.

An alternate means of preparation involved the use of prereacted CMS powder with MgO. The prereacted CMS was prepared by dry mixing the reagent salts and heating at  $1650^\circ\text{C}$  for 16 h in a gas/air Bickley furnace. After cooling, the material was crushed to a fine powder. Another compact containing 5% CMS was made by hot pressing a mixture of MgO and 15% prereacted CMS at  $1650^\circ\text{C}$  long enough to extrude the proper amount of liquid phase, as described by Stoops.<sup>9</sup> These specimens were designated as Type EX.

The density of all specimens was measured using a displacement technique, with mercury as the displacement medium. The density of the CMS powder was determined using a helium gas pycnometer. Standard X-ray diffraction techniques were used to determine the crystalline phases present.

Specimens for microscopic examination were polished on a Syntron vibrator with  $\alpha\text{-Al}_2\text{O}_3$  in  $\text{H}_2\text{O}$ , or in a solution of kerosene, glycerine, and  $\text{H}_2\text{O}$ , to minimize relief. The average size of MgO grains for each specimen was determined from photomicrographs using a cross-sectional area technique which accounted for the area occupied by the boundary phase. It was assumed that the volume fraction of the boundary phase was equal to its fractional area in a polished section.

## (2) Mechanical Testing

Specimens for mechanical testing were cut from the compacts using a diamond blade. All specimens had a length to width ratio of approximately 2:1 and nominal dimensions of 0.6 in. x 0.3 in. x 0.3 in. Specimens were polished using a series of Buehler emery papers and then mounted in a special jig and sanded on both ends to ensure that the ends were flat, parallel to each other, and perpendicular to the loading axis.

Stress-strain tests in the temperature range  $1200^\circ\text{C}$ - $1400^\circ\text{C}$  were made in compression with a constant loading rate using equipment described previously by Hulse and Copley<sup>10</sup> (Apparatus III). A continuous record of load and engineering strain up to fracture was obtained using Daytronic differential transformer units. Stresses were calculated from the indicated load and the initial specimen cross-sectional area. All strains reported herein are true strains, the natural logarithm of one

plus the engineering strain,

### III. Results and Discussion

#### (1) Specimen Characterization

The measured densities are presented in Table I. The calculated theoretical values for the compositions included in the table were based on the measured values of  $3.580 \text{ g/cm}^3$  for MgO single crystals and of  $3.08 \text{ g/cm}^3$  for prereacted CMS. While the density of CMS has been reported by Rigby<sup>11</sup> as  $3.20 \text{ g/cm}^3$ , a calculated density from the lattice parameters measured by Sahama and Hytonen,<sup>12</sup> and by Roy,<sup>13</sup> was found to be  $3.05 \text{ g/cm}^3$ . This value is in good agreement with the measured value of  $3.08 \text{ g/cm}^3$ .

From Table I, the measured densities of the specimens are seen to be less than the theoretical values. For specimens containing CMS these differences were attributed to the presence of an undetermined phase. It is thus appropriate to consider the possible phase changes taking place during firing.

Phase equilibrium studies of the system CaO-MgO-SiO<sub>2</sub> by Ricker and Osborn<sup>14</sup> indicate that under stable equilibrium conditions CMS melts incongruently to form merwinite (Ca<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>) and MgO at 1487°C, MgO and liquid at 1508°C, and liquid at 1650°C. The reverse should occur on cooling. Another possible cooling path is the direct metastable congruent crystallization to CMS, a phenomenon similar to that described by Aksay and Pask<sup>15</sup> for mullite, and by Eitel<sup>16</sup> for complex silicates in general. The prereacted CMS powder which was cooled rapidly from 1650°C showed only CMS by X-ray diffraction and no glassy phase on microscopic examination, suggesting the second cooling path.



Heating of the mixtures equivalent to MgO and CMS, however, resulted in densities lower than theoretical values. An examination of the phase relationships indicates that at 1550°C the equilibrium phases are the MgO grains and a MgO-deficient CMS liquid. Equilibrium cooling would require a peritectic reaction of this liquid with the MgO grain surfaces; this reaction would depend on diffusion through the reaction product forming on the surfaces and would be a slow process. If the liquid then cools independently in an equilibrium manner, according to the phase diagram CMS and akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ) would form. Alternatively, metastable cooling could form CMS and liquid or amorphous phase which would account for the lower measured densities listed in Table I. Only MgO and CMS phases were detected by X-ray diffraction in these specimens, so that a mixture of CMS and amorphous phase should constitute the material in the grain boundary regions in the microstructures shown in Fig. 1. All specimens were translucent after firing.

The ratio of the MgO-MgO contact area to the total interfacial area for each specimen was determined using a method described by Stephenson and White.<sup>17</sup> A number of straight lines were drawn on photomicrographs of each specimen and the number of intersections made with MgO-MgO ( $N_{ss}$ ) and MgO-intermediate phase ( $N_{s1}$ ) boundaries were noted. The ratio was then determined as

$$\frac{\text{MgO-MgO interfacial area}}{\text{Total interfacial area}} = \frac{N_{ss}}{N_{ss} + N_{s1}} \quad (1)$$

The spatial distribution of a liquid phase relative to solid particles has been shown by Smith<sup>18</sup> to depend on the equilibrium dihedral angle. As this angle approaches  $0^\circ$ , the degree of penetration of the liquid between solid grains increases until all of the grains are isolated. In the system MgO-CMS an equilibrium dihedral angle of  $25^\circ$  has been reported;<sup>19</sup> it is thus expected that a significant amount of MgO grain-grain contacts will be present at equilibrium. The number, however, should also be a function of the amount of liquid. The ratios determined for each material are given in Table I. For the specimens of Type HPA, the amount of MgO grain-grain contacts was found to decrease as the amount of CMS was increased. However, for the 5% CMS specimens of Type EX, the boundary area ratio was essentially the same as for the 15% CMS specimens of Type HPA, indicating that the distribution of phases was essentially determined by the initial content of liquid and that extrusion simply reduced the amounts of liquid between the MgO grains. This suggests that the method of liquid extrusion can be quite useful in developing multiphase materials with more uniformly dispersed boundary phases.

Average sizes for MgO grains for the specimens tested are also given in Table I. While the smallest addition of secondary phase resulted in an increase in the rate of growth of MgO grains compared to the case of no addition, further additions slowed the growth. Since the CMS additions result in the presence of a liquid phase at annealing temperatures, it is expected that grain growth occurs by a solution-diffusion-precipitation process. Also, since there is no reason to suspect that solution and precipitation rates are dependent on the amount of liquid present,

diffusion is probably the rate-controlling step. The diffusion paths are the shortest for the compacts with the smaller amounts of liquid. Grain growth in similar MgO-silicate systems has been studied by Stephenson and White,<sup>17</sup> and by Buist et al.<sup>20</sup> with similar results.

## (2) Stress-Strain Tests

Figure 2 shows stress-strain relations for the MgO-CMS materials tested for the polycrystalline MgO prepared in the manner described for specimens of Type HPA. The 0.2% offset yield stress, the maximum stress before fracture, and the strain at fracture for each specimen are listed in Table II.

It is evident that for all specimens both the yield stress and fracture stress decrease as the temperature is increased, and also that the yield stresses and their temperature sensitivity are greater for the composites than for MgO. Furthermore, for specimens of Type HPA, the yield and fracture stresses increase as the amount of CMS is increased, while the total strain at fracture remains relatively constant and small. In comparison MgO specimens have higher fracture stresses and much higher strains at fracture. The type EX 5% CMS specimens had yield stresses and fracture stresses comparable to the 15% CMS specimens of Type HPA at comparable temperatures. To explain these observations the distribution of the boundary phase must be considered.

The fraction of MgO grain-grain interfacial area, defined by Eq. (1) and with values listed in Table I, can be taken as a measure of the continuity of the MgO grain framework. The significance of the fraction as an indicator of mechanical behavior is evident by the similarity in behavior of the Type HPA specimens containing 15% CMS with an area

fraction of 0.26, and the Type EX specimens containing 5% CMS with an area fraction of 0.28. However, the 5% CMS specimens of Type HPA having an area fraction of 0.51 yield and fracture at stress levels significantly lower than do the Type EX specimens with the same CMS content. In general, as the continuity of the grain boundary phase increased, i.e. as the area ratio decreased, the high temperature mechanical behavior of these materials was improved.

All of the mixtures were essentially brittle as indicated by the comparatively small strain at fracture in each test. The generally lower fracture stresses compared to the polycrystalline MgO specimens can be associated with the more brittle nature of these compacts. However, the greater spread in yield stress data between 1200°C and 1400°C in comparison with MgO suggests that a decrease in the rigidity of the boundary phase with increasing temperature due to decreasing viscosity of the grain boundary phase may play a significant role in determining deformation characteristics.

In a previous paper,<sup>4</sup> the stress-strain and creep behavior of polycrystalline MgO of Type HPA were discussed. Deformation was due to extensive dislocation motion, and it was noted that the yield stresses for this polycrystalline material were in good agreement with average values reported by Copley and Pask<sup>21</sup> for MgO single crystals in <001> and <111> orientations. In the MgO-CMS materials presently being considered, the role of a relatively temperature-sensitive rigid boundary phase in determining mechanical behavior is dependent on whether the MgO grain or grain boundary phase tends to be continuous. At 1200°C, the yield stresses are higher and approach the value for MgO with the

development of an MgO framework, i.e. as the area ratio increases. At 1400°C, the yield stresses decrease below that for MgO with the development of an MgO framework of reduced cross-section compared to dense polycrystalline MgO. Thus at 1200°C stress-strain behavior of these composite materials must be controlled by the relatively rigid boundary phase, while at 1400°C the boundary phase controls deformation only when the MgO grain-grain contact area is low.

#### IV. Summary and Conclusions

A model system has been developed to study the effect of the presence of a boundary phase on the high temperature mechanical behavior of MgO materials. Specimens of polycrystalline MgO containing up to 15% of a silicate phase equivalent to CMS were fabricated by hot pressing or by hot pressing and annealing techniques. Phase diagram analysis and X-ray diffraction indicated the presence of CMS and suggested in addition the presence of an amorphous phase in the boundary material.

The high temperature stress-strain behavior of these specimens was studied in compression over the temperature range 1200-1400°C. Behavior was found to be strongly dependent on the degree of continuity of the boundary phase. At 1200°C the stress-strain behavior was concluded to be controlled by the relatively rigid boundary phase, while at 1400°C deformation was controlled by the boundary phase only when the MgO grain-grain contact area was low.

#### Acknowledgment

This work was supported in part by a grant provided by the Foundation in Refractories Education and in part by the U. S. Energy Research and Development Administration.

References

1. W. F. Ford, A. Hayhurst, and J. White, "The Effect of Bond Structure on the High Temperature Tensile Behavior of Basic Bricks," *Trans. Brit. Ceram. Soc.*, 60 [8] 581-601 (1961).
2. B. H. Baker and P. Schroth, "High Hot Strength in Basic Brick," *Bull. Am. Ceram. Soc.*, 47 [7] 623-626 (1968).
3. H. J. S. Kriek and B. B. Segal, "Effect of the Silicate Constitution of Magnesite Bricks on the High-Temperature Strength," *Trans. Brit. Ceram. Soc.*, 66 [2] 65-83 (1967).
4. W. E. Snowden and J. A. Pask, "High-Temperature Deformation of Polycrystalline Magnesium Oxide," *Phil. Mag.*, 29 [3] 441-455 (1974).
5. S. M. Copley and J. A. Pask, "Deformation of Polycrystalline MgO at Elevated Temperatures," *J. Am. Ceram. Soc.*, 48 [12] 636-642 (1965).
6. R. B. Day and R. J. Stokes, "Mechanical Behavior of Polycrystalline Magnesium Oxide at High Temperatures," *J. Am. Ceram. Soc.*, 49 [7] 345-354 (1966).
7. A. G. Evans, D. Gilling and R. W. Davidge, "The Temperature Dependence of the Strength of Polycrystalline MgO," *J. Matl. Sci.*, 5 187-197 (1970).
8. T. G. Langdon and J. A. Pask, "Effect of Microstructure on Deformation of Polycrystalline MgO," *J. Am. Ceram. Soc.*, 54 [5] 240-246 (1971).
9. R. F. Stoops, "Liquid Extrusion Forming of Powdered Refractory Materials into High Density Parts;" presented at 68th Annual Meeting, the American Ceramic Society, Washington, D.C., May 11, 1966 (Refractories Div., No. 28-R-66); for abstract see *Am. Ceram. Soc.*

- Bull., 45 [4] 449 (1966).
10. C. O. Hulse and S. M. Copley, "High Temperature Compressive Deformation Equipment," Am. Ceram. Soc. Bull., 45 [5] 530-534 (1966).
  11. G. R. Rigby, "Mineralogy of Ceramic Materials," Brit. Refractories Res. Assn., Stoke-on-Trent, 1948.
  12. T. G. Sahama and K. Hytonen, "Calcium-Bearing Magnesium-Iron Olivines," Am. Min., 43 862-81 (1958).
  13. D. M. Roy, "The System  $\text{Ca}_2\text{SiO}_4\text{-CaMgSiO}_4$ ," Min. Mag., 31 187 (1956).
  14. R. W. Ricker and E. F. Osborn, "Additional Phase Equilibrium Data for the System  $\text{CaO-MgO-SiO}_2$ ," J. Am. Ceram. Soc., 37 [3] 133-139 (1954).
  15. I. A. Aksay and J. A. Pask, "The Silica-Alumina System: Stable and Metastable Equilibria at 1.0 Atmosphere," Science, 183 69-71 (1974).
  16. W. Eitel, Silica Melt Equilibria (Rutgers Univ. Press, New Brunswick, N.J., 1951), 25-29.
  17. I. M. Stephenson and J. White, "Factors Controlling Microstructure and Grain Growth in Two-Phase (One Solid + One Liquid) and in Three-Phase (Two Solid + One Liquid) Systems," Trans. Brit. Ceram. Soc., 66 [9] 443 (1967).
  18. C. S. Smith, "Grains, Phases and Interfaces: An Interpretation of Microstructure," Trans. AIME, 175 [1] 15-51 (1948).
  19. B. Jackson, W. F. Ford and J. White, "The Influence of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  on the Wetting of Periclase Grains by Liquid Silicate," Trans. Brit. Ceram. Soc., 62 [7] 577-601 (1963).
  20. D. S. Buist, B. Jackson, I. M. Stephenson, W. F. Ford, and J. White, "The Kinetics of Grain Growth in Two Phase (Solid-Liquid) Systems,"

Trans. Brit. Ceram. Soc., 64 [4] 173-209 (1965).

21. S. M. Copley and J. A. Pask, "Plastic Deformation of MgO Single Crystals up to 1600°C, J. Am. Ceram. Soc., 48 [3] 139-146 (1965).



Table I. Density, grain size, and grain boundary contact area ratio data

Composition	% Theor. Density	Density, gm/cm <sup>3</sup>		G.S.	MgO grain-grain area ratio*
		Measured	Calculated		
<u>Type HPA</u>					
100% MgO	98.5	3.550	3.580	17 $\mu$ m	1.00
5% CMS, 95% MgO	98.1	3.498	3.552	30 $\mu$ m	0.51
10% CMS, 90% MgO	97.7	3.459	3.525	25 $\mu$ m	0.37
15% CMS, 85% MgO	99.2	3.420	3.499	22 $\mu$ m	0.26
<u>Type EX</u>					
5% CMS, 95% MgO	98.4	3.496	3.552	31 $\mu$ m	0.28

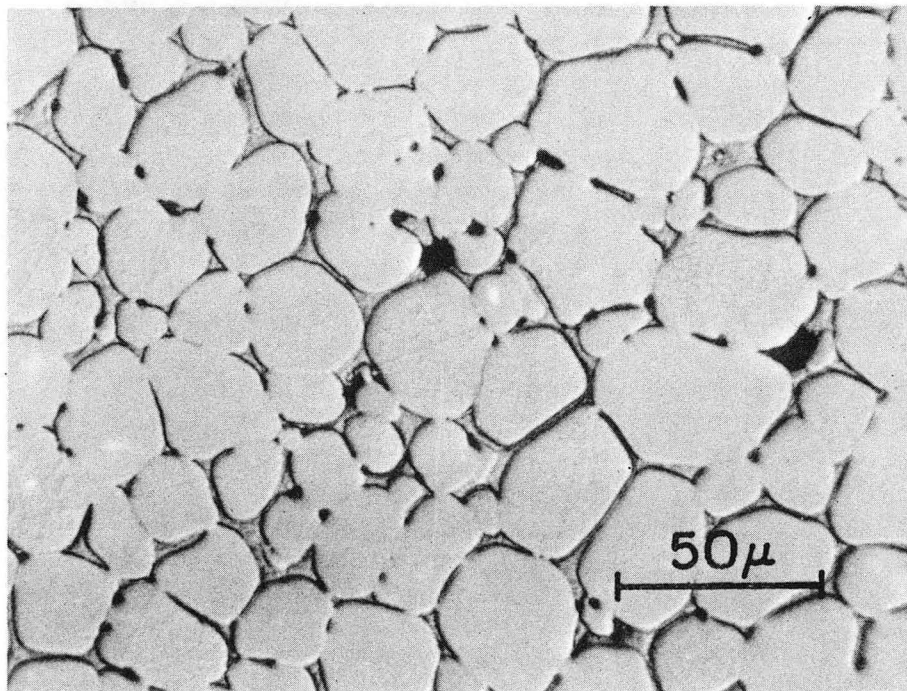
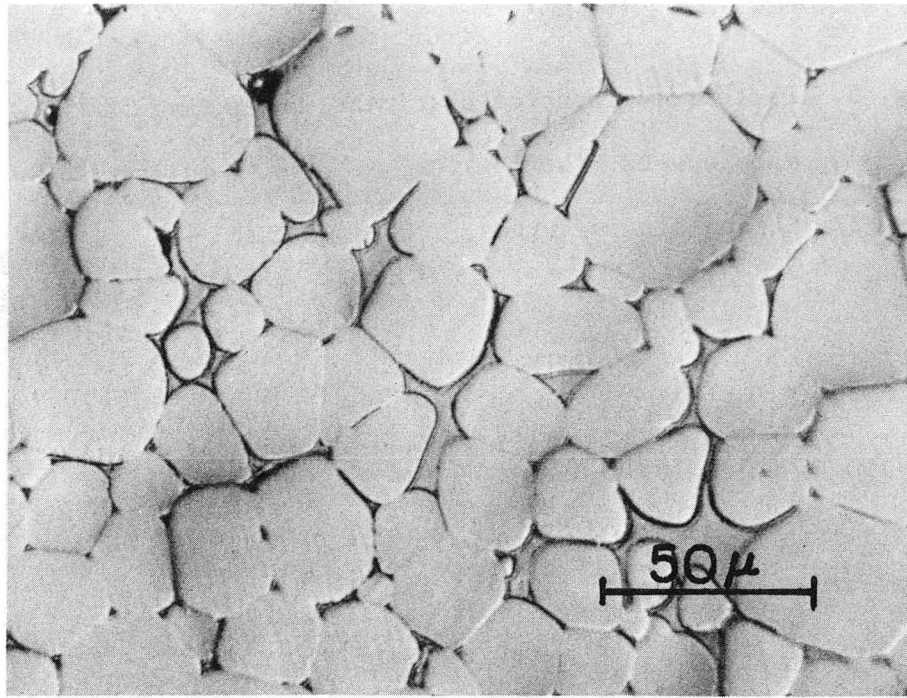
\*Ratio is  $N_{ss}/N_{s1} + N_{s1}$  where  $N_{ss}$  is number of MgO-MgO interface interceptions and  $N_{s1}$  is number of MgO-boundary phase interface interceptions measured by linear intercept method.

Table II. Stress-strain data

Composition	Yield Stress	Fracture Stress	Strain at Fracture
<b>Type HPA</b>			
<u>100% MgO</u>			
1200°C	10,400 psi	23,800 psi	13.2%
1300°C	8,100	16,400	13.0%
1400°C	7,800	12,500	> 8.0%
<u>5% CMS</u>			
1200°C	11,300	13,600	2.3%
1300°C	5,800	7,500	2.4%
1400°C	4,000	6,600	2.2%
<u>10% CMS</u>			
1200°C	14,000	17,600	2.7%
1300°C	7,900	10,000	2.3%
1400°C	4,500	6,900	2.2%
<u>15% CMS</u>			
1200°C	16,400	22,400	5.2%
1300°C	12,400	16,500	4.2%
1400°C	8,000	10,100	3.1%
<b>Type EX</b>			
<u>5% CMS</u>			
1200°C	15,500	22,840	2.5%
1300°C	11,400	18,560	4.2%
1400°C	7,600	10,580	2.8%

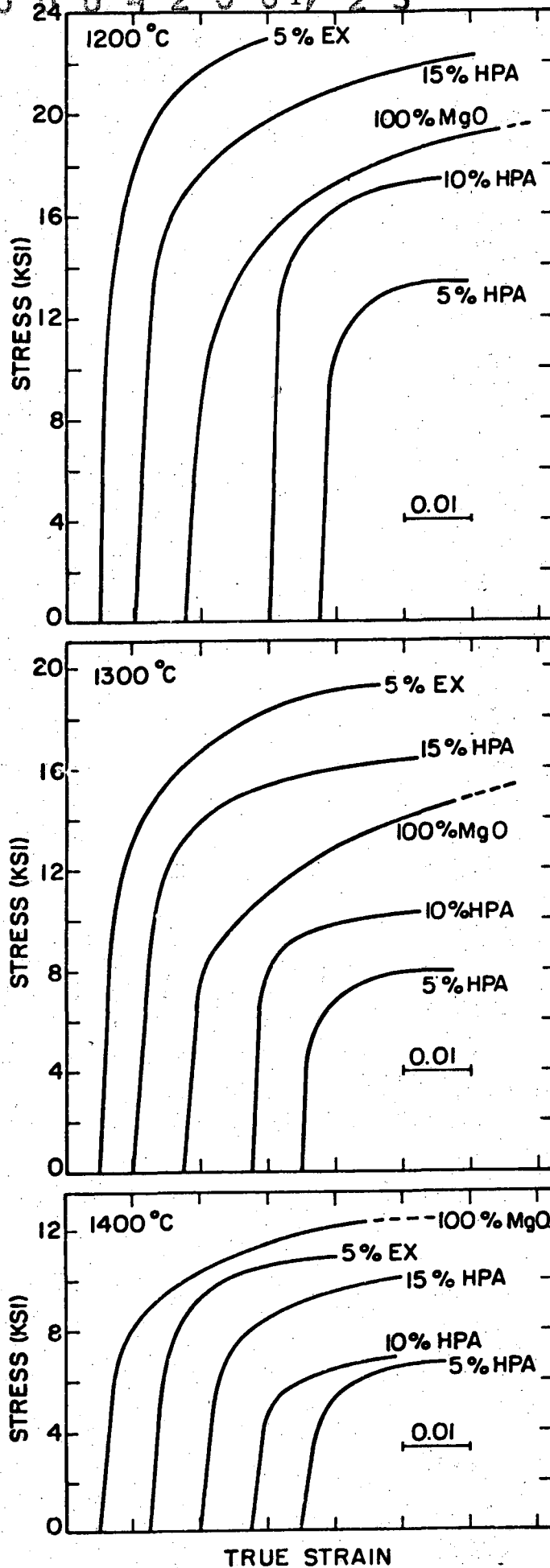
## Figure Captions

- Fig. 1.** Photomicrographs of specimens containing 5% CMS, Type HPA (top) and Type EX. (bottom).
- Fig. 2.** Stress-strain curves, 1200-1400°C.



XBB-715-2115

Fig. 1.



XBL 7411-7564

Fig. 2.

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