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PERMEATION OF SILICATES IN MAGNESIA AND FORSTERITE COMPACTS

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May 1972

ABSTRACT

$CaO(K_2O)$-MgO-SiO_2 liquids permeated into magnesia and forsterite compacts when continuous or "open" channels were available at the liquid-solid interface. Solid-solution formation at the liquid-forsterite interface resulted in the closing off of the open channels. The sessile drop and permeation experiments provided information that was used in the interpretation of microstructure development.

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I. Introduction

The wetting behavior of grains and the nature of solid-liquid interfacial reactions are critical in determining the performance of refractory materials during a slag attack. With the permeation of a liquid, the resistance to erosion and the high temperature strength of a refractory are dependent upon the nature of the liquid distribution.

The distribution of a liquid in a two-phase body at the firing temperature is governed by the interfacial energy relationships of the contained phases, as shown schematically in Fig. 1a. The relationship of the dihedral angle, ϕ, as measured through the liquid, to the solid-solid interfacial energy (grain boundary energy), γ_{ss}, and solid-liquid interfacial energy, $\gamma_{s\ell}$, is represented by

$$\gamma_{ss} = 2\,\gamma_{s\ell}\cos(\phi/2) \qquad (1)$$

As $\gamma_{s\ell}$ decreases in magnitude, ϕ approaches zero and when $\gamma_{s\ell}$ is equal to or less than $(1/2)\,\gamma_{ss}$, the liquid "penetrates" the grain boundary with its elimination.

Jackson et al.[1,2] successfully demonstrated the importance of this phenomenon in their studies on the influence of Cr_2O_3, Fe_2O_3, Al_2O_3 and TiO_2 on the wetting relationships in magnesia (MgO)-monticellite ($CaO{\cdot}MgO{\cdot}SiO_2$) bodies. They found that, at 1550°C, the addition of Cr_2O_3 markedly increased dihedral angles and promoted an appreciable degree of solid-solid bonding. In contrast to Cr_2O_3, the addition of Fe_2O_3, Al_2O_3 and TiO_2 decreased the dihedral angle and the degree of

solid-solid bonding. The effects of Cr_2O_3 were not so marked at 1725°C.

Sessile drop experiments, also shown schematically in Fig. 1b, provide some information on the $\gamma_{s\ell}$ by application of Young's equation

$$\gamma_{sv} - \gamma_{s\ell} = \gamma_{\ell v} \cos \theta \qquad (2)$$

where γ_{sv} is the solid-vapor and $\gamma_{\ell v}$ is the liquid-vapor interfacial energy, and θ is the contact angle measured through the liquid phase. Under chemical equilibrium or steady state conditions at the interface, an acute angle indicates that the solid is wet by the liquid, or $\gamma_{sv} > \gamma_{s\ell} > \gamma_{\ell v}$ and $(\gamma_{sv} - \gamma_{s\ell}) < \gamma_{\ell v}$. If a reaction occurs between the liquid and solid, then the contribution of the free energy of reaction to the driving force for wetting $(\gamma_{sv} - \gamma_{s\ell})$ may exceed $\gamma_{\ell v}$ and spreading of the liquid will occur.[3] The contact angle, then, is measured as 0° but is actually indeterminate.

Permeation of a liquid phase into a porous compact is expected to be dependent upon the interfacial energies and any reactions. Thus, contact and dihedral angle measurements may provide some understanding of the mechanism of slag permeation into porous refractories. Also, when a liquid phase is part of a refractory composition, similar types of measurements may be helpful in the understanding of the microstructure formation.

The objective of this study was to correlate the interfacial energies and reactions with the mechanism of liquid permeation into magnesia or forsterite (Mg_2SiO_4) compacts. In order to gain additional information on the microstructure development of basic refractories,

CaO-MgO-SiO_2 liquids, which are common in these refractories, were used.

II. Experimental Procedures

Magnesia and forsterite substrates of varying porosities were prepared for liquid permeation studies. Magnesia compacts with 69, 90 and 98% theoretical density were made by cold pressing and sintering at 1550°C for 15 h. The MgO powders used were (1) reagent grade powder* of sub-micron particle size for the higher density compacts, and (2) coarse powder of 40-53μ particle size obtained by grinding single crystals of MgO† for the ρ_{th} = 69% compact. A few experiments were performed using cold pressed compacts without presintering with ρ_{th} = 50%. Forsterite compacts of 82 and 94% theoretical density were prepared by cold pressing forsterite powder§ and sintering at 1650°C for 15 h. A forsterite compact of 69% theoretical density was also prepared by adding 10% napthalene to the prefired body. The substrates were disks of approximately 1/2 in. diameter and 1/8 in. thickness polished on one side. Pressed disks of the unmelted composition of a liquid prepared from reagent grade powders of $CaCO_3$#, $MgCO_3$≠, Cr_2O_3#, Fe_2O_3#, and SiO_2**, of approximately the same size as the substrate, were placed on the polished surface of the substrate. After heating for 3 h at 1550° or 1650°C and cooling to room temperature, the specimens were mounted in resin and cut perpendicular to the interface. The cut sections were

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* Allied Chemical Corp., Morristown, N.J.: 99% MgO after ignition.
† Muscleshoals Electrochemical Company, Tuscumbia, Alabama.
§ Merck Co., South San Francisco, California
\# J. T. Baker Chem. Co., Phillipsburg, N.J.
≠ Mallinckrodt Chem. Works., St. Louis, Mo.
**Ottawa Silica Co., Ottawa, Ill.

polished and examined in reflected light to determine the permeation of liquid into the compact. The results obtained were in agreement with those of a few experiments repeated with disks of the premelted batches.

Compacts for microstructure studies were prepared using unreacted powders to form MgO or Mg_2SiO_4 with 15 to 45% liquid by weight. After mixing, the powders were pressed into disks and sintered in air in a gas-fired furnace at 1550° or 1650°C for 50 h, depending on the liquid composition.

Sessile drop experiments were performed using magnesia single crystals, magnesia compacts of 90% theoretical density, forsterite single crystals,* and forsterite compacts of ρ_{th} = 94%. The single crystal substrates were formed by cleaving, or cutting and polishing along (001) planes. The batches for the liquid phase were mixed in isopropyl alcohol and melted for 2 h at 1600°C in platinum crucibles. A piece of about 1/2 gm was then placed on a substrate, and the assembly was heated in a gas-fired furnace at 1550° or 1650°C for 3 h and quenched below the solidification temperature of the drop within a minute. Contact angle measurements were made at room temperature using a telescope equipped with a filar-micrometer eyepiece. Angles were measured directly using a graduated protractor connected to the eyepiece.

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*F.R. Charvat, Crystal Products Dept., Union Carbide Corp., San Diego, Calif. 92112

0 0 0 0 3 6 0 0 2 2

III. Results and Discussion

1. MgO-Liquid Systems

Disks corresponding to monticellite (CMS) composition melted and permeated sintered MgO compacts of 69 and 90% theoretical density but not one of ρ_{th} = 98%, when heated at 1550°C for 3 h. The microstructure of the compact with ρ_{th} = 90% is shown in Fig. 2a; its appearance after permeation, in Fig. 2b. Figure 2a shows regions of higher porosity but no grain boundary separations. After permeation, a thin film of liquid is clearly seen along many of the grain boundaries, and rounding of corners has occurred indicating that redistribution of material was achieved by a solution-precipitation process. The grain boundaries that have not been penetrated by the liquid form dihedral angles with the liquid showing an average of about 25°. The boundaries forming dihedral angles must have lower values for γ_{ss} due to a favorable crystallographic orientation of the grains.[4] In the absence of open channels or capillaries, as in the 98% dense compact, no liquid permeation occurs.

Permeation experiments using unsintered MgO compacts of ρ_{th} = 50% were also made with CMS, CMS + 1% Fe_2O_3, and CMS + 1% Cr_2O_3 liquids. In every case the liquids permeated the compacts readily resulting in rounded grains exhibiting limited growth as seen in the lower part of Fig. 3, which is a vertical cross-section of the specimen permeated by the Cr_2O_3-containing liquid. In this case the grains close to the interface (in the upper part of the photograph) are more angular and greenish. These effects were minimized as the MgO grains depleted the Cr_2O_3 from the liquid permeating toward the center of the specimen (the

lower part of the photograph). Thus, a solid solution of Cr_2O_3 in MgO leads to strong crystallographic anisotropy of the surface energies.

Specimen containing 15% CMS liquid by weight, approximately 17% by volume, were prepared by heating a compacted mixture at 1550°C for 50 h. Although the amount of liquid was greater than in the permeated compact shown in Fig. 2b, which has about 3-4% liquid by volume, the nature of the distribution of the liquid and the average dihedral angles were similar. They were also similar to the observations reported by Jackson et al.[1,2]

Sessile drop experiments at 1550°C of CMS on single crystal and polycrystalline MgO showed a contact angle of 47° and no reactions. An acute contact angle indicates wetting of the solid which provides the driving force for the capillary permeation of the compacts by the liquid.

2. Forsterite-Liquid Systems

Permeation studies were made using forsterite compacts and liquids: (1) (CaO 28%, MgO 30, SiO_2 42), (2) (MgO 36%, SiO_2 64), and (3) (K_2O 20%, MgO 28, SiO_2 52). Liquids (1) and (2) are in equilibrium with forsterite at 1550° and 1565°C, respectively, according to the CaO-MgO-SiO_2 phase diagram.[5] Similarly, liquid (3) is in equilibrium with forsterite at 1565°C.[6] No permeation of these liquids occurred in the compacts of ρ_{th} = 82% (Fig. 4a) and 94%, with corresponding open porosities of 15 and 5.5%. However, permeation did occur in the compact of ρ_{th} = 69% with 28.8% open porosity (Fig. 4b). Sessile drop experiments of these liquids on single crystal and most dense forsterite compact showed spreading which indicates the occurrence of a reaction[3] and thus chemical non-equilibrium between the substrate and the liquid.

Since the phase diagram[5] shows limited solid solution between CMS (CaO 36%, MgO 26, SiO_2 38) and forsterite, it would be expected that a solid solution of CaO and/or SiO_2 would also occur in forsterite when in contact with liquids (1) and (2). This deduction is in agreement with Pluschkell and Engell's[7] indication of SiO_2 solubility in forsterite (34.4 mol% SiO_2 at 1400°C) by electrical conductivity measurements. Also, an electron beam microprobe examination of the specimens with liquid (3) indicated some solubility of K_2O in forsterite. These solid solution reactions would then explain the lack of permeation of the liquids into forsterite compacts of even 15% open porosity. Channels at the solid-liquid interface are closed off as the forsterite grains grow at the interface during solid-solution formation. Any liquid that permeates into the compact before the channels are closed off disappears as it reacts with forsterite to form a solid solution.

The microstructure of a compact containing 45% of liquid (1) by weight after sintering at 1550°C for 50 h is shown in Fig. 5a. Figure 5b shows the microstructure of a specimen containing 25% of liquid (3) after 50 h at 1650°C. The degree of grain bonding and the anisotropic nature of the grains are more pronounced in the former. The microstructure of the compacts with liquid (2) was similar to that with liquid (3). Furthermore, the nature of the liquid distribution is similar to that in the compacts permeated by the same liquids (Fig. 4b).

IV. Conclusions

Permeation of silicates into magnesia and forsterite compacts occurred when the solid was wet by the liquid and when a continuous or

"open" pore structure was present. When the solid was unsaturated with respect to at least one of the components of the liquid phase, the solid-solution reaction at the interface resulted in the closing off of the open channels even at relatively high porosities.

The permeation experiments provide useful information in predicting the microstructure of a compact containing a liquid with a similar composition. The nature of the distribution of a given liquid distribution is similar in a porous compact permeated by a liquid in comparison with a compact of equivalent overall composition made from a mixture of batch materials.

Acknowledgment

Grateful acknowledgment is extended to George Dahl for assistance in the preparation of polished sections and to George J. Georgakopoulos for assistance in electron beam microprobe analyses.

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0 0 0 0 3 6 0 7 3 2 3

References

1. B. Jackson, W. F. Ford, and J. White, "The Influence of Cr_2O_3 and Fe_2O_3 on the Wetting of Periclase Grains by Liquid Silicate," Trans. Brit.Ceram. Soc., 62 [7] 577-601 (1963).

2. B. Jackson and W. F. Ford, "A Quantitative Study of Bonding in Basic Refractories," Trans. Brit. Ceram. Soc., 65 [1] 19-39 (1966).

3. I. A. Aksay, C. E. Hoge, and J. A. Pask, "Thermodynamics and Mechanics of Wetting," to be published.

4. Thermodynamics of Solids, R. A. Swalin, section 12.4, John Wiley and Sons, Inc., New York, 1962.

5. E. F. Osborn and A. Muan, Figure 598 in Phase Diagrams for Ceramists, E. M. Levin, C. R. Robbins, and H. F. McMurdie, J. Am. Ceram. Soc., Ohio, 1964.

6. E. W. Roedder, Figure 399, ibid.

7. W. Pluschkell and H. J. Engell, "The Ionic and Electronic Conductivity in Magnesium Orthosilicates," Ber. Dtsch. Keram. Ges. 45 [8] 388-94 (1968).

Figure Captions

Figure 1. Equilibrium of forces (a) between a grain boundary and two equivalent solid-liquid interphase boundaries, and (b) on the periphery of a sessile drop of an acute contact angle. B is the resultant balancing force equal and of opposite direction to $\gamma_{\ell v}$.[3]

Figure 2. (a) Sintered MgO compact of ρ_{th} = 90%, and (b) the microstructure of the same compact after permeation of CMS liquid at 1550°C for 3 h.

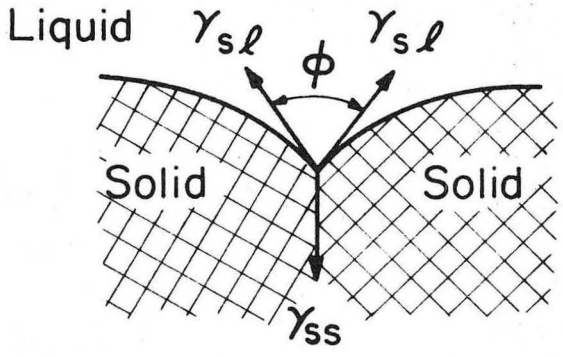
Figure 3. Permeation of CMS + 1% Cr_2O_3 liquid into a MgO compact of ρ_{th} = 50% at 1550°C for 3 h.

Figure 4. (a) The interface between liquid (1) (CaO 28%, MgO 30, SiO_2 42) and a forsterite compact of ρ_{th} = 82%, at 1550°C for 3 h, and (b) the microstructure of a forsterite compact of ρ_{th} = 69% after permeation of liquid (1) at 1550°C for 3 h.

Figure 5. The forsterite compact containing (a) 45% of liquid (1) after 50 h at 1550°C, and (b) 25% of liquid (3) (K_2O 20%, MgO 28, SiO_2 52), after 50 h at 1550°C.

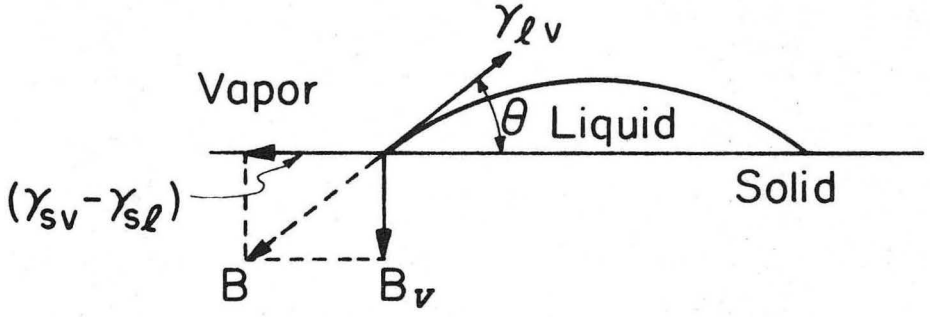
0 0 0 0 3 6 0 7 0 2 4

(a)



$$\gamma_{ss} = 2\gamma_{s\ell} \cos(\phi/2)$$

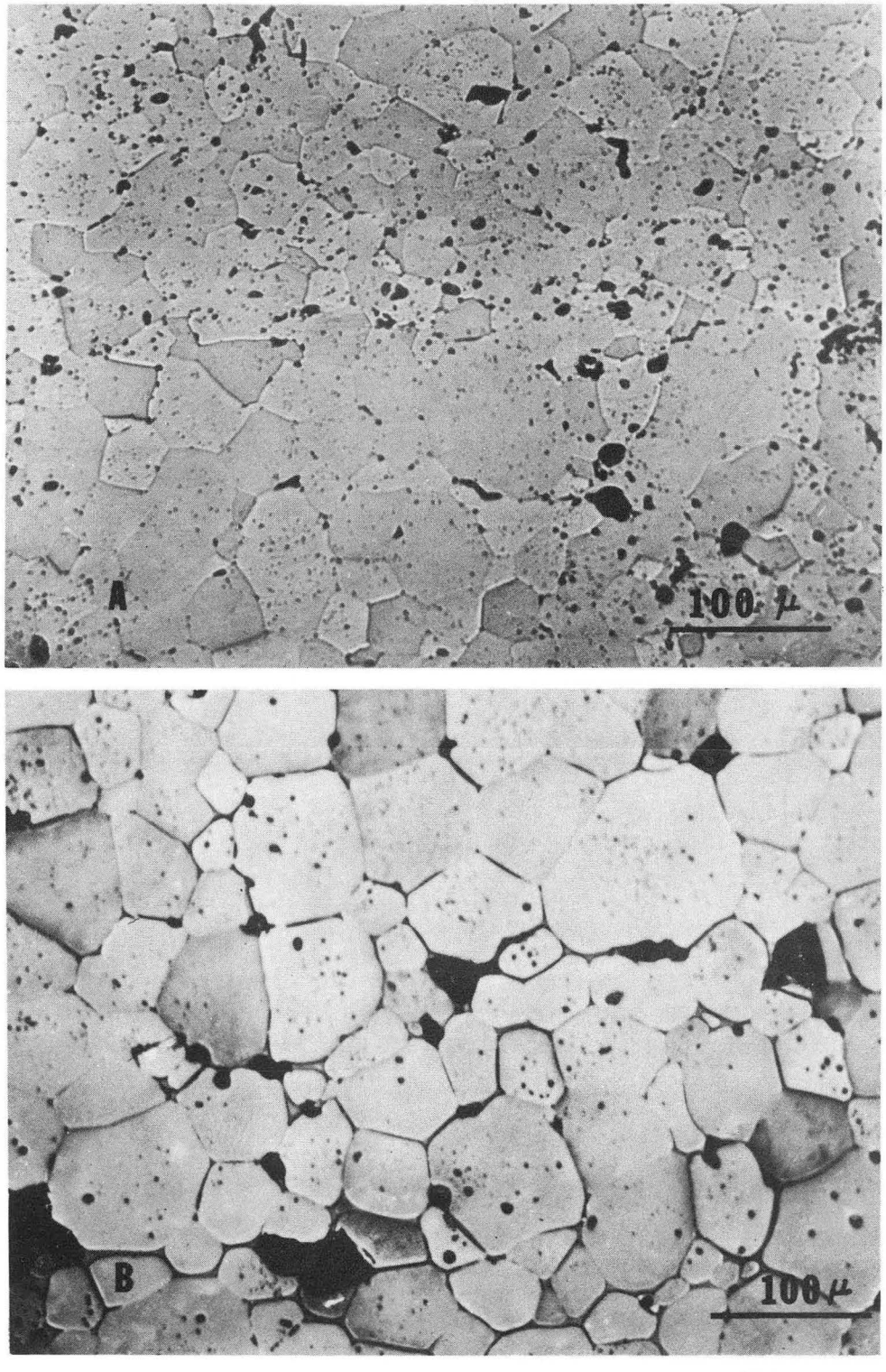
(b)



$$\gamma_{sv} - \gamma_{s\ell} = \gamma_{\ell v} \cos\theta$$

XBL724-6200

Fig. 1



XBB688-5021

Fig. 2

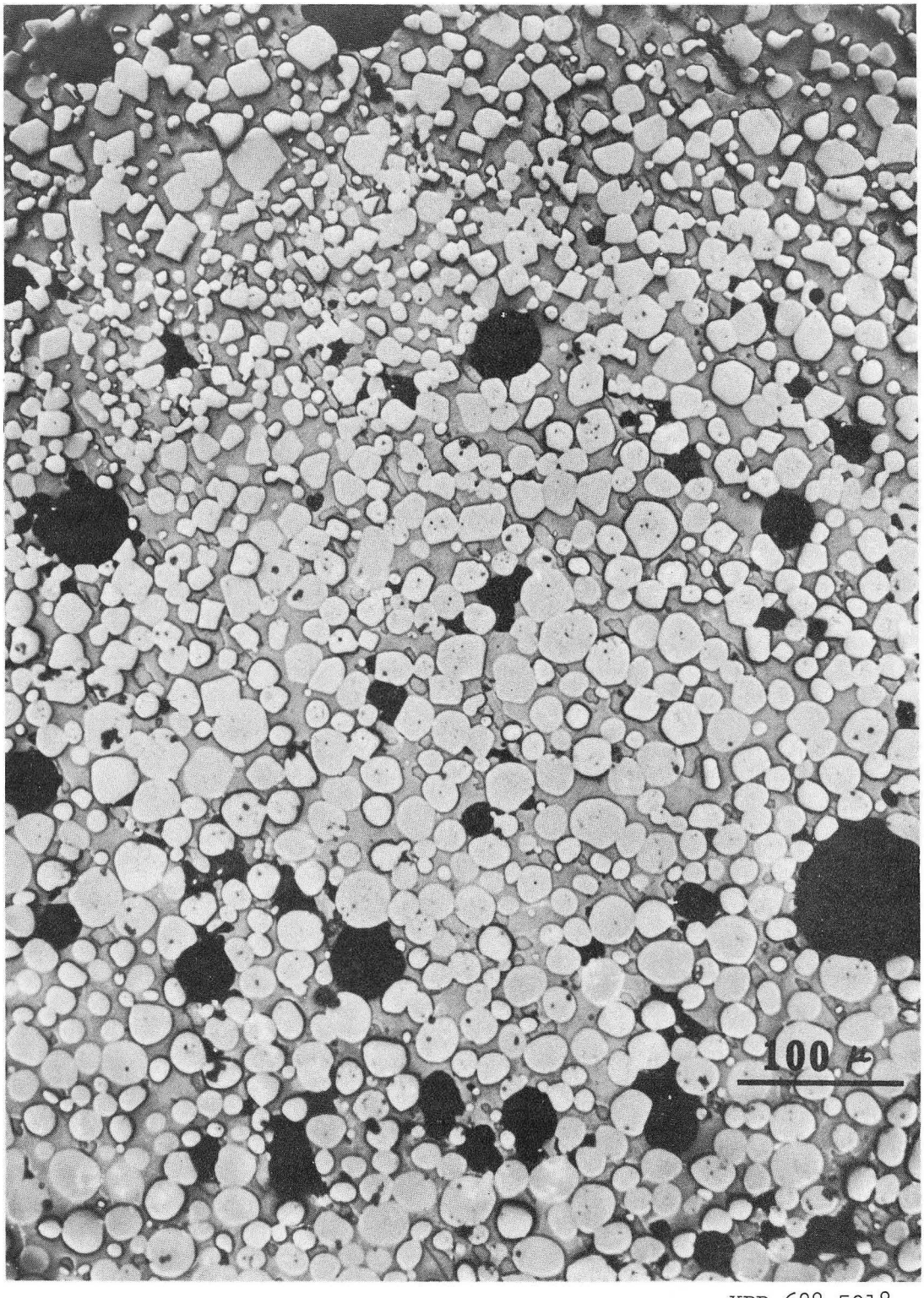


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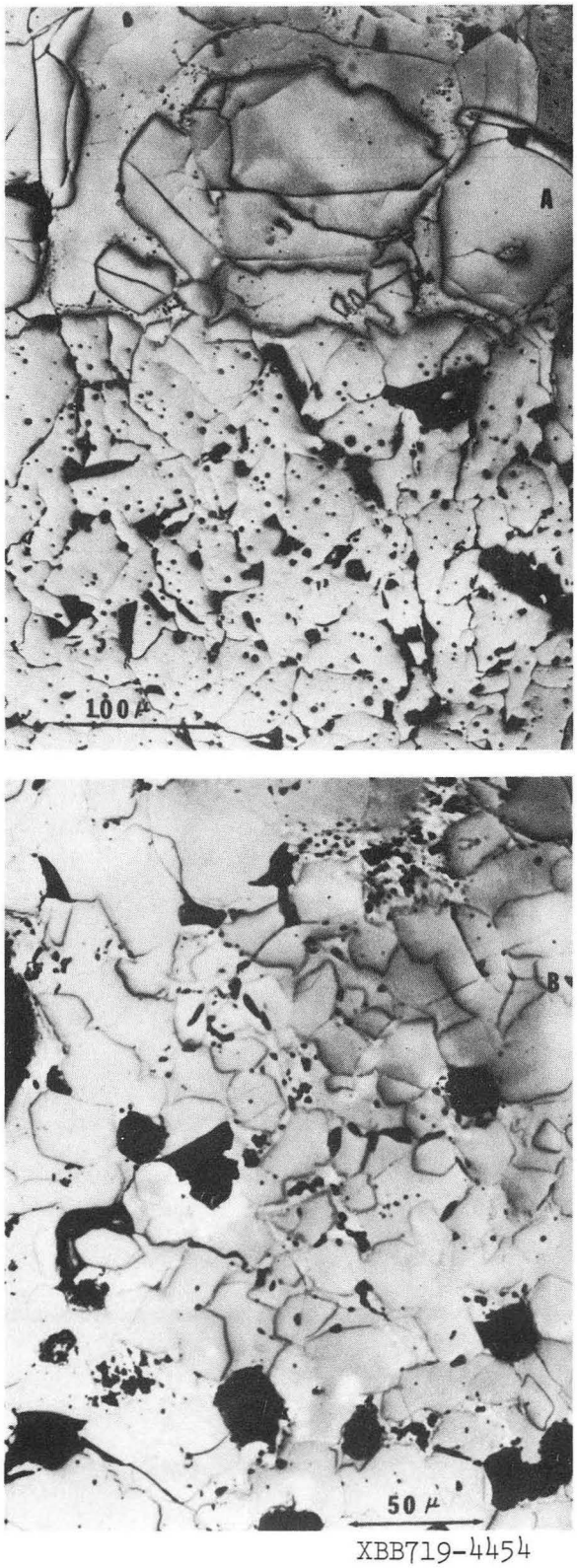
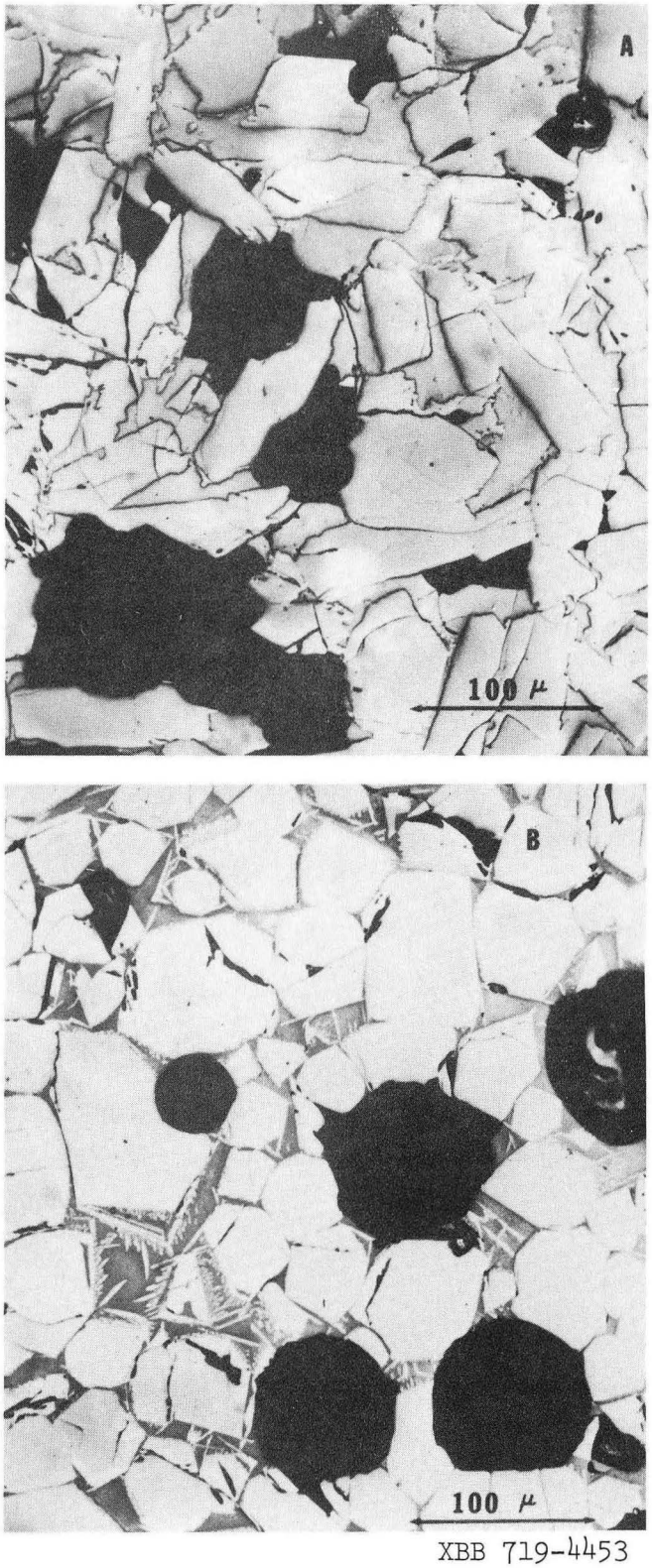
Fig. 3



XBB719-4454

Fig. 4



XBB 719-4453

Fig. 5

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