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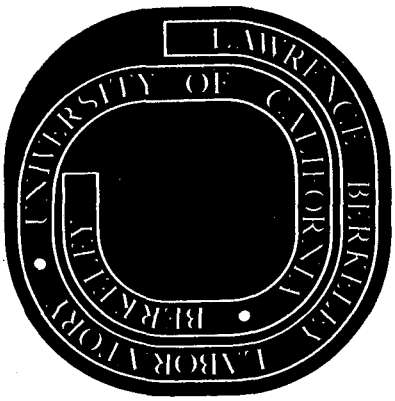


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# PERMEATION OF SILICATES IN MAGNESIA AND FORSTERITE COMPACTS

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## ABSTRACT

$CaO(K_2O)$-MgO-$SiO_2$ liquids permeated into magnesia and forsterite compacts when 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 could be used in the interpretation of microstructure development.

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*Presently with Zenith Radio Corp., Microcircuit Facility, Elk Grove, Ill.

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## I. Introduction

The wetting behavior of solid 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 its 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, $\phi$, as measured through the liquid, to the solid-solid interfacial energy (grain boundary energy), ${}_s\gamma_s$, and solid-liquid interfacial energy, ${}_s\gamma_\ell$, is represented by

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

As ${}_s\gamma_\ell$ decreases in magnitude, $\phi$ approaches zero and when ${}_s\gamma_\ell$ is equal to or less than $(1/2)\,{}_s\gamma_s$, the liquid "penetrates" the grain boundary with its elimination. The classic example of this phenomenon is due to Smith[1] who showed the influence of the presence of bismuth on the distribution of the phases in the copper-lead alloy system and the corresponding effect on the ductility.

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

$$ {}_s\gamma_v - {}_s\gamma_\ell = {}_\ell\gamma_v \cos\theta \qquad (2) $$

where ${}_s\gamma_v$ is the solid-vapor and ${}_\ell\gamma_v$ is the liquid-vapor interfacial energy, and $\theta$ 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 ${}_s\gamma_v > {}_s\gamma_\ell > {}_\ell\gamma_v$ and $({}_s\gamma_v - {}_s\gamma_\ell) < {}_\ell\gamma_v$. If a reaction occurs between the liquid and solid, then the driving force for wetting $({}_s\gamma_v - {}_s\gamma_\ell)$ may exceed ${}_\ell\gamma_v$ and spreading of the liquid will occur.[2] The contact angle, then, is measured as $0^\circ$ 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 present in a refractory, 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 (MgO) 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 basic refractories, were used.

## II. Literature

Several investigators have studied the slag attack on basic linings of oxygen converters. Herron, et al.[3] studied the attack of tar-impregnated magnesite brick by slags containing mainly CaO, MgO, $SiO_2$, MnO, and FeO. Lack of wetting between the liquid slag and carbon was found to hinder the permeation of the slag into the brick structure. Thus, the permeation rate was controlled by the oxidation rate of the

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carbon by the slag. Similar results were obtained by Hodson and Richardson[4] on the slag attack of tar-impregnated magnesite and dolomite refractories. They also observed that fusion-cast magnesite-chrome refractories were attacked by slags rich in dicalcium ferrite but not by siliceous slags as the intergranular spinel was dissolved.

Van Vlack[5] investigated the microstructure of silica-iron oxide compacts in relation to wettability and distribution of the phases by measuring dihedral angles under various oxidation levels. His studies showed that the dihedral angles, and thus the distribution of liquid around the solid grains, were independent of iron oxide content and oxidation level employed. Large dihedral angles were always observed and the microstructure thus possessed a crystalline skeleton structure. Such a structure is responsible for the high strength of silica bricks at high temperatures.

In magnesiowüstite- and periclase-liquid systems, Van Vlack and Riegger,[6] and Reigger et al.[7] observed low dihedral angles and the presence of liquid along most grain boundaries. With the appearance of a second solid phase, however, an intergranular bridge was formed. Both olivine [$(Mg,Fe)_2SiO_4$] and spinel ($FeAl_2O_4$ and $FeFe_2O_4$) type phases provided contact between magnesiowüstite grains. Silicate liquids were observed to penetrate more extensively between periclase grains than do ferrite liquids.

Jackson et al.[8] studied the influence of $Cr_2O_3$ and $Fe_2O_3$ on the wetting relationships in 85% periclase, 15% monticellite mixtures fired 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 $Fe_2O_3$ decreased the dihedral angle and the degree of solid-solid bonding. Their studies also showed that when the solubility limit was exceeded, the spinel crystals preferred to grow from the periclase grains. Jackson and Ford[9] extended similar studies up to 1725°C and investigated the effect of $Al_2O_3$ and $TiO_2$ on wetting and distribution of various phases, in addition to $Cr_2O_3$ and $Fe_2O_3$. The effects of $Cr_2O_3$ were not so marked at 1725°C. $Al_2O_3$ and $TiO_2$, like $Fe_2O_3$, reduced the dihedral angles, and thus the degree of solid-solid bonding. The dihedral angles were found to be independent of the amount of liquid. The degree of solid-solid bonding between the magnesia grains at 1725°C was found to increase as the $CaO/SiO_2$ molar ratio of the silicate increased above 0.5, and the effect of $Cr_2O_3$ was greatly enhanced as the ratio approached 2.

Stephenson and White[10] investigated the factors controlling the grain growth and geometry of microstructures in (1) $CaO-MgO-Fe_2O_3-SiO_2$ and $CaO-MgO-Al_2O_3-SiO_2$ mixtures containing lime, periclase, and a liquid phase at the firing temperature and (2) $MgO-MgCr_2O_4-CaMgSiO_4$ mixtures containing periclase and a liquid phase at the firing temperature. In all three systems, the presence of a liquid phase between unlike grains was less than between like grains.

## III. 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

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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 $\rho_{th}$ - 69% compact. A few experiments were performed using cold pressed compacts without any presintering with $\rho_{th}$ = 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% naphthalene 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 polished and examined in reflected light to determine the permeation of liquid into the compact.

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.

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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.

Sessile drop experiments were performed using MgO single crystals, MgO compacts of 90% theoretical density, and forsterite compacts of $\rho_{th}$ = 94%. The single crystal substrates were formed by cleaving along (100) 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. 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.

## IV. Results and Discussion

### 1. MgO-Liquid Systems

Disks corresponding to CMS ($CaO \cdot MgO \cdot SiO_2$, monticellite) composition melted and permeated sintered MgO compacts of 69 and 90% theoretical density but not one of $\rho_{th}$ = 98%, when heated at 1550°C for 3 h. The microstructure of the compact with $\rho_{th}$ = 90% is shown in Fig. 2a; its appearance after permeation, in Fig. 2b. Although no grain boundary separations are observed in the former, after permeation a thin film of liquid is clearly seen along many of the grain boundaries which is also associated with a zero dihedral angle. The regions which show greater permeation correspond to the more porous portions as observed in the upper part of Fig. 2a. This behavior indicates that the liquid has permeated into the compact through the open channels and a redistribution of material has occurred without affecting the boundaries whose grains were oriented to result in a low $_s\gamma_s$; these boundaries formed dihedral

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angles with the liquid. However, when the open channels or capillaries were absent, as in a 98% theoretically dense compact, there was no liquid permeation.

Permeation experiments using unsintered MgO compacts of $\rho_{th}$ = 50% were also made with CMS, CMS + 1% $Fe_2O_3$, and CMS + 1% $Cr_2O_3$ liquids. A cross-section of the latter specimen is shown in Fig. 3. The grains close to the interface (in the upper part of the photograph) can be seen to be more angular; they were also greenish. As the MgO grains depleted the $Cr_2O_3$ content from the permeating liquid, the greenish color diminished away from the interface (toward the lower part of the photograph) and the grains became more rounded. The latter appearance and the size of grains were about the same throughout the cross-sections for the other two liquids. Thus, a solid solution of $Cr_2O_3$ in MgO leads to strong crystallographic anisotropy of the surface energies.

Specimens containing 15% liquid by weight at the sintering temperature were prepared by heating at 1550°C for 50 h. The microstructure of the MgO compact with an addition equivalent to CMS is shown in Fig. 4. The nature of the distribution of the liquid and the average dihedral angles (about 25°) are similar to those in the MgO compact permeated by CMS at 1550°C (Fig. 2b) and to the observations reported by Jackson, et al.[8]

Sessile drop experiments at 1550°C of CMS on single crystal MgO showed a contact angle of 47°. 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.[11] Similarly, liquid (3) is in equilibrium with forsterite at 1565°C.[12] No permeation of these liquids occurred in the compacts of $\rho_{th}$ = 82% (Fig. 5a) and 94%, with corresponding open porosities of 15 and 5.5%. However, permeation did occur in the compact of $\rho_{th}$ = 69% with 28.8% open porosity (Fig. 5b). Sessile drop experiments of these liquids on the most dense forsterite compact showed spreading which indicates the occurrence of a reaction.[2]

Since the phase diagram[11] 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 $SiO_2$ would also occur in forsterite when in contact with liquids (1) and (2). This deduction is in agreement with Pluschkell and Engell's[13] 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. 6a. Figure 6b 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. 5b).

## V. Conclusions

Permeation of silicates in magnesia and forsterite compacts occurred when the solid was wet by the liquid and when open channels were available at the liquid-solid interface. 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 high porosities.

The sessile drop experiments provide information that could be used in the interpretation of liquid permeation into compacts. They are also useful in studying some systems because they indicate the presence of reactions by the spreading phenomenon.

The permeation experiments provide useful information for the development of microstructure. The nature of the liquid distribution after permeation indicates the dihedral angles that would occur in a body with equivalent solid and liquid phase compositions. The liquid distribution also provides information on the homogeneity of the porous compact.

## ACKNOWLEDGMENT

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## 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 balancing force equal and opposite direction to $\ell\gamma_v$.(2)

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

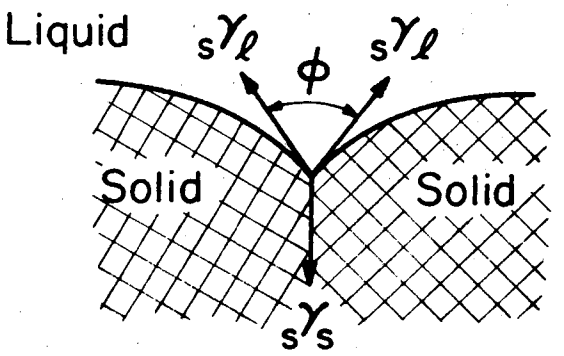
Figure 3. Permeation of CMS + 1% $Cr_2O_3$ liquid into a MgO compact of $\rho_{th}$ = 50% at 1550°C for 3 h.

Figure 4. The microstructure of MgO compact containing 15% of CMS liquid, after 50 h at 1550°C.

Figure 5. (a) The interface between liquid (1) (CaO 28%, MgO 30, $SiO_2$ 42) and a forsterite compact of $\rho_{th}$ = 82%, at 1550°C for 3 h, and (b) the microstructure of a forsterite compact of $\rho_{th}$ = 69% after permeation of liquid (1) at 1550°C for 3 h.

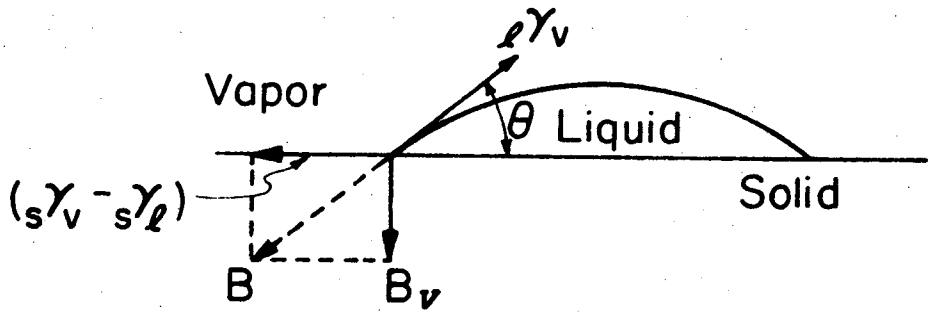
Figure 6. The forsterite compact containing (a) 45% of liquid (1) after 50 h at 1550°C, and (b) 25% of liquid (3) ($K_2O$ 20%, MgO 28, $SiO_2$ 52), after 50 h at 1550°C.

(a)




$$_s\gamma_s = 2\ _s\gamma_\ell \cos(\phi/2)$$

(b)




$$_s\gamma_v - _s\gamma_\ell = _\ell\gamma_v \cos\theta$$

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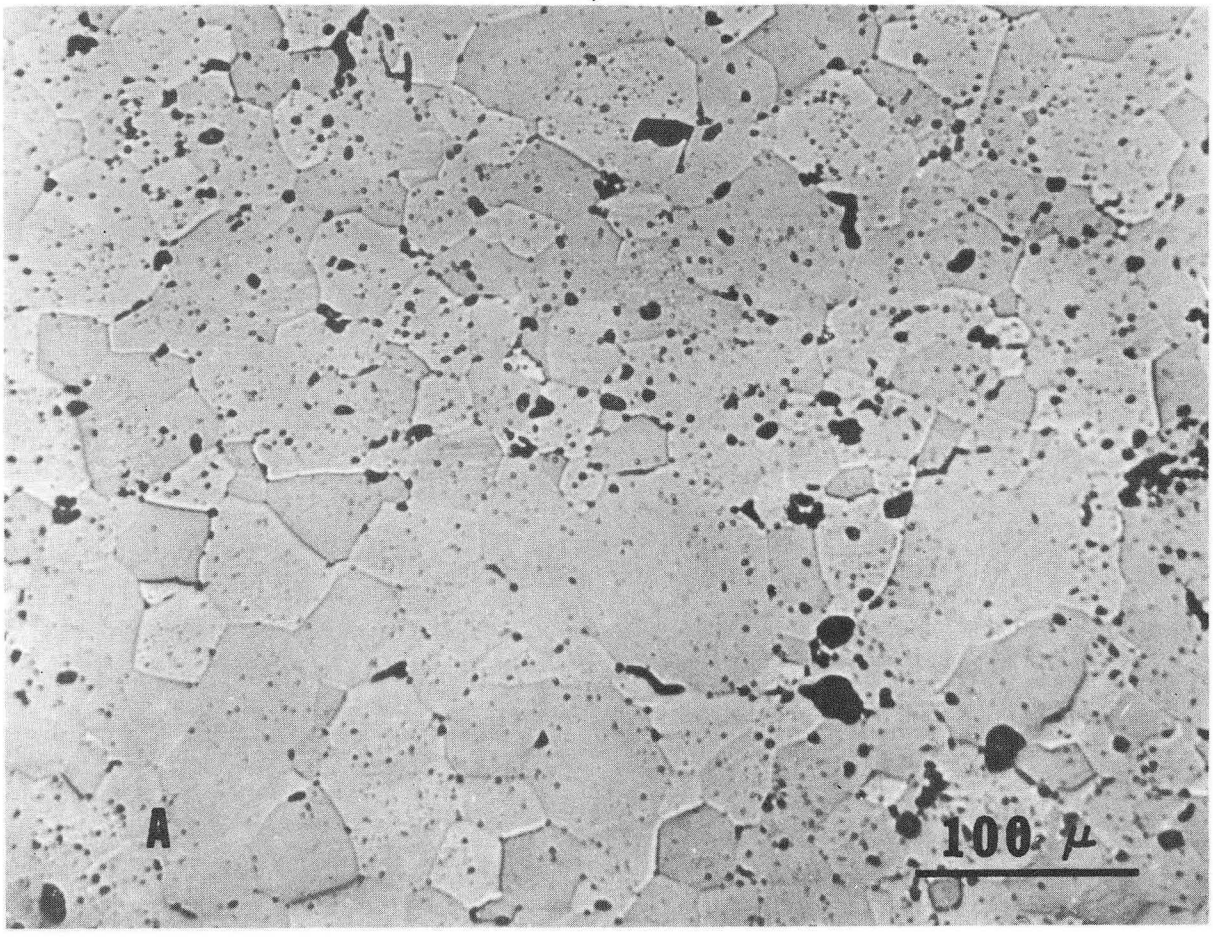
Fig. 1



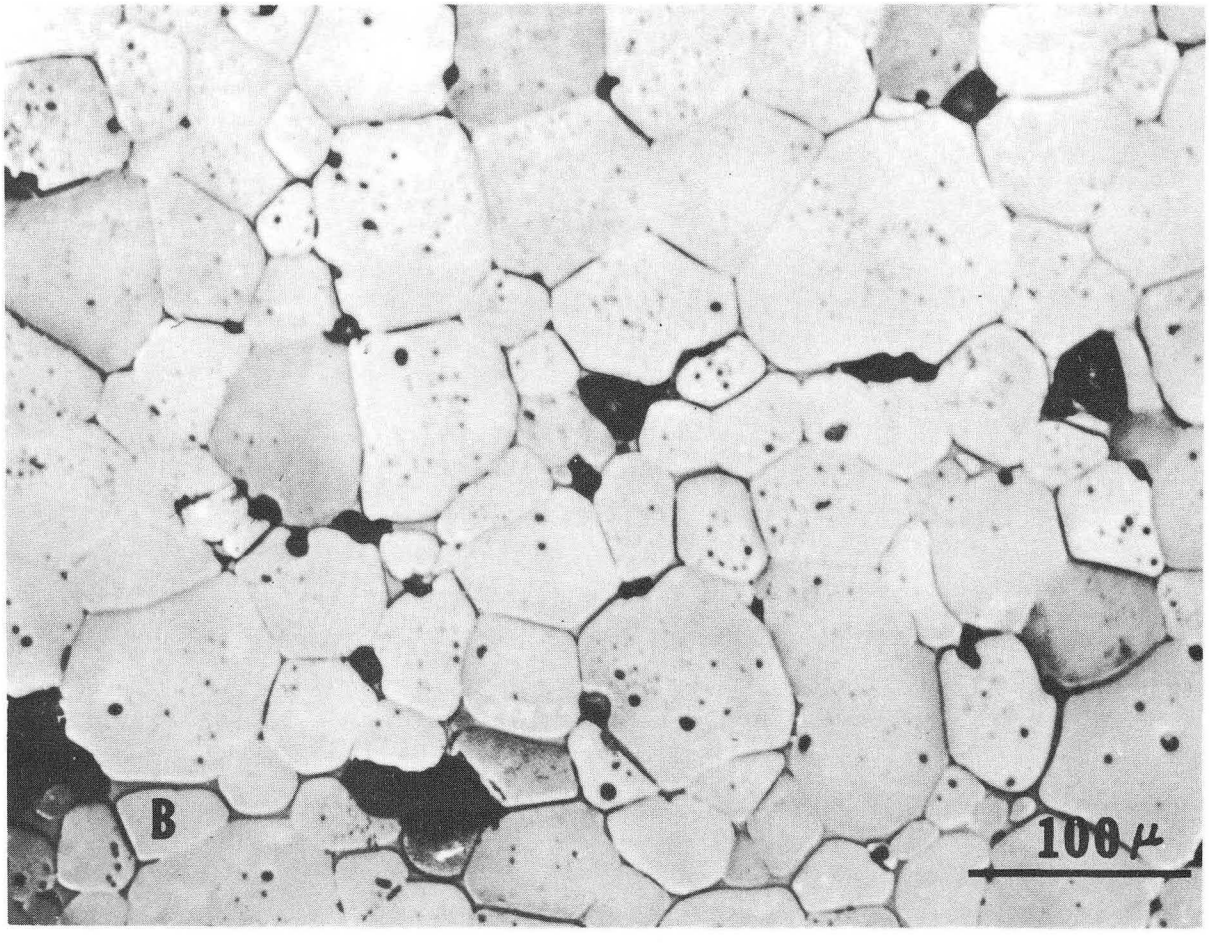




Fig. 2

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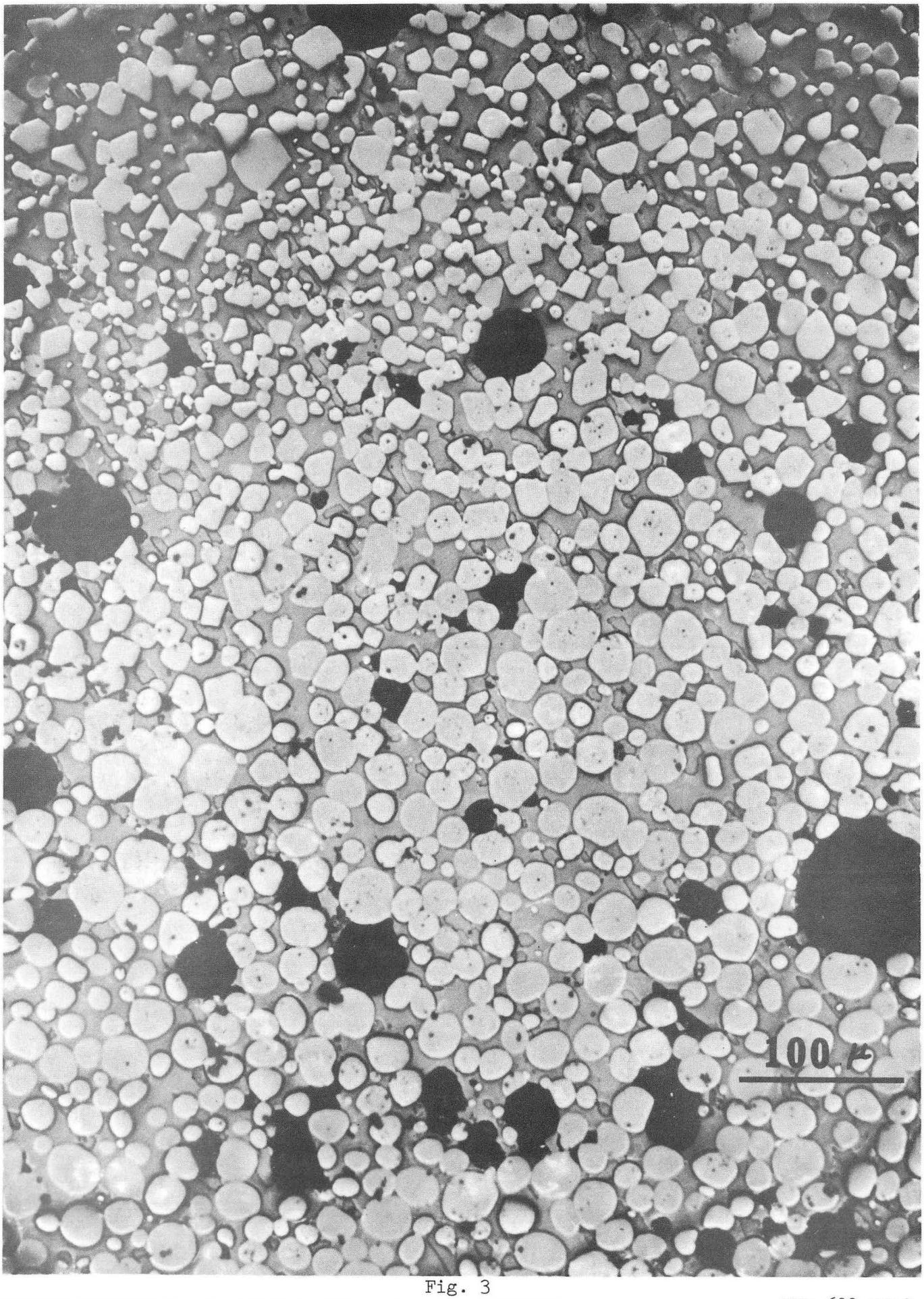


Fig. 3

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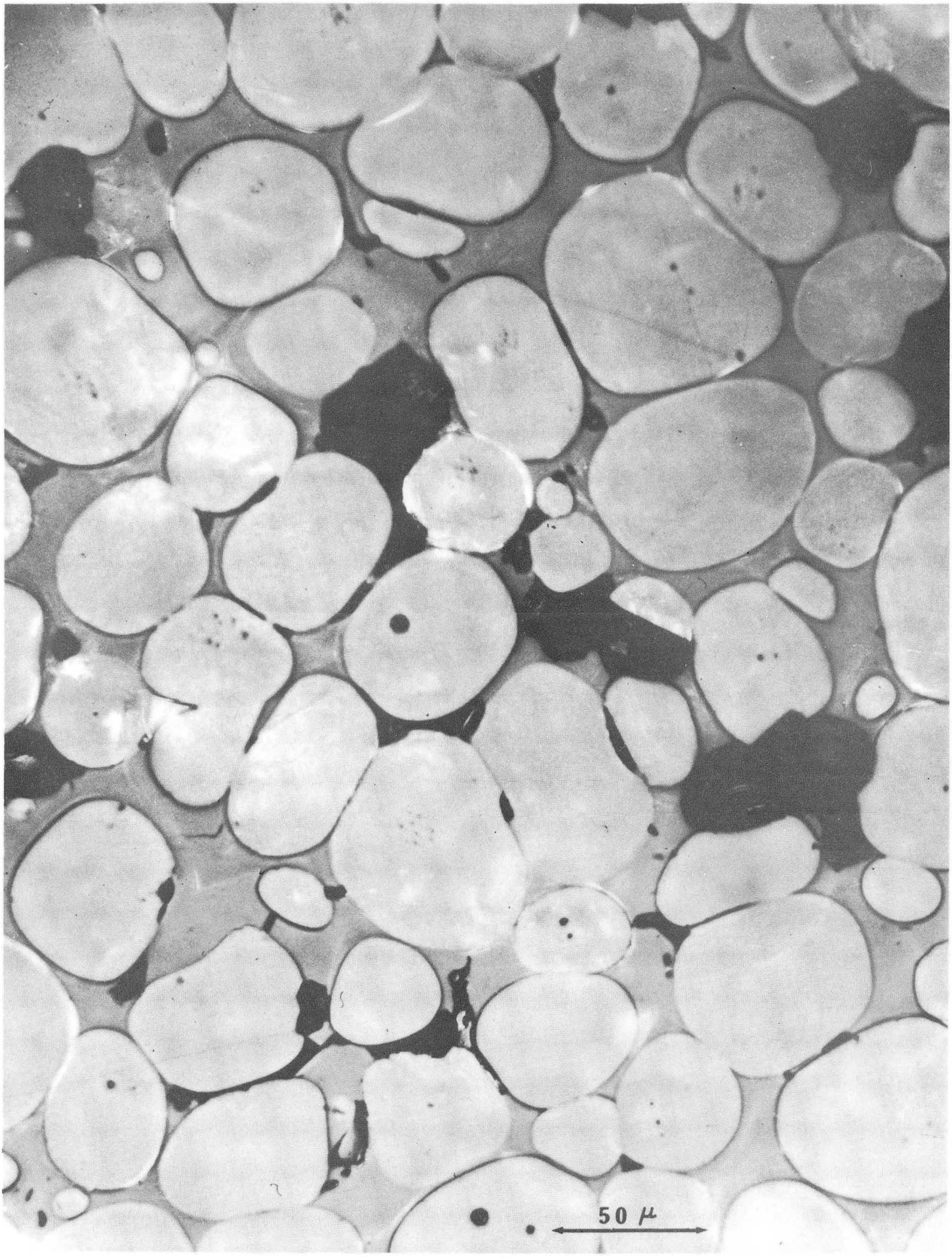


Fig. 4

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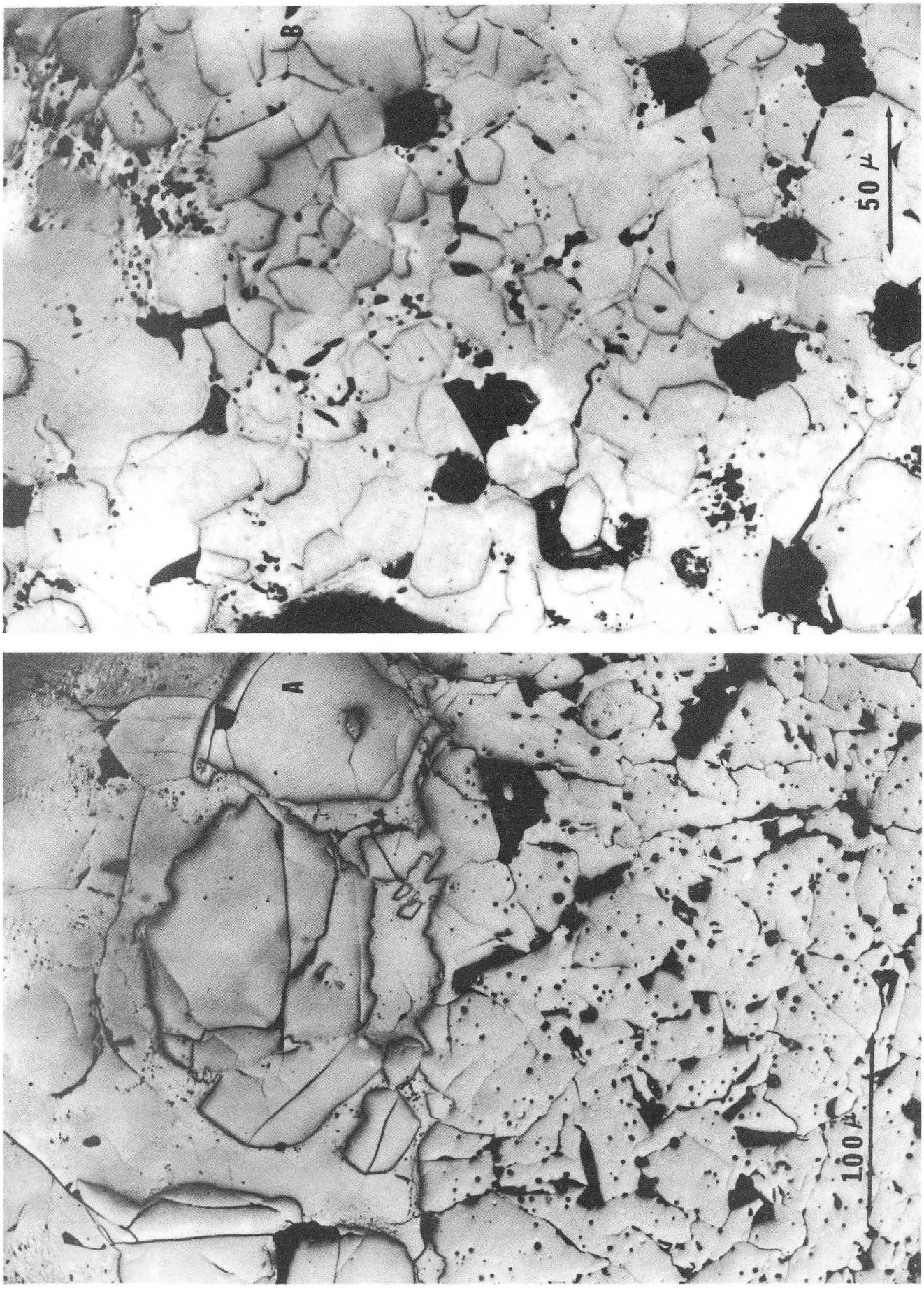


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Fig. 5

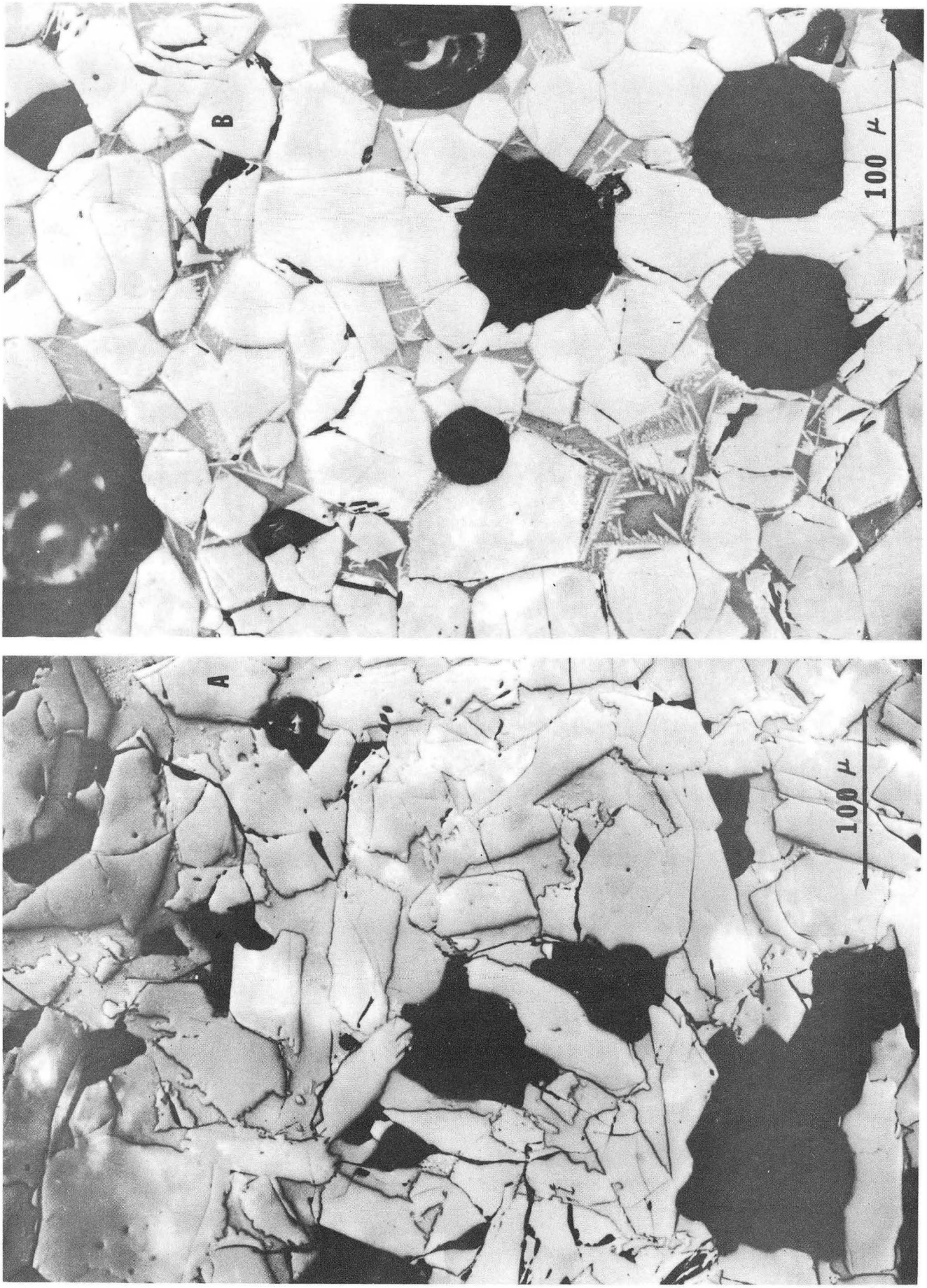


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Fig. 6

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