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### Authors

Jonghe, L.C. De

Schmid, H.

Chang, M.

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L.C. De Jonghe, H. Schmid and M. Chang

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Interreaction Between  $Al_2O_3$  and a  $CaO-Al_2O_3$  Melt

Lutgard C. De Jonghe, Herbert Schmid and Mei Chang

Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
and  
Department of Materials Science and Mineral Engineering  
University of California at Berkeley  
Berkeley California, 94720

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Interreaction Between  $\text{Al}_2\text{O}_3$  and a  $\text{CaO-Al}_2\text{O}_3$  Melt

Lutgard C. De Jonghe,\*† Herbert Schmid\*‡ and Mei Chang\*†§

\*Materials and Molecular Research Division  
Lawrence Berkeley Laboratory  
and

†Department of Materials Science and Mineral Engineering  
University of California at Berkeley  
Berkeley, California 94720

Abstract

Polycrystalline and single crystalline and  $\alpha$ -alumina was reacted with a eutectic C-A<sup>§</sup> melt at 1530°C. A reaction zone develops in which a strongly textured  $\text{CA}_6$  layer, as well as a  $\text{CA}_2$  layer forms, with a remaining layer of unreacted C-A melt. Silica, an impurity, in the  $\alpha$ -alumina is rejected by the advancing  $\text{CA}_6$  phase and accumulates as calcium alumina silicates in channels that assist in the reaction as fast transport paths. Reaction mechanisms and welding is briefly discussed.

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‡ Now at the Max Planck Institut für Metallforschung, Stuttgart, Germany.

§ Now at Applied Materials, Santa Clara, California.

§ C = CaO; A =  $\text{Al}_2\text{O}_3$

## I. Introduction

The calcium oxide - aluminum oxide system is the basis of an important class of high temperature refractories (1). Typically, such refractories are prepared by firing a hydrated cement mix at elevated temperatures. A complex set of dehydration, interreactions and bonding processes accompanies the firing and a variety of phases are formed. These phases, and their distribution will in the first place limit the performance of the refractory. High alumina refractories with  $C/A > 2$  should in principle be useful to temperatures approaching the  $CA_2$  peritectic transformation temperature of about  $1760^\circ\text{C}$  (2). The behaviour of such refractories will, however, strongly depend on the nature of the intergranular or bonding phases that may be present. Such phases develop as the result of the high temperature reaction between the calcia rich phase and the alumina that are the usual starting constituents of the unfixed bodies.

In this paper we report on the structure of the interreaction zone between dense, polycrystalline alumina and a C-A melt with a composition near that of the  $1360^\circ\text{C}$  eutectic.

The phase distribution and micromorphology were examined by microscopy methods. The findings should be relevant to processes taking place during reactive sintering in the  $\text{CaO-Al}_2\text{O}_3$  system, and to the understanding of bonding in some highly fired, high alumina-calcium aluminate bonded refractories.

Solid state interreaction between  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  have been previously studied by Kohatsu and Brindley (3), and by Ito et al.

(4,5). For  $\text{CaO-Al}_2\text{O}_3$  couples, reacted below the lowest eutectic temperature in the C-A system, a layered succession of phases was observed that corresponded to an isothermal cross-section of the phase diagram. Platinum marker experiments clearly indicated that calcium was the dominantly transported cation establishing the thickness of the various reaction layers. Grainboundary transport appeared to enhance significantly the interreaction rate. In the present case, where  $\text{Al}_2\text{O}_3$  is reacted with a C-A eutectic melt, the structure of the interreaction zone was found to be more complex, while impurities in the  $\text{Al}_2\text{O}_3$ , such as Si and Mg, appeared to have an important role.

## 2. Experimental Procedure

$\text{Al}_2\text{O}_3$  and  $\text{CaCO}_3$  powders were mixed to give a C/A ratio of 1 by weight, corresponding approximately to the  $1360^\circ\text{C}$  eutectic composition. The powder was melted and homogenized in a platinum crucible, for 1 hour, at  $1420^\circ\text{C}$  in air. Pieces of this pre-melted material were put into contact with the interface between two polished blocks of dense, polycrystalline alumina.\* The impurities in the alumina and in the melt were determined spectroscopically, and are listed in Table I. The assembly was heated, in air, at a rate of  $10^\circ\text{C}/\text{min}$  to  $1530^\circ\text{C}$ . The melt penetrated, through capillary action, between the alumina blocks, to produce a chemical weld. The sample was held at temperature for 4 hours, and then cooled at  $10^\circ/\text{min}$ . The specimen configuration is shown in Figs. 1a and 1b. Similar experiments were also performed using corundum single crystals with 00.1 contact faces.

Thin slices of the reaction zone were cut with a diamond saw perpendicular to the reaction zone, and prepared for transmission electron microscopy. It was necessary to mechanically pre-thin the reactive zone with a dimple polisher\*\* to about  $15\mu\text{m}$ , to minimize the effects of preferential etching in the subsequent foil preparation by ion milling. This technique also permitted a more accurate pre-selection of the area to be examined by transmission electron

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\*Hot pressed polycrystalline alumina prepared by AVCO Systems, Wilmington, Massachusetts 01887.

\*\*VCR Group, 65000 Meadow Brook Drive., San Francisco, California. Philips Corp., Eindhoven, Netherlands.



microscopy. Thin foils were examined in a Philips 400 scanning transmission electron microscopy with an X-ray micro analyzer. The microscope was operated in the micro diffraction mode for element detection, so that area of about  $0.1\mu\text{m}$  in diameter could be analyzed chemically. Some high resolution work was performed with a Siemens 102 transmission electron microscope.<sup>†</sup> Polished sections were also examined by scanning electron and optical microscopy. These samples were briefly etched in hot  $\text{H}_3\text{PO}_4$ .

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<sup>†</sup>Siemens Corp, Stuttgart, West Germany.

### 3. Results and Discussions

A scanning electron micrograph of a polished and etched reaction zone cross section is shown in Fig. 2. This zone contains several layers parallel to the reaction front. A in Fig 2a is the unreacted  $\alpha$ -alumina. The first layer, B in Fig 2a consist of dense, platelike grains preferentially aligned in the reaction direction. Channel-like features, arrowed in Fig. 2a, have been etched out in this layer. Transmission electron microscopy and selected area diffraction revealed that the B layer consisted mainly of  $CA_6$  grains. This is in agreement with the observation of Kohatsu and Brindlely (3) and Ito et al. (4,5) on solid state reacted samples. The size of the  $CA_6$  grains varies around about  $50\mu m$ , while that of the original  $\alpha$ -alumina is only a few microns. The development of  $CA_6$  is thus accompanied by a process that has aspects similar to that of abnormal grain growth. The  $CA_6$  grains are heavily faulted, as shown in Fig. 3. The faults are a stacking sequence disorder, accommodating some deviations from the C/6A stoichiometry. They recently have been analyzed in some detail by Schmid and De Jonghe (6). Additionally, evidence of basal plane dislocation activity was also found frequently. An example is shown in Fig. 4, where some basal plane dislocations in the  $CA_6$  phase have been arrowed.

Within the  $CA_6$  layer, channel-like features can be observed as arrowed in Fig 2a. Transmission electron microscopy of such regions showed that these features appear to consist of large  $CA_6$  grains or

grain bundles with elongated inter- and transgranular pores, Fig. 5. Close examination showed, however, that in these pores remains of an amorphous aluminum-calcium-silicate containing phase could be found, as shown in Fig. 6. Strong preferential thinning of the glassy phase in the pores is thus likely to have caused the appearance of empty pores in the channel-like features. Presumably the silicate phase formed as a result of rejection of silica at the advancing  $\text{Al}_2\text{O}_3/\text{CA}_6$  reaction interface, and accumulated in the channel-like pore bundles. These silicate filled channels may thus also provide an additional path for ions that are not readily transported in the  $\text{CA}_6$  phase. Thus, the silicate impurity phase is likely to be involved in enhancing the interreaction rate kinetics for the impure, polycrystalline alumina. The reaction of the eutectic C-A melt with  $\alpha$ -alumina single crystals is significantly slower, as is shown in Fig. 7. The  $\text{CA}_6$  layer phase is now only 10-15 $\mu\text{m}$  wide, which for polycrystalline material, reacted under similar conditions, is about 45 $\mu\text{m}$  wide. The  $\text{Al}_2\text{O}_3/\text{CA}_6$  or  $\text{CA}_6/\text{CA}_6$  grain boundaries do thus not solely account for this significant difference in reaction rates, as reported by Kohatsu and Brindley (3), since such boundaries are evident in both cases.

Since the molar volume of the  $\text{CA}_6$  phase is about 18 larger than that of  $6\text{Al}_2\text{O}_3$ , and the formation of  $\text{CA}_6$  is known to be attributable to CaO transport (3), significant stresses should arise in the reaction morphology shown in Fig. 7; where the layer is thin, at A in Fig. 7, more rapid growth should take place, requiring a relative displacement of A with respect to B. Since  $\text{CA}_6$  is a layered compound, slip in

the basal plane is likely to be significantly easier than normal to it, so that differential growth stresses could be more easily relieved for grains growing along basal planes rather than normal to it. Basal plane dislocation activity were indeed found in the  $CA_6$  phase, as shown in Fig. 4. Additionally, CaO transport is also likely to be quite anisotropic, since such transport anisotropies are known to be extreme in the related sodium- $\beta$  and - $\beta''$  alumina structures (7). Both the expected case of basal plane slip and the transport anisotropy should significantly contribute to making the basal plane the preferred growth direction during C-A interreaction. Thus, no preferred orientation relationships need be invoked to account for the strong texture development observed in the  $CA_6$  layer for the C-A interreaction.

Next to the  $CA_6$  layer, marked B in Fig. 2, a second reaction layer, C, is observed. This layer consisted mainly of a mixture of the calcium rich phase  $CA_2$  and an Mg containing phase. The Mg containing precipitate phase is likely to be spinel, according to the known phase relationships (8) and the cubic morphology of the precipitate.

The remaining layer, D in Fig. 2, was a mixture of CA and  $C_3A$ , as would be expected from the cooling of the unreacted melt.

It was also interesting to note that the strength of the calcium aluminate bonding of the  $\alpha$ -alumina blocks depended significantly on the amount of melt that was allowed to penetrate the contact area. For larger amounts of melt penetration, at a wider separation of the two alumina blocks (Fig. 1a), increasing amounts of porosity developed

at the weld interface, after complete reaction of the melt to  $CA_6$ . Such porosity is shown in Fig. 9. The increased porosity resulted in a considerably weaker weld. Local variations in the reaction rate cause the  $CA_6$  surface at the weld interface to be rough, so that good contact is not maintained. Such roughness appears to increase with increasing reaction time, leaving increasing weld porosity. It is possible that similar problems might arise during reactive liquid phase sintering in the C-A system, and lead to poor powder densification behavior.

#### 4. Conclusions

The interreaction zone between polycrystalline  $\alpha\text{-Al}_2\text{O}_3$  and a C-A eutectic melt, at  $1530^\circ\text{C}$ , produces a reaction zone that differs in several significant aspects from the one observed for C-A solid state interreaction. Only a strongly textured  $\text{CA}_6$  layer is clearly defined. Additional layers are complex phase mixtures. Silica, a common impurity in sintered alumina, is rejected by the advancing  $\text{CA}_6$  phase and accumulates in channels that provide easy transport paths enhancing reaction kinetics.

Complete reaction of the C-A melt with an  $\alpha$ -alumina junction produces a porous weld. The weld porosity increases with increasing amounts of melt, leading to poorer mechanical properties.

## 5. Acknowledgement

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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### Figure Captions

Fig. 1. a. Reaction geometry

b. Cross-section of a reacted sample

Fig. 2. a. Cross section of the reaction layer. A = unreacted alumina; B =  $CA_6$  phase; C =  $CA_2$  + spinel; D = CA -  $C_3A$  mixture. Some channel-like features in the  $CA_6$  layer have been arrowed.

b. Spinel precipitates, arrowed, in the C layer.

c,d,e. X-ray dispersive analysis of the B, C, and D layers showing the changing C/A ratios.

Fig. 3. Basal plane faulting in the  $CA_6$  phase. Such faulting can accommodate deviations from the C/6A stoichiometric ratio.

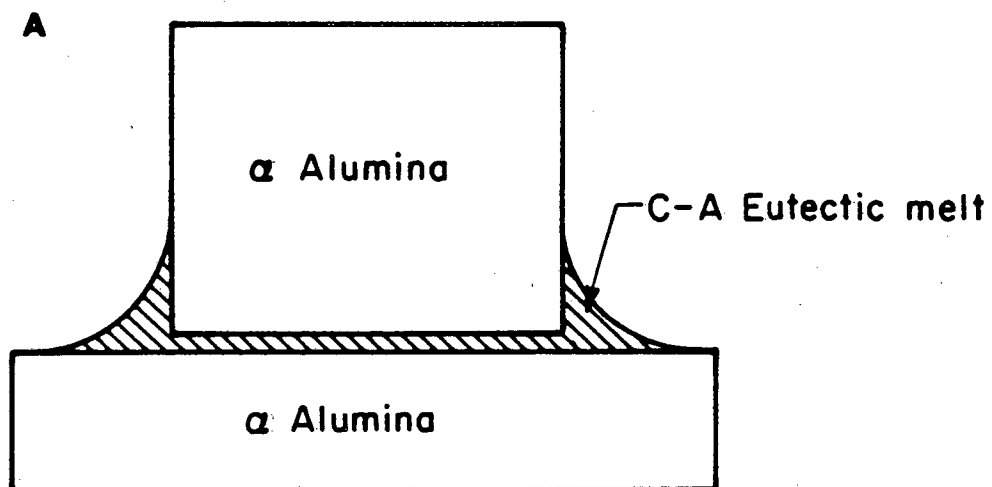
Fig. 4. Basal plane dislocation activity, arrowed, in  $CA_6$  phase.

Fig. 5. Porous  $CA_6$  grains in channel features marked in Fig. 2a.

Fig. 6. a. Remaining silicate phase found in some pores and intergranular regions of areas such as shown in Fig. 5. The X-ray dispersive spectrum is from the area marked A, and shows the presence of Si. The fringes are 00.2 lattice fringes of the  $CA_6$  phase.

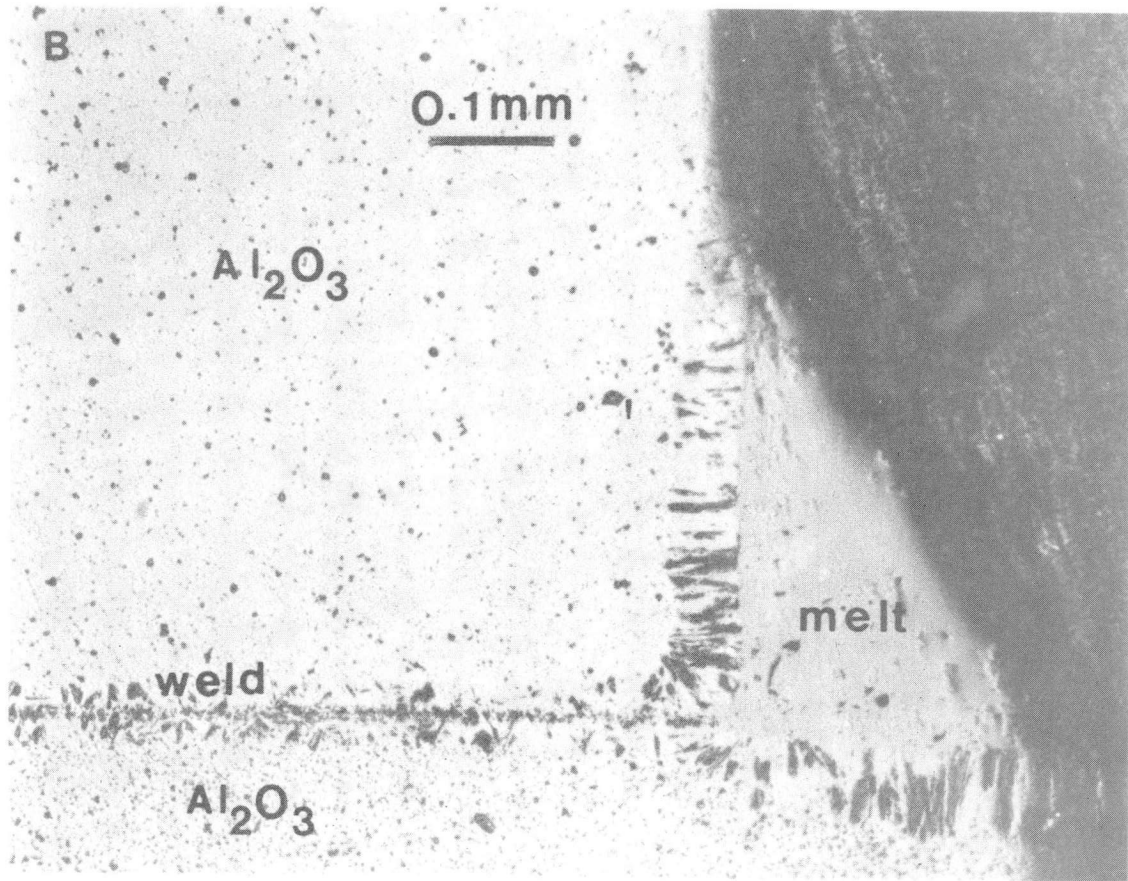
Fig. 7.  $CA_6$  formation for reaction at C-A melt with  $\alpha$ -alumina single crystal. The 00.1 direction of the alumina is normal to the reaction front. A Ca microanalysis tracing is superimposed for a scan along the line A-B.

Fig. 8. Remaining porosity at the weld interface between two alumina blocks, after complete reaction of penetrated C-A melt to  $CA_6$ .



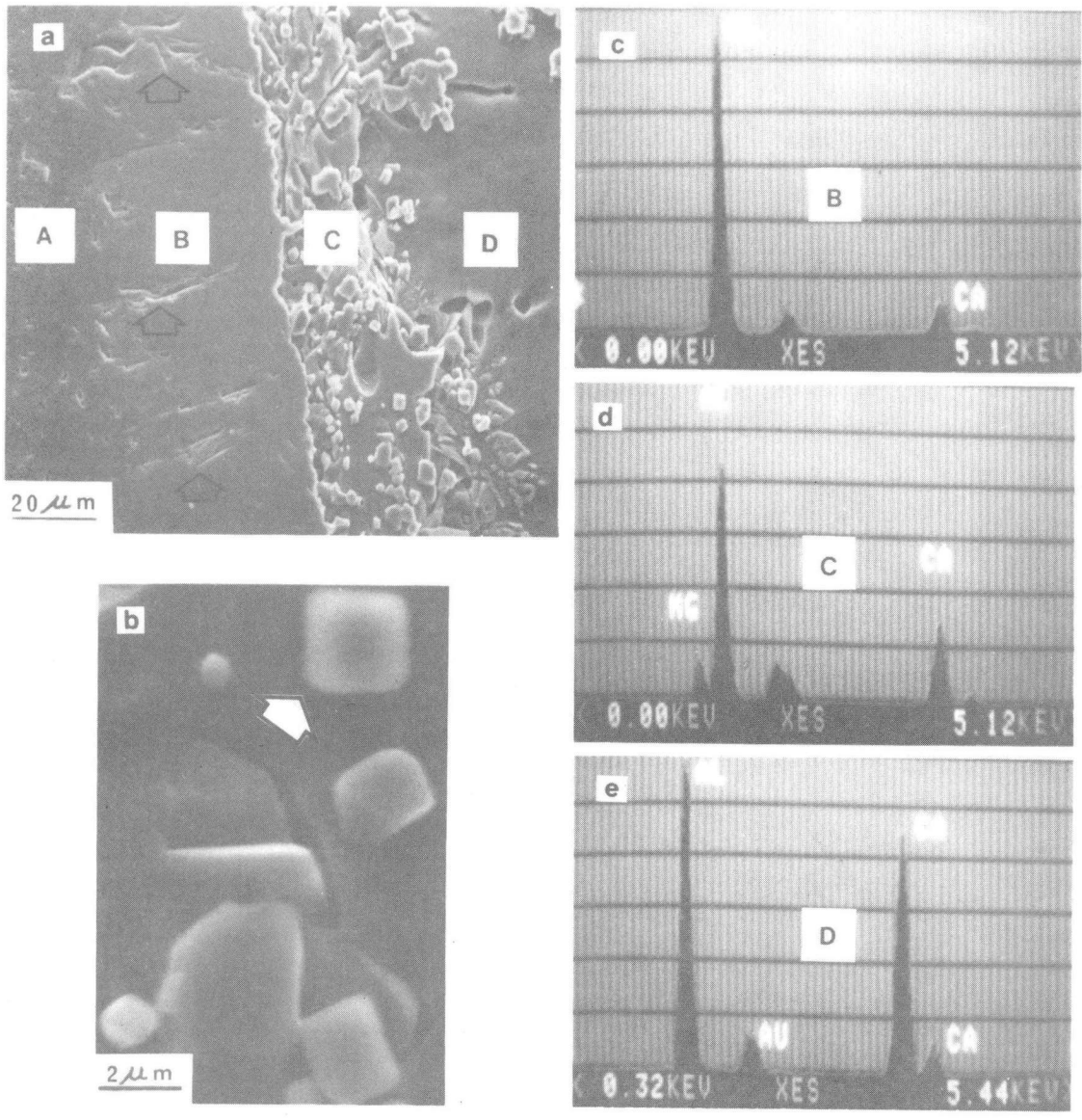
XBL 833-116

Fig. 1a



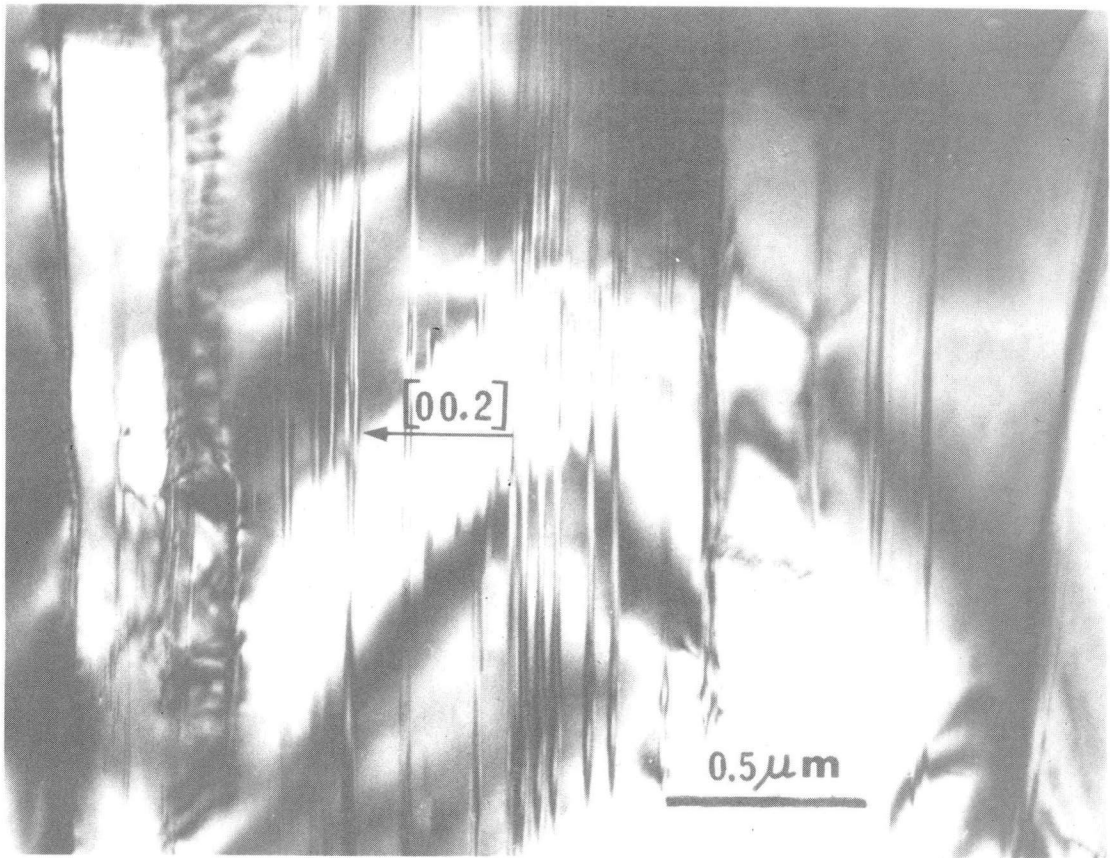
XBB 833-2602

Fig. 1b



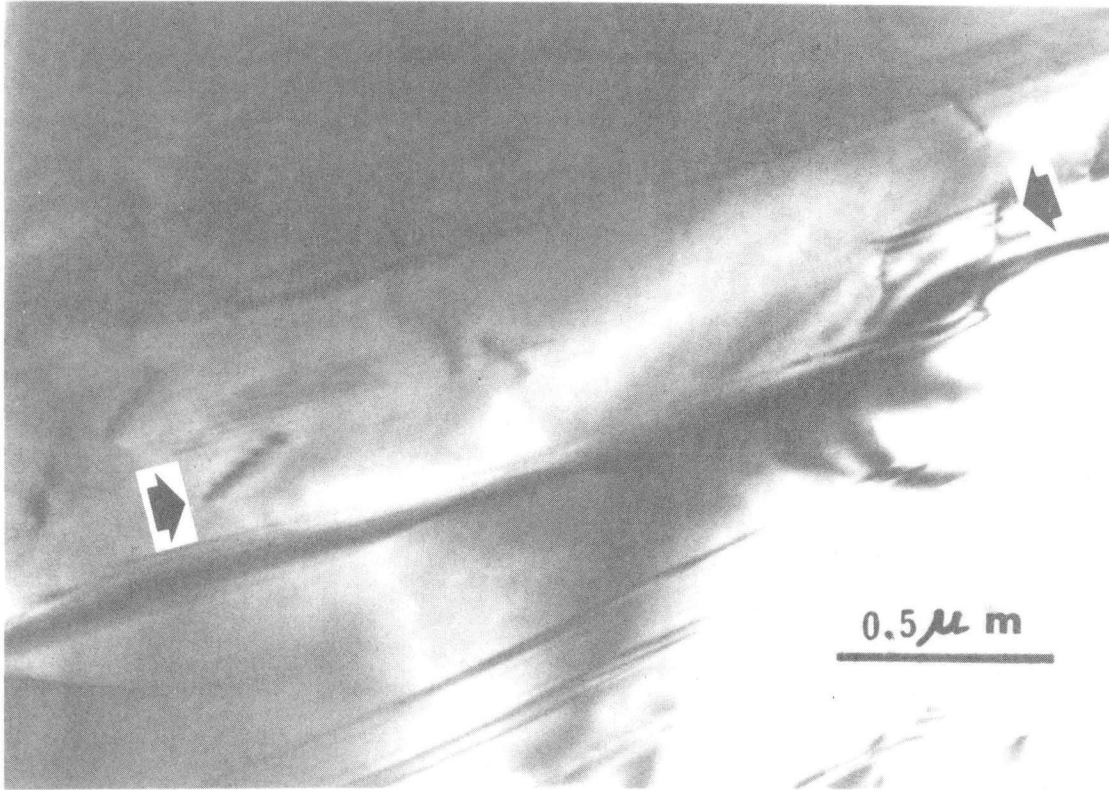
XBB 833-2608

Fig. 2



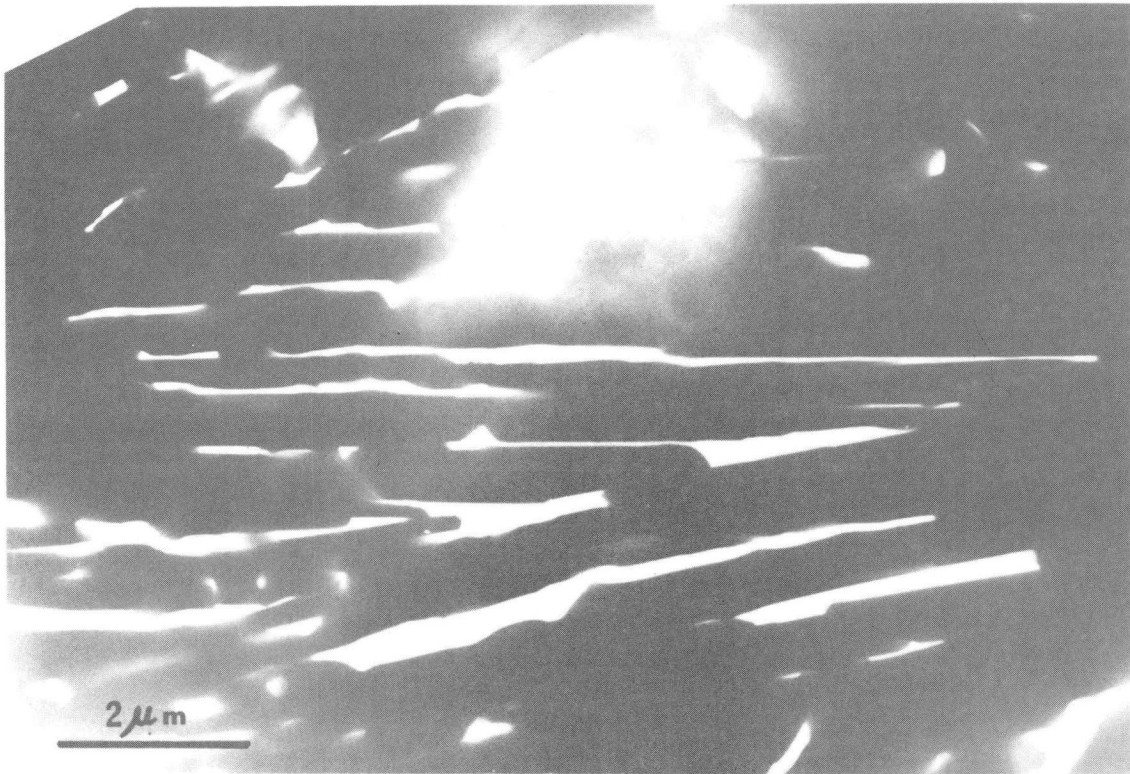
XBB 833-2603

Fig. 3



XBB 833-2604

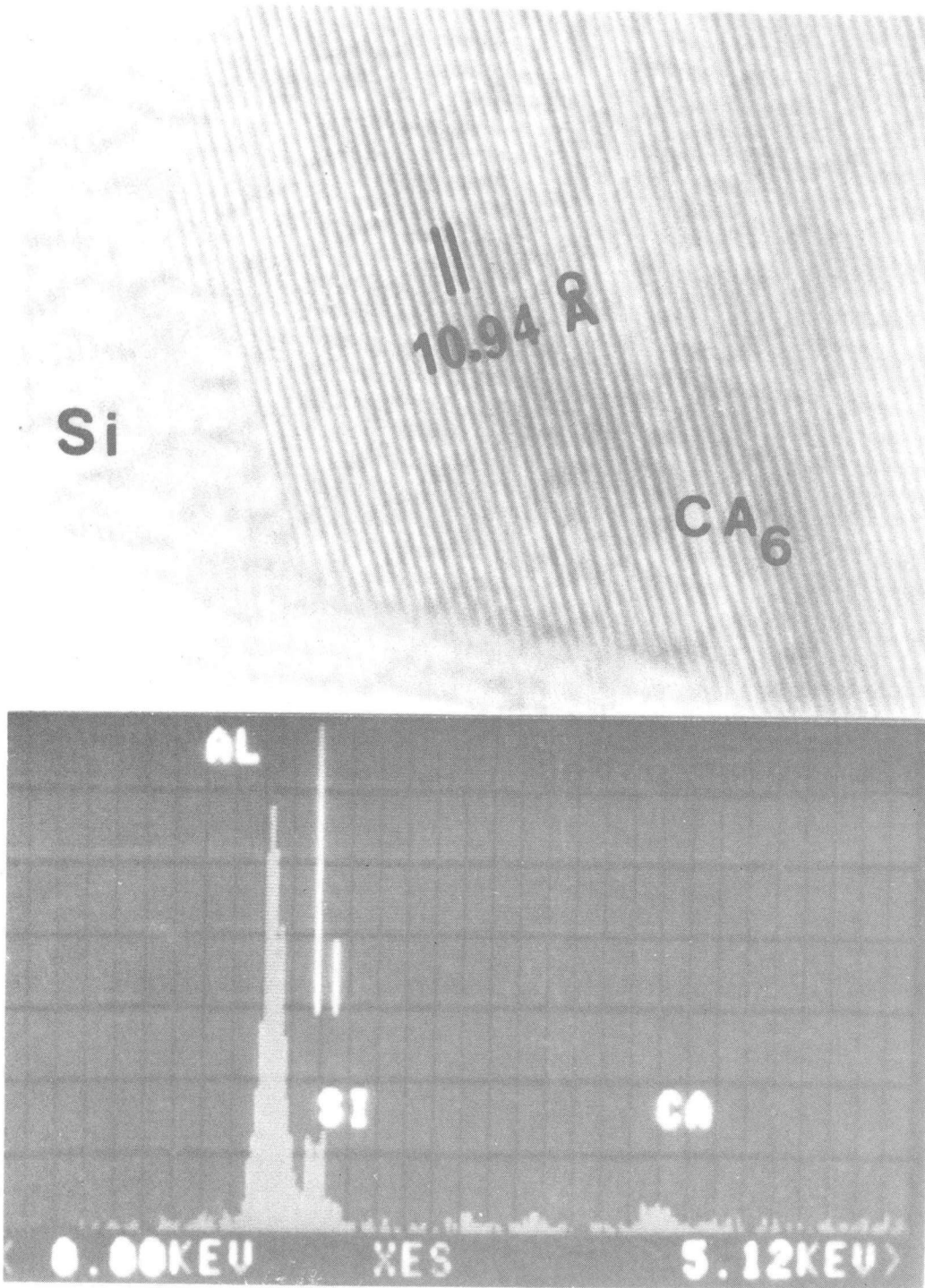
Fig. 4



XBB 833-2607

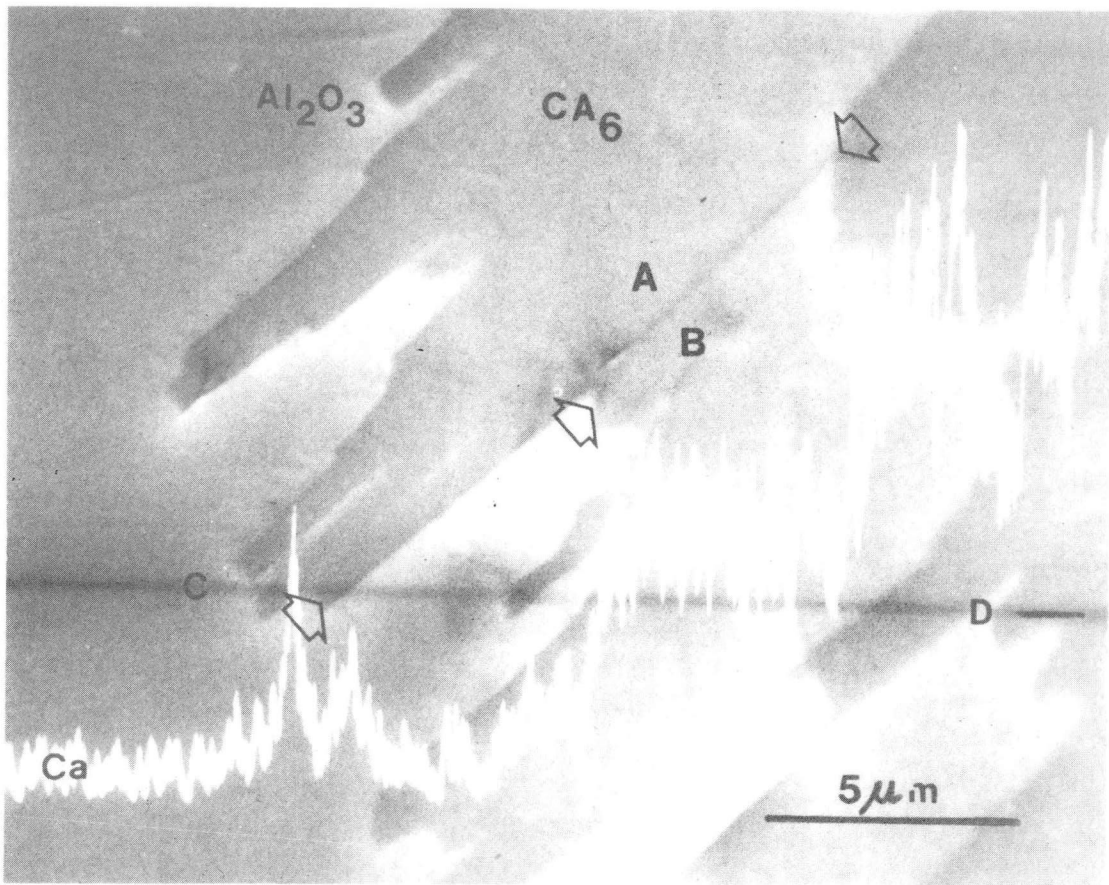
Fig. 5





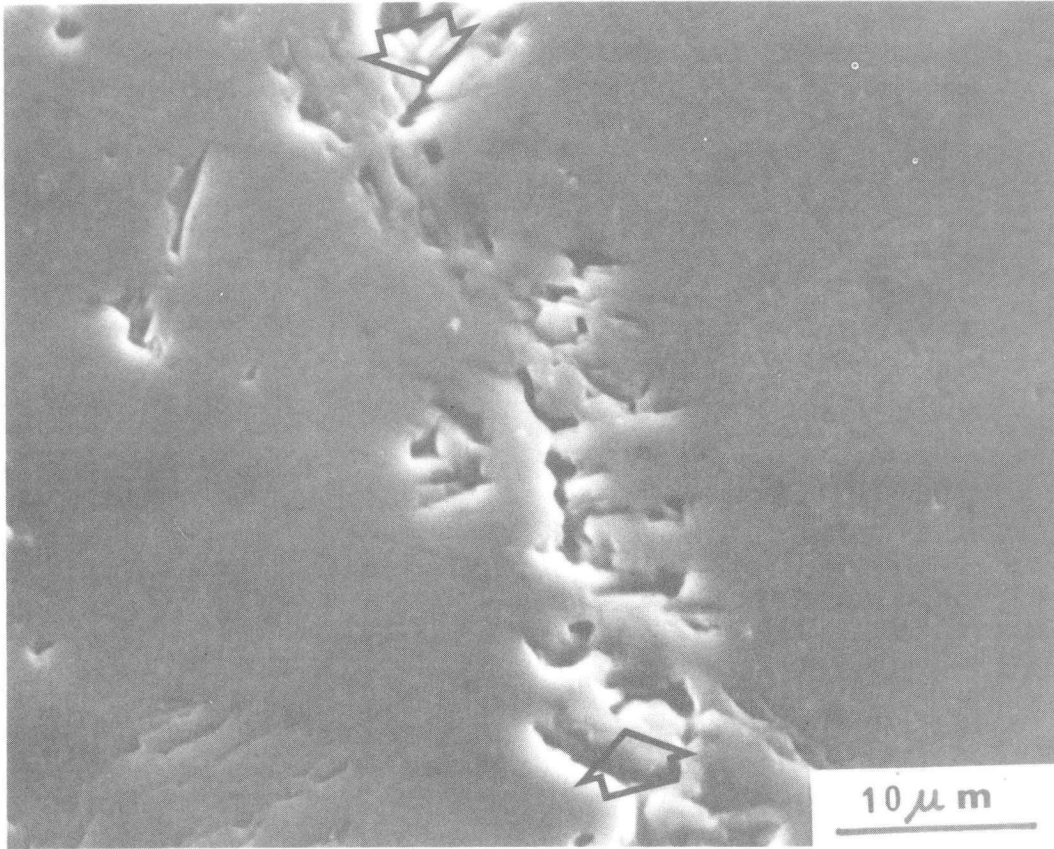
CBB 833-2609

Fig. 6



XBB 833-2606

Fig. 7



XBB 833-2605

Fig. 8

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