BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 295—299 (1966)

Twinning in Electric Furnace-fused Corundum

By Goro YAMAGUCHI, Yasushi KUBO and Hiroshi OGAWA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

(Received July 20, 1965)

In an investigation into the fracture properties of thin-sectioned corundum crystals, it was noticed that microcracks in electrically-fused corundum obey a hexagonal symmetry in spite of the rhombohedral symmetry of the corundum structure. This fact suggests that the corundum crystals consist of several twins, which have the same optical direction and which cannot be distinguished microscopically. The X-ray Laue back-reflection and etching techniques were applied to commercial 16-mesh grains of electric furnace-fused alumina abrasives. Corundum crystals grown over the crystal size of hundreds of μ to 1 mm. in electric-furnace fusions were found to be generally composed of several penetration twins with a twinning plane (0001). The twins are considered to be growth twins arising in the cooling process. The impurity composition and heat treatment have no marked effect on twinning. The twin junction is highly stable both mechanically and chemically. Cleavage cracks generated in individual crystals are stopped at the twin boundary.

Recently many studies have been made of the imperfection structures of corundum as background for such applications as alumina ceramics, jewel instruments, lasers and masers.

In one investigation into the effect of imperfection sturctures on the abrasive properties of corundum, it was noticed that corundum crystals from electric-furnace-fused ingot consist of several twins ranging in size from hundreds of μ to 1 mm.; these twins have the same optic direction and can not be distinguished microscopically. This fact was initially noticed in examining microcracks generated in thin-sectioned corundum crystals,[1]

1) G. Yamaguchi, Y. Kubo and H. Ogawa, This Bulletin, **39**, 287 (1966).

which obey a hexagonal symmetry in spite of the rhombohedral symmetry of the corundum structure.[2] X-Ray Laue back-reflection and etching techniques were applied, thus revealing the characteristic features of this fine basal twinning with the penetration twin boundary. The cause of twinning and the effect on the abrasive properties will be discussed.

Experimental

Specimens.—Most of the specimens examined were commercial 16-mesh grains of electric-furnace-fused alumina abrasives obtained from Carborundum Company, with the impurity contents given in Table I. These specimens were obtained from large ingots of electric-furnace-fusions and were composed predominantly of corundum with crystal sizes of from 2 mm. to 1/10 mm. and of impure minerals forming a matrix or included in corundum crystals. Of these impurities, only titania was present in a conceivable amount in corundum in a solid solution. The texture varies depending on the raw materials and on the processing. A detailed description of the texture of these products may be found in the article by Baumann.[3]

TABLE I. IMPURITY COMPOSITION OF THE SPECIMENS

Specimen	SiO_2	Fe_2O_3	TiO_2	
C32	0.51	0.12	2.46	
R41	0.49	0.15	2.49	
C37	0.26	0.04	tr.	
Japanese commercial abrasives	0.86	0.21	2.43	# 24 as received
	0.10	0.10	1.50	# 220 treated by Na_2CO_3-K_2CO_3-H_3BO_3 flux

The specimens, designated G52, C32, R41 and C37, are so-called high or low-titania fused aluminas widely used for abrasives. C36 is an electric-furnace made white alumina made from Bayer-process raw material; it contains beta alumina as impurity. R71 is a special alumina containing a considerable amount of ZrO_2; in it corundum crystals grow as dendrite or fine euhedral crystalites in a matrix of impurities. Commercial Verneuil corundum and hydrothermally-synthesized corundum were also studied for the sake of comparison.

The effect of heat treatment on twinning was examined using as received Japanese commercial 24-mesh abrasive alumina containing titania in a solid solution; it has been heat-treated in air at 1250°C for 1 hr.

The Observation of Cleavage Cracks in Thin Sections.—When corundum crystals were ground in thin sections, numerous microcracks, regular or irregular, appeared in various places. These microcracks were not observed until the section was ground to a thickness of less than 5/100 mm.; they were closely related to the crystallographic orientation of the ground section.

When the ground section made an angle of from 50° to 80° with the basal (0001) plane and one of from 60° to 90° with the rhombohedral $\{10\bar{1}1\}$ plane, cleavage cracks parallel to the $\{10\bar{1}1\}$ plane took place predominantly.

The orientation of the c-axis and the cleavage crack normals with respect to the section normal was determined on thin-sectioned corundum crystals approximately 2/100 mm. thick using a universal stage and expressed in terms of stereographic projection. The symmetry exhibited by the cleavage cracks was then examined.

X-Ray Laue Back-reflection Photographs.—By the Laue back-reflection method, the orientation of the crystal in thin sections was examined and compared with the data determined by the measurement of cleavage cracks. Crystals with the c-axis nearly perpendicular to the section plane were selected in thin sections. Laue back-reflection photographs of them were then taken, and the symmetry of the reflection patterns was examined. The Laue pattern obtained from the single corundum crystal should be of a trigonal symmetry, so the hexagonal crystal gives evidence of basal twinning.

Etching on the Basal (0001) Surface.—In order to examine the twin junction and the size of twin individuals, the basal (0001) surface was etched. Etching techniques developed by Scheuplein and Gipps[4] using phosphoric acid and by Stephens and Alford[5] using potassium bisulfate were applied.

Results

The Arrangement of Cleavage Cracks in Thin Sections.—The orientations of the section normal (T), the c-axis (C) and the cleavage crack normals (P_1, P_2 and P_3) as determined on a thin-sectioned corundum crystal of Fig. 1(a), which exhibits three sets of cleavage cracks, are shown in Figs. 1(b) and 1(c) by stereographic projection to show the symmetry of the cleavage cracks.

These cleavage cracks correspond to the rhombohedral $(10\bar{1}1)$ plane, with an angle of 57°35′ with relation to the basal plane. The arrangement of cracks, however, can only be interpreted as of a hexagonal symmetry. By careful observation of Fig. 1(a) it can be seen that the sets of cleavage cracks never intercross with each other and that they separates a crystal into regions, in each of which one of the sets predominates. Almost all of the crystals exhibiting more than two sets of cleavage cracks were found to possess hexagonal crack patterns.

A Laue Back-reflection Photograph.—One of the Laue back-reflection photographs taken along the c-axis of nearly basal sections of electric-furnace-fused corundum is given in Fig. 2(a); the corundum is seen to be made up, by basal twinning, of the superposition of the usal trigonal pattern of a single corundum crystal and its 180° rotated or mirror-reflected pattern.

2) J. D. Dana & E. S. Dana, "The System of Mineralogy," 7th ed., Vol. 1, John Wiley & Sons, Inc., New York (1944), p. 520.
3) H. N. Baumann, Jr., *Am. Ceram. Soc. Bull.* **37**, 179 (1958).
4) R. Sheuplein, *J. Am. Ceram. Soc.*, **43**, 458 (1960).
5) W. J. Alford, ibid., **46**, 193 (1963).

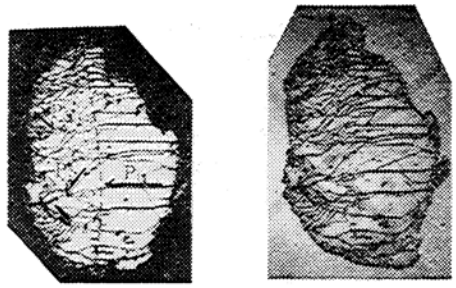
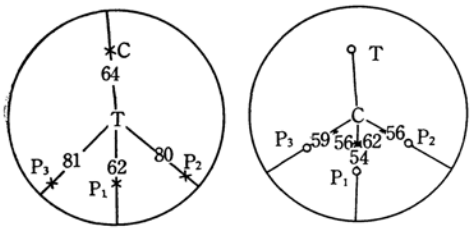


Fig. 1(a). A crystal made up of two twin individuals, one of which includes cleavage crack P_1, another includes P_2 and P_3. Each arrow is drawn parallel to the trace of cleavage crack on thin section. The twin boundary presumed from the distribution of cleavage cracks is shown by dotted line.



1(b) 1(c)

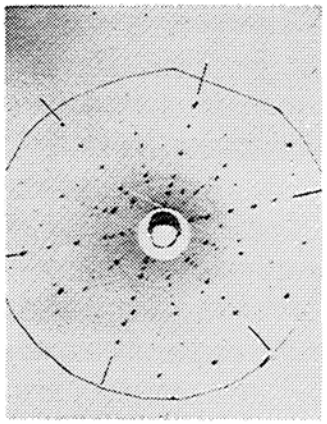
Fig. 1(b). Stereographic projection of cleavage cracks on the section plane.

1(c). Stereographic projection of cleavage cracks on the basal plane.

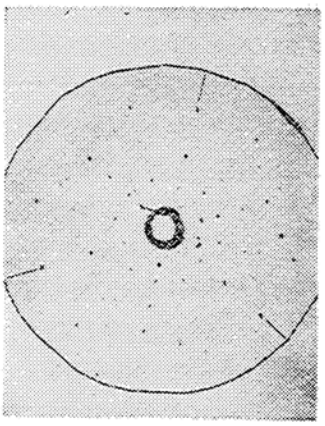
The Twin Structure Revealed by Etching on the Basal (0001) Plane.—Etch pits on the (0001) surface showed the region of twin individuals by means of the reversal of the triangular etch pits. Twin junctions were not affected at all or were only obscurely etched, as is shown in Fig. 3 and Fig. 4; this differs from Alford's observation of the basal twin of flux crystals, where the trace of the composition plane $(10\bar{1}0)$ on the basal plane was marked by a row of rectangular or diamond-shaped etch pits.[5]

The twin boundaries drawn from the distribution of etch pits are shown in Fig. 5. The size of the individual crystal is determined to vary from hundreds of μ to 1 mm. in diameter, and the twin boundary is not planar but interpenetrating.

The Effect of Impurities, Texture, and Heat Treatment on Twinning.—The presence of twinning was examined on each of the specimens, which differ in impurity composition and in texture. The results are shown in Fig. 6, where measured grains are marked at positions on the abscissa expressing the crystal size in mm.; the single crystal is marked by a one-sided arrow head, and twin composed of more than two individuals, by a two-sided arrow head.



2(a)



2(b)

Fig. 2(a). Laue photograph taken along the c-axis of electrically-fused corundum crystal. An X-ray beam with about 1 mm. in diameter is applied. The hexagonal distribution of the spots confirms the twinning of the crystal.

2(b). Laue photograph taken along the c-axis of Verneuil corundum crystal. An X-ray beam with about 1 mm. in diameter is applied. The trigonal distribution of the spots is that of single crystal's.

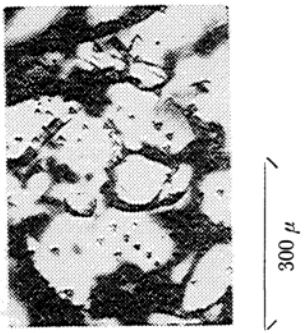


Fig. 3. Twin structure revealed by etching on the basal plane. Twin junction was not affected at all.

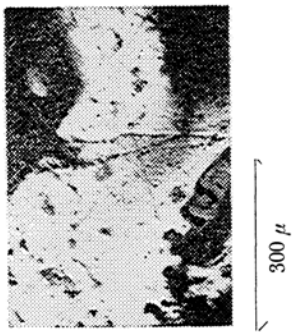


Fig. 4. Same as Fig. 3. Twin junction was obscurely etched.

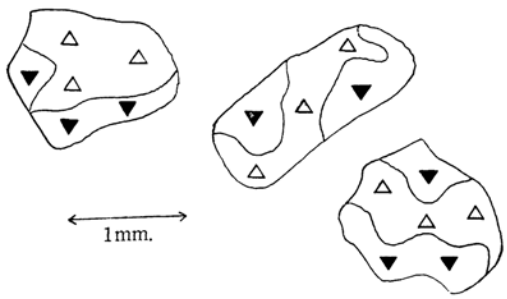


Fig. 5. Twin boundaries drawn from the distribution of etch pits.

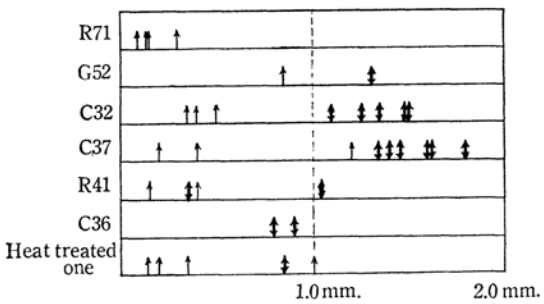


Fig. 6. Relations between crystal size and twin formation.
Crystal size is expressed by $(a+b)/2$ in mm.
a: The longest diameter
b: The diameter perpendicular to the direction of a
↕ Twin composed of more than two individuals
↑ Single crystal

Except for the R71 sample, which has a singular composition and texture, no striking difference was observed between the specimens with regard to twin formation. In any specimen corundum crystals grown over the crystal size of hundreds of μ are composed of interpenetrating basal twins. Heat treatment in air at 1300°C on titania-containing crystals caused no change in the twin structure.

Discussion

The twinning of corundum has been described in the literature as follows; commonly with a twinning plane $(10\bar{1}1)$ and less commonly with (0001), the latter being usually lamellar and producing a lamellar structure and striae on $c(0001)$ and $r(01\bar{1}1)$, and even less commonly, penetration twins or, rarely, arrowhead twins with tabular crystals parallel to $(11\bar{2}0)$.[2]

Recently, Stephans and Alford[6] reported that a basal twinning with a $(10\bar{1}0)$ composition plane and a (0001) twin axis, which was observed by Mekczer as a rare form on natural corundum, is generally present on flux crystals grown from PbO-PbF_2 flux systems at temperatures up to 1250°C. Pressure twinning produced on $(10\bar{1}1)$ and on (0001) under pressures of from 13000 to 18000 atmospheres was studied in detail by Veit[7] and interpreted on the basis of dislocation mechanisms by Kronberg.[8] This study has shown another form of twinning in electric-furnace fused corundum crystals.

Skeletal crystals (so designated by Baumann), which grow on the surface of shrinkage pipes in cooled ingots, were also found to be basal twins coupled on a longitudinal twin boundary, on each side of which rhombohedral corundum crystals pile up along the c-axis, thus forming a skeletal needle, on which no comment was made by Baumann.

The cause and process of twin formation can only be inferred qualitatively. The observed twins are considered to be growth twins arising from the strain peculiar to the cooling of large ingots of electric-furnace fusions. The cohesion of a twin junction is as strong as the internal cohesion of a single crystal; the etch pits usually observed in other cases on the traces of a twin boundary are not revealed, and the cleavage cracks generated in the region of single crystals are stopped at the twin boundary, not propagating beyond it, as is shown in Fig. 1(a).

The fracture properties of electrically-fused corundum are supposed to be affected by twinning. Whether twinning increases the toughness of corundum or not remains to be established, however.

Conclusion

1) Corundum crystals grown over the crystal size of from hundreds of μ to 1 mm. in electric-furnace fusions have been found generally to be composed of several penetration twins with a twinning plane (0001).

6) W. J. Alford, *J. Am. Ceram. Soc.*, **47**, 81 (1964).
7) K. Veit, *Jb. Min. Beil.*, **45**, 121 (1921).
8) M. L. Kronberg, *Acta. Met.*, **5**, 507 (1957).

2) These twins have been considered to be growth twins arising in the cooling process. The impure content and heat treatment have no marked effect on the twinning.

3) The twin junction is highly stable, both mechanically and chemically. Cleavage cracks generated in individual single crystal are stopped at the twin boundary. By chemical etching on the basal plane, the trace of the twin boundary is not affected at all or, in some cases, is only obscurely etched.

4) The fracture properties of corundum may be supposed to be affected by twinning, but the relation between the toughness of abrasives and the twinning remains to be established.