Oriented overgrowth of hematite on beta-alumina

By E. R. Segnit

Division of Building Research, Commonwealth Scientific and Industrial Research Organization, Highett, Victoria, Australia

Summary. An alkali-alumina-silica slag from the interior of a kiln used for the firing of refractories was found to contain recrystallized mullite, corundum, and beta-alumina. Isolated areas of the slag were also rich in iron oxides; in these areas beta-alumina crystallized from the melt as hexagonal plates, and at a later stage small hexagonal plates of hematite grew on the 0001 face of the beta-alumina plates in a regular fashion.

Introduction

EPITAXY, or oriented overgrowth of one type of crystal on another from the vapour phase, from solution (generally aqueous) and in the solid state is a phenomenon that has been widely observed and studied by chemists and metallurgists. The phenomenon also occurs in nature and numerous cases have been described by mineralogists. Van der Merwe (1949) has prepared an exhaustive list of examples of the pheno-menon, mostly non-mineralogical, and has discussed the theory of the development of oriented overgrowth.

In this paper an example of the overgrowth of hematite on beta-alumina is described. This occurred during the crystallization of the phases from a molten silicate slag formed on the refractory lining of a kiln; epitaxial growth under such conditions does not appear to have been described before.

Conditions of formation

The slag occurred on the walls of a downdraught kiln used for firing alumino-silicate refractories. Firing temperatures were in the region of 1300° C, and the slag was formed chiefly by the reaction of alkali driven from the bricks with the refractories of the kiln walls. A viscous, mottled brown glazed layer several mm thick formed on the wall and largely prevented further corrosion. Under the microscope the glazed slag layer was rather inhomogeneous, with parts being predominantly crystalline, and other parts mainly glassy. In the more crystalline parts the slag had reacted with firebrick fragments causing abundant

crystallization of mullite needles, and, in places, thick hexagonal basal plates of corundum.

In the glassy parts of the slag where the alkali content was higher, very thin hexagonal plates of the so-called beta-alumina ($Na_2O.11Al_2O_3$) had crystallized. Where iron oxide particles had reacted with the glassy part of the slag it was coloured brown, and both red-brown hexagonal plates of hematite and skeletal crystals of magnetite had formed. Rapid crystallization of the latter had depleted the surrounding liquid slag of iron, leaving each grain of magnetite with a halo of colourless glass in the solid slag. It was in these iron-rich areas that an oriented overgrowth of hematite platelets had developed on beta-alumina crystals.

The nature of the overgrowth

The substrate crystals were thin colourless hexagonal plates. Their habit, together with the occurrence in the more soda-rich part of the slag, indicated that the phase was beta-alumina rather than corundum. In parts of the slag where the iron concentration was lower, very thin crystals of beta-alumina were free from overgrowth; as the iron concentration began to increase, trains of very small poorly formed hematite crystals formed on the substrate in lines parallel to the edges of the larger crystal. The hematites were larger and well formed where the iron content was at its highest (fig. 1).

The beta-alumina crystals show some step growth on the 0001 surfaces which can be seen in fig. 2, where a complete triangular step is shown outlined by hematite crystals. The hematites occur as small, very thin hexagonal plates, and, as can be seen in fig. 1, they form in rows parallel to the edges of the substrate crystal. The striking feature of this regular overgrowth, however, is that the individual hematite platelets are oriented at 30° to the substrate crystal. They also appear to have nucleated along growth steps on the 0001 surface of the larger crystal. The steps can seldom be seen on the substrate itself, but show up as a more or less continuous line through the rows of hematite crystals (fig. 2). The development of the rows of platelets appears to have been controlled in most cases by the surface features of the substrate, although at times the substrate is apparently microscopically flat (fig. 3). Growth steps on the larger beta-alumina crystals reach a maximum of one micron in height, but they are mostly much less than this; those illustrated in fig. 2 are too small to be measured microscopically although on other crystals up to 24 steps could be counted over a height of 2 microns.

The hematite platelets were very small and poorly formed where the
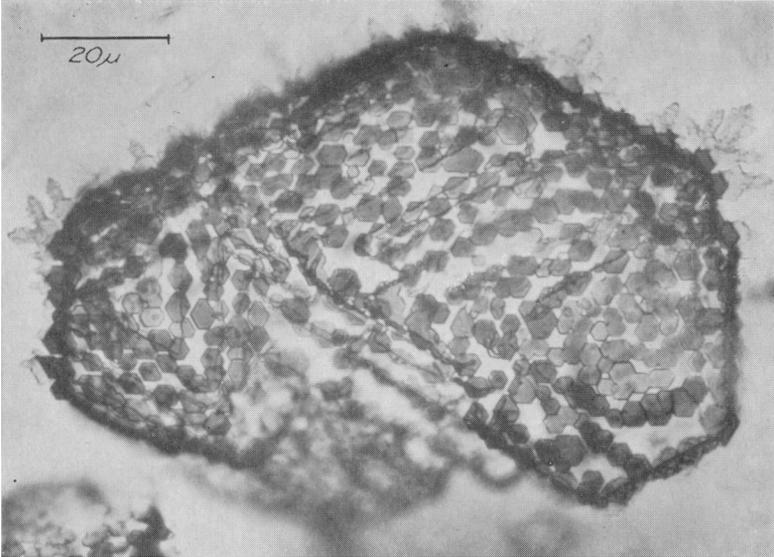
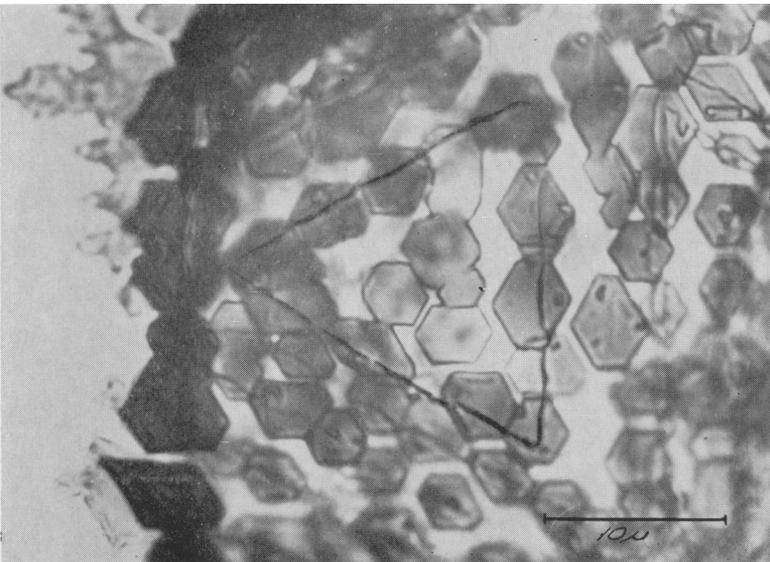FIG. 1. Crystal of beta-alumina with oriented overgrowth of hematite.

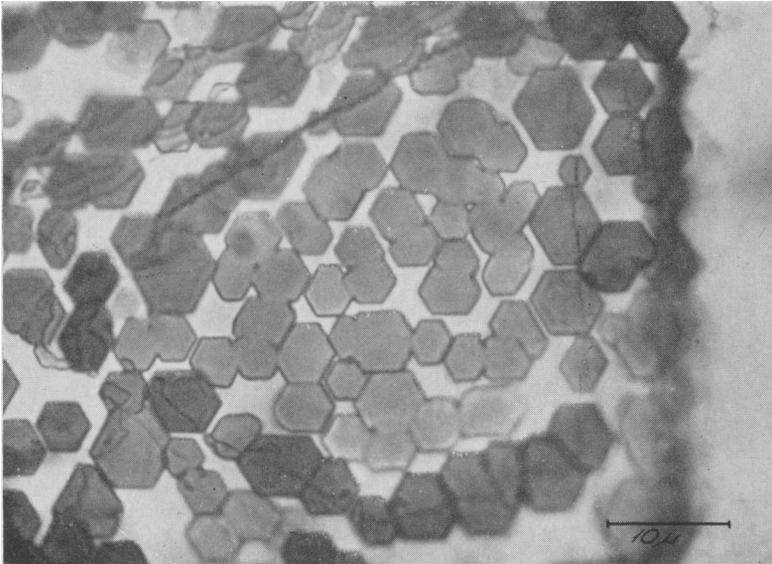FIG. 2. Left hand portion of crystal shown in fig. 1, showing triangular growth step.

FIG. 3. Right-hand portion of crystal shown in fig. 1, showing oriented hematite crystals on a microscopically flat surface.
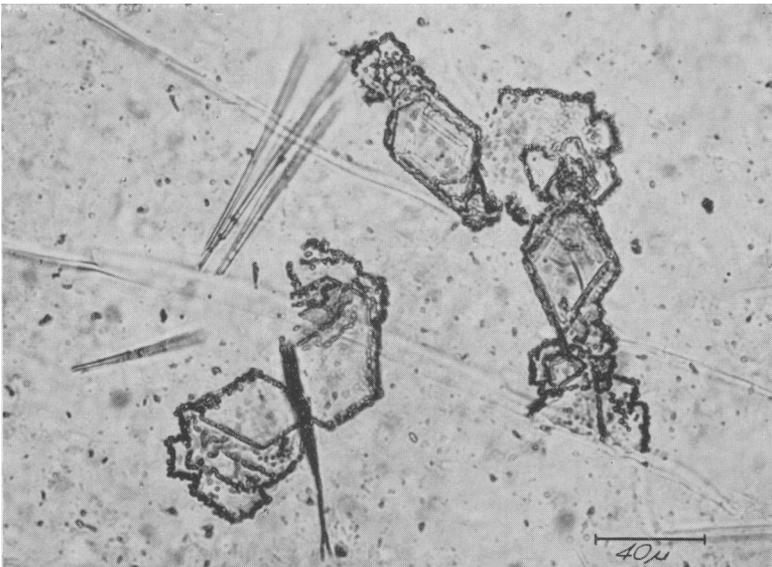

FIG. 4. Beta-alumina crystals in iron-poor part of slag. Very small, poorly formed hematite crystals have nucleated along growth steps of the substrate.

liquid phase was low in iron. However, they still developed along lines parallel to the sides of the beta-alumina crystal, particularly at the edges. This is illustrated by the group of crystals in fig. 4; here the beta-alumina crystals are outlined by chains of very small hematites, one to two microns in diameter. On some of these crystals growth steps can be seen (top right) and chains of very small hematites can be seen outlining such steps (lower right).

Discussion

Beta-alumina was first described by Rankin and Merwin (1918) as a form of alumina. However, it was shown by later workers that crystals of the compound always contained a small amount of alkali, and Ridgway, Klein, and O'Leary (1936) in a detailed survey of the problem showed that it was, in fact, a sodium or a potassium aluminate with the suggested formula $Na_2O.12Al_2O_3$ or $K_2O.12Al_2O_3$. Pablo-Galan and Foster (1959) investigated the occurrence of beta-alumina in the ternary system $Na_2O–Al_2O_3–SiO_2$, and have shown that there is probably a large primary phase field for the compound. Bor (1950) described the occurrence of both beta-alumina and corundum in glass tank refractories; the habits of the crystals in his samples were very similar to the habits of the corresponding crystals found in the present work.

Bragg, Gottfried, and West (1931) first described the basic structure, which was later detailed by Beevers and Ross (1937), who stated that 'It consists of blocks of cubic close-packed oxygen atoms of the thickness of four close-packed layers, adjacent blocks being held together by a layer of oxygen and alkali atoms which is not close-packed'. A composition of $Na_2O.11Al_2O_3$ fitted the structure, which had an hexagonal unit cell. This structure results in a good basal cleavage, and explains the tendency to form very thin, basal plates on crystallization.

Hematite, however, has the rhombohedral corundum structure (Bragg, 1930). The crystalline habit can vary considerably, although it mainly tends to form hexagonal plates bounded by prism or small rhombohedral faces. The oxygen atoms are in approximate hexagonal close packing, with two-thirds of the available cation positions occupied by the $Fe^{...}$ ions.

From a consideration of the structural arrangement of the oxygen atoms, which are fundamentally close packed in both structures, the overgrowth of hematite on beta-alumina appears at first sight quite straightforward. The free surface of beta-alumina can be considered as a close packed layer of oxygen atoms surmounted by a layer of open
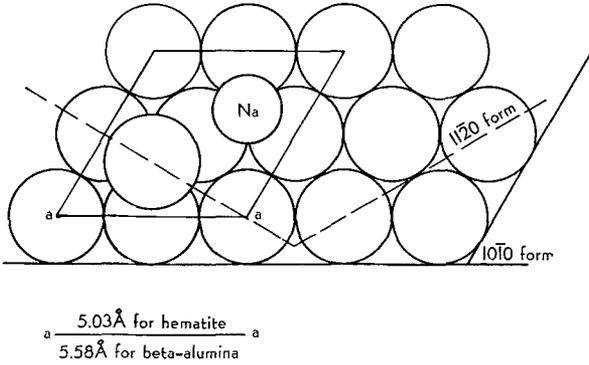
(a)
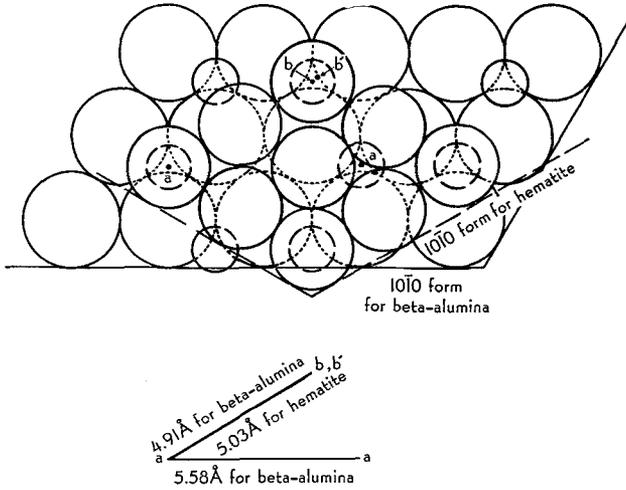
(b)

FIG. 5 (a). Top of beta-alumina unit cell showing position of Na and non-close packed O atom. (b) Hematite 0001 structure rotated 30° and superimposed on 0001 close packing of beta-alumina. Smallest circles represent Fe atoms.

spaced alkali and oxygen atoms. The lower surface of the hematite crystal can also be considered as a close packed layer of oxygen atoms which could grow on the alkali-oxygen layer as if a further beta-alumina layer were to be formed. The a cell dimension of beta-alumina is 5·58 Å, while the corresponding dimension of hematite is 5·03 Å, giving a 9·5 % misfit. This is very close to the 9 % limit for epitaxial growth as calculated by van der Merwe (1949), although he points out that some cases of epitaxy considerably exceed this limit.

If this is the structural scheme of the present overgrowth, the explanation of the 30° difference in orientation of the two phases would seem to be a mere difference in habit of the two types of crystals. In this case, the substrate could be considered to have developed a first order prism ($10\bar{1}0$), while the hematite overgrowth formed a second order prism ($11\bar{2}0$) or rhombohedron (1121). The positions of these faces in relation to the oxygen packing is shown in fig. 5a.

If, however, the crystal habits are the same, there must be a 30° structural misorientation between the two crystals. It is possible that this could happen along a direction in the structure at 30° to the oxygen rows in the substrate. In fig. 5b the cell edge distance a–a for beta-alumina is 5·58 Å, and a–b' for hematite is 5·03 Å. However, the distance a–b for beta-alumina is 4·91 Å, which would represent a misfit with the a–b' dimension of hematite of only 2 %. In this case the two structures may be thought of as being linked by Fe$\cdots$ with the relative orientations shown in fig. 5b. Two-thirds of the Fe$\cdots$ atoms would be in normal tetrahedrally co-ordinated positions, while the remainder would occupy positions of apparent octahedral co-ordination.

Conclusions

This paper describes an example of oriented overgrowth occurring during crystallization from a silicate melt. The epitaxy of the two related structures showed a difference in orientation of 30°, which could be ascribed either to a difference in habit of the two types of crystal, or to a difference in structural orientation. On the material available it was not possible to decide between the two possibilities. The overgrowth phenomenon showed the classical features of regular orientation of crystals which had nucleated along growth steps on the substrate.

References

BEEVERS (C. A.) and ROSS (M. A. S.), 1937. Z. Krist., vol. 97, p. 59.
BOR (L.), 1950. Journ. Amer. Ceram. Soc., vol. 33, p. 375.
BRAGG (W. L.), 1930. The atomic structure of minerals, Cornell Univ. Press, Ithaca, N.Y., p. 93.
—— GOTTFRIED (C.), and WEST (J.), 1931. Z. Krist., vol. 77, p. 255.
PABLO-GALAN (L. DE) and FOSTER (W. R.), 1959. Journ. Amer. Ceram. Soc., vol. 42, p. 491.
RANKIN (G. A.) and MERWIN (H. E.), 1918. Amer. Journ. Sci., vol. 45, p. 301.
RIDGWAY (R. R.), KLEIN (A. A.), and O'LEARY (W. J.), 1936. Trans. Electrochem. Soc., vol. 70, p. 71.
VAN DER MERWE (J. H.), 1949. Crystal Growth. Faraday Society Disc., No. 5, p. 201.