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Etch Pits in Flux-Grown Corundum

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Procedures have been developed for chemically polishing and etching {0001}, {10$\bar{1}$1}, {10$\bar{1}$2}, {11$\bar{2}$0}, and {1$\bar{1}$00} planes in crystals of ruby and sapphire grown from a PbF_2 flux. The shape and the orientation of the etch pits were found to be characteristic for each plane and the density of the pits was 10^2 to $10^4/cm^2$. Similar pits were produced in flame-fusion material, but the density was 10^6 to $10^8/cm^2$. Ruby and sapphire crystals grown by the same process behaved similarly. There is evidence that etch pits reveal dislocations which emerge normally to the basal or to the prismatic planes, since similar patterns of pits were produced after the removal of successive layers of material parallel to these planes, and a correlation was found between the pit patterns on opposite {0001} faces. Inconclusive evidence on this point was obtained for the rhombohedral planes.

1. Introduction

Crystals of corundum (α-alumina) were first produced artificially by Verneuil [1] at the beginning of the century. Since that time, his flame-fusion technique has been used to produce considerable quantities of synthetic sapphire (undoped Al_2O_3) and ruby (Al_2O_3 doped with Cr_2O_3). Most of this material is used as artificial gemstones, watch and instrument bearings, and record-player styli. For such uses, the main properties of corundum that are important are its hardness, chemical inertness, and optical transparency coupled with a relatively high refractive index; chemical impurities and imperfections on an atomic scale are relatively unimportant, unless they lead to gross strain.

Until comparatively recently, there was little demand to produce any material of better quality. The last few years, however, have led to the use of ruby and sapphire in circumstances where the requirements are more stringent; for example, in masers and lasers, as substrates for epitaxially grown, microelectronic devices, and in the form of whiskers for reinforcement of metals. The more sophisticated applications require material of higher quality and have provided the impetus for the development of methods of growing better crystals and to the quest for techniques for determining the degree of purity and perfection.

The etch-pit method is probably the simplest and most convenient method of revealing dislocations in crystals, but it is often difficult to produce the etch pits in a repeatable and reliable manner. Since the object is usually to study the dislocations introduced during growth or subsequent mechanical deformation or heat treatment, it is also important to ensure that any surface damage, introduced for example in mechanical polishing, is removed by chemical polishing or some other means before the etching is carried out.

In 1926, Seebach [2] developed a technique for producing etch pits on the surface of small spheres of natural corundum using a $KHSO_4$ flux. More recently, Scheuplein and Gibbs [3] developed a technique for producing etch pits on the basal {0001} planes and planes near {20$\bar{2}$1}* in flame-fusion ruby and sapphire using boiling orthophosphoric acid (H_3PO_4). The surfaces to be etched were prepared by mechanical polishing and subsequent flame polishing. In 1963, Alford and Stephens [4] used orthophosphoric acid to polish the prismatic {11$\bar{2}$0} planes. They etched both these surfaces with fused potassium hydrogen sulphate

*Throughout this paper morphological indices are used, based on $c/a = 1.365$.

($KHSO_4$). Later these authors [5] used the same techniques in a limited study of the {0001} and {11$\bar{2}$0} faces of lightly doped sapphire crystals grown from PbO-PbF_2 fluxes. Janowski and Conrad [6] also used $KHSO_4$ to carry out a detailed mapping of the dislocation structure on the {0001} and {11$\bar{2}$0} planes in Verneuil ruby; indistinct pits were formed on the rhombohedral {10$\bar{1}$1} planes. Barber and Tighe [7] used an orthophosphoric acid thinning, polishing and etching technique to study the {0001}, {10$\bar{1}$2}, {12$\bar{3}$4}, {11$\bar{2}$0}, and {1$\bar{1}$00} planes, and used a concentrated potassium hydroxide etchant on the basal plane. Heuer and Roberts [8], while mainly concerned with thermal etching, did carry out some chemical etching, producing, for example, etch pits on the basal plane with borax at 1000° C. Most of the authors mentioned worked with flame-fusion material and obtained etch-pit densities in the region of $10^6/cm^2$. Stephens and Alford [5] reported densities in flux-grown crystals of less than 10^2, rising to $10^7/cm^2$ in areas associated with flux inclusions.

The present etch-pit study arose from the desire to monitor the dislocation content of ruby and sapphire crystals during the development of a fluxed-melt method of growth, to compare them with similar crystals grown by other methods, and to provide a tool for estimating the density and distribution of dislocations introduced during mechanical deformation. One advantage of using fluxed-melt crystals is that they grow with well-defined natural faces. For example, spontaneously nucleated crystals generally grow in tabular form parallel to the {0001} planes; the other principal planes are {10$\bar{1}$1} and {10$\bar{1}$2}. This feature enables crystals to be orientated directly without the need to use X-rays.

In the present work, the recipes used by previous workers were examined and additional ones tried. Conditions have been established for chemically polishing and etching the basal {0001} planes, the rhombohedral planes {10$\bar{1}$1} and {10$\bar{1}$2}, and the prismatic planes {11$\bar{2}$0} and {1$\bar{1}$00} for ruby and sapphire crystals grown by the fluxed-melt method. It was subsequently checked that the same conditions also produced pits in Verneuil material, although the density of the pits was much greater than in flux-grown crystals.

Previous authors [3, 5-7] have presented evidence that supports the hypothesis that etch pits produced by several etchants reveal dislocations in Verneuil material. The present work includes investigations of the effect on the etch-pit pattern of repeated chemical polishings and etchings, and the correlation between pits on opposite {0001} faces. These observations indicate that the etches described in this paper reveal dislocations in flux-grown corundum.

2. Preparation of Crystals

The corundum crystals produced in this laboratory were grown out of a solution in fused lead fluoride, by a technique similar to that described by White [9] and White and Brightwell [10]. Several variations of this fluxed-melt technique have been employed, however. In one, a nearly saturated solution of alumina in lead fluoride is held at about 1150° C for a day to equilibrate, and is then cooled slowly at a rate of about 1° C/h to 800° C. The fluxed melt is contained in a sealed platinum crucible and heated in a closely regulated muffle furnace. The crystals grow either by spontaneous nucleation in the form of tablets or onto previously inserted seed crystals. Ruby crystals can be grown by adding a small amount of Cr_2O_3 to the melt.

In a variation of the technique, growth takes place under virtually isothermal conditions, but with a temperature gradient along the crucible. Material is transported from the hotter region containing the nutrient to the cooler part where growth takes place, either onto a seed crystal or by spontaneous nucleation. It has been found that growth occurs not only when the hotter region is at the bottom of the crucible, but also when it is at the top. In the former instance, material is transported mainly by convection, but in the latter by diffusion. For either method, an internal baffle of platinum and an external refractory baffle are desirable to maintain a temperature differential of about 50° C. Although somewhat slower, the second method possesses some advantages over the first. For example, when spontaneously nucleated crystals are formed, they have fewer growth steps, virtually no flux entrapment, fewer twin boundaries, and a greater thickness in the [0001] direction. These improved properties may be associated with the fact that, in the second method, spontaneously nucleated crystals grow completely immersed in the flux instead of floating on the surface.

To extract the crystals at the end of a growth run, molten solvent is poured off and the last traces of lead fluoride are removed by boiling in 50% nitric acid.

All crystals selected for etch-pit study were free from visible flux inclusions. The results of a chemical analysis on typical crystals are shown in table I.

TABLE I Spectrographic analysis of flux-grown corundum crystals (ppm by weight).

	Cr	Fe	Pb	Mg	Si	Cu
Ruby	880	80	20	0.1	0.4	0.1
Sapphire	< 1	125	30	0.1	0.4	0.1

No other impurity elements were detected.

3. Experimental Procedure and Results

All the chemical polishing and etching was carried out in platinum crucibles. Unless otherwise stated, chemicals were "Analar" grade, used once and then discarded. Temperatures were measured with a Pt-13% Rh/Pt thermocouple and maintained to within ±5° C. Specimens were secured on the end of a short length of platinum wire and, to minimise thermal shock, were preheated to approximately the temperature of the crucible.

To cut faces of various orientations, a diamond-impregnated disc was used. The cut face was first ground with a diamond-impregnated wheel and then polished with successively finer grades of carborundum paper, followed by diamond dust.

When crystals were etched directly after mechanical polishing without any intermediate chemical polishing, numerous polishing scratches were revealed which tended to obscure the pattern of pits which would otherwise be obtained. Away from scratch marks, however, the etch-pit density appeared to be similar to that obtained by etching after chemical polishing or etching an as-grown face.

Conditions for polishing and etching varied considerably from face to face. Consequently, separate procedures were developed for the basal plane, the prism planes, and the rhombohedral planes. Interferometry measurements indicated that the depth of the pits produced by these various procedures was generally 1.5 to 2 μm. The chemical polishing schedules remove slightly more than this thickness of material.

3.1. Basal Plane {0001}

Immersion in concentrated (88%) orthophosphoric acid for 150 sec at 425° C was found to produce a satisfactory chemical polish on the basal plane.

Three types of etchant were found to produce pits. The optimum conditions were: (i) immersion in fused potassium hydrogen sulphate at 700° C for 20 to 25 sec; (ii) immersion in concentrated orthophosphoric acid whose temperature was raised gradually to 290° C over a period of about 75 min (this was achieved by lowering the crucible into a constant temperature bath at 300° C); and (iii) preheated crystals immersed for 10 min in a 10N aqueous solution of KOH maintained at 325° C.

(ii) gave slightly more consistent pits than (i) and is preferable if speed is not essential. Both etchants produced triangular-shaped pits with edges parallel to $<11\bar{2}0>$ directions (fig. 1).

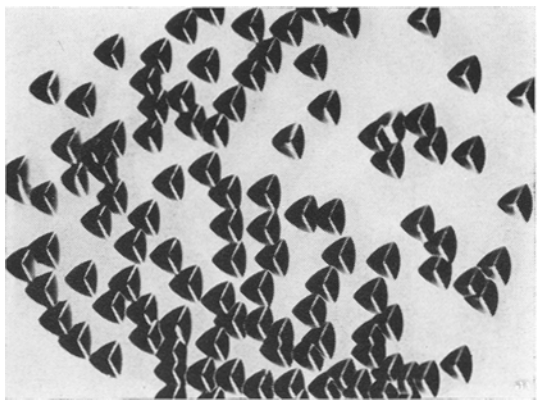

Figure 1 Etch pits produced by orthophosphoric acid on {0001} plane of a flux-melt ruby crystal. $<11\bar{2}0>$ direction vertical (×140).

Generally, (iii) produced sharper and more regular pits than either (i) or (ii) (fig. 2). The etchant was, however, less pleasant to work with, and the apparatus was more difficult to clean afterwards. Occasionally, pits produced by this etch were hexagonal rather than triangular: this tendency was more noticeable at lower temperatures (~250° C). The pits were initially triangular; as their size increased their corners became truncated (fig. 3) with their edges parallel to $<11\bar{2}0>$ directions.

It was noticed that the shape of the pits was very sensitive to orientation. When the etched face was accurately perpendicular to the c axis, the pits were symmetrical with their deepest point in the geometrical centre. If, however, a face was cut a few degrees from the basal plane,

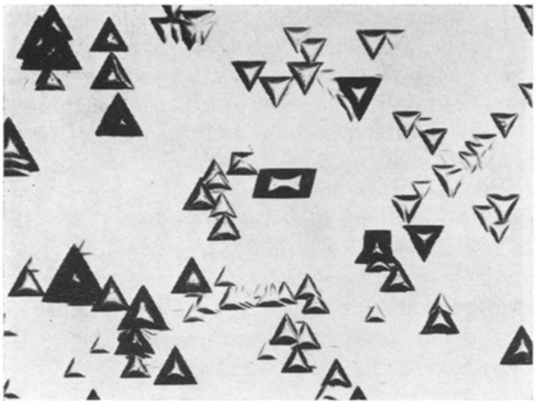

Figure 2 Pits produced on a similar crystal by KOH solution. $\langle 11\bar{2}0\rangle$ direction horizontal. A twin boundary runs from top left to bottom right ($\times$140).

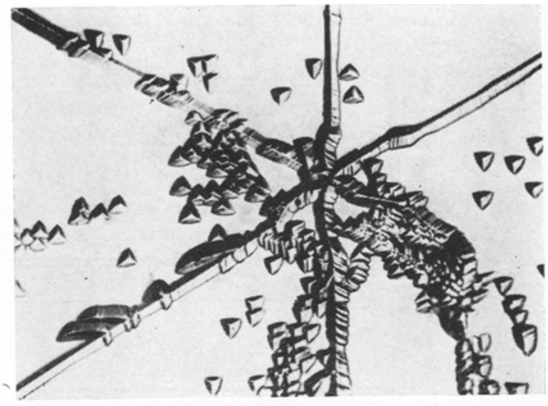

Figure 4 Pits produced by orthophosphoric acid on $\{0001\}$ plane near centre of a flux-melt ruby crystal. Note the meeting of several twin boundaries ($\times$70).

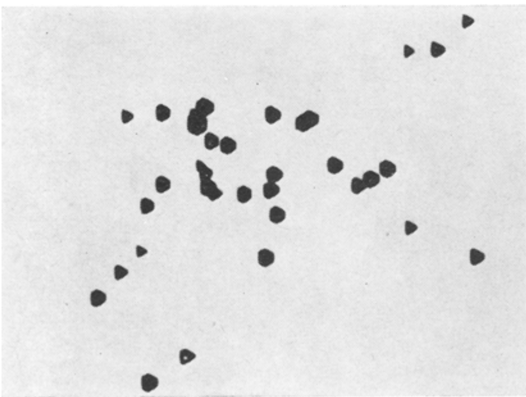

Figure 3 Pits produced by KOH solution on $\{0001\}$ plane of a flux-melt ruby, showing the transition to hexagons. $\langle 11\bar{2}0\rangle$ direction vertical ($\times$140).

the pits produced were assymetrical in shape, but their form was just that predicted by solid geometry from a symmetrical pit on the basal plane.

Fig. 2 shows a 180° rotation of the etch pits across a twin boundary, similar to that reported by Stephens and Alford [5]. Fig. 4 shows pits produced by the phosphoric acid etch in the central region of a fluxed-melt platelet where several twin boundaries meet. Some thin platelet crystals, ~1 mm thick, were etched on both $\{0001\}$ faces and viewed through a microscope. On racking down the microscope, first the pits on the top surface could be seen and then those on the bottom: it was observed that the triangular pits on one face were rotated through 180° with respect to those on the other. A one-to-one correlation was noticed between a number of the pits on the top and bottom surfaces, indicative that pits occur at the ends of line imperfections (i.e. dislocations) passing normally through the specimen. In addition, it was generally found that etch pits on the $\{0001\}$ faces were aligned with the edges formed by the meeting of the basal and $\{10\bar{1}1\}$ growth faces. The shape and alignment of the pits, as indicated in fig. 10, reflect the trigonal symmetry of corundum which belongs to the $\bar{3}m$ point group.

Several crystals were etched and photographed, then polished, re-etched, and photographed again. It was found that the pit pattern was reproduced very accurately. Even after four or five etchings and polishings, corresponding to the removal of about 10 μm of material, the movement of pits relative to fixed features on the periphery of the crystal was less than 3 μm, although occasionally pits would disappear or others appear elsewhere. These experiments add further evidence to indicate that etch pits correspond to dislocations which probably emerge normally at the surface.

3.2. Rhombohedral Planes $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$

Both these planes were polished with a mixture of cryolite ($AlF_3.3NaF$, ordinary grade; "Analar" not available) and sodium tetraborate in the ratio of 2:1 at 1000° C for 60 sec. Larger proportions of cryolite removed more material but left a rough surface, whereas more borax produced a smooth surface but did not remove much material.

The etchant was a mixture of $KHSO_4$ and cryolite in the ratio of $3\frac{1}{2}$:1. Good pits were

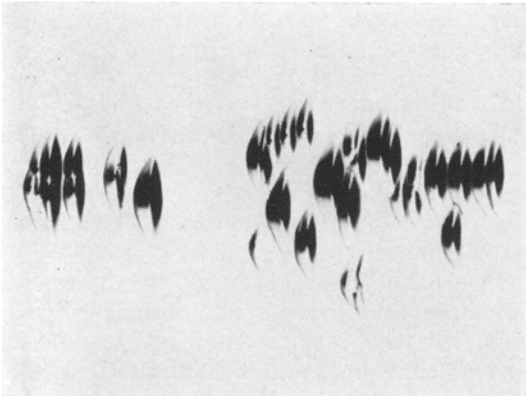

Figure 5 Etch pits on a $\{10\bar{1}2\}$ type face of a flux-melt ruby produced by mixture of $KHSO_4$ and $AlF_3.3NaF$. $<1\bar{2}10>$ direction vertical ($\times 140$).

Figure 7 Less common type of pits formed on $\{10\bar{1}1\}$ face. Similar crystal and etch. $<1\bar{2}10>$ direction horizontal ($\times 210$).

formed after 120 sec at 750° C. Fig. 5 shows pits on a $\{10\bar{1}2\}$ face. The shape of the pits varied with some crystals, especially on the $\{10\bar{1}1\}$ faces; two types of pits are shown in figs. 6 and 7. The orientation of the pits is indicated in fig. 10.

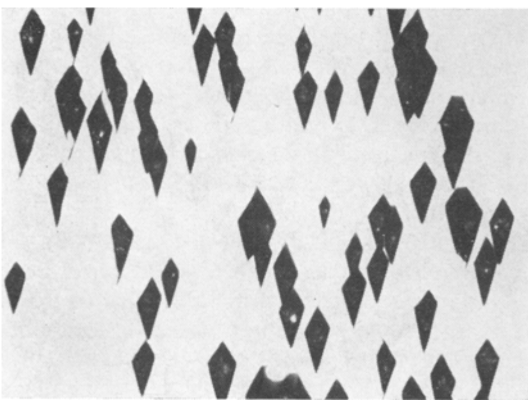

Figure 6 Pits produced on $\{10\bar{1}1\}$ face of a flux-melt crystal. Same etch as for fig. 5. $<1\bar{2}10>$ direction horizontal ($\times 280$).

3.3. Prism Planes $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$

Three different methods were used for polishing the prism planes.

(*a*) In that used most frequently, the crystal was immersed in concentrated orthophosphoric acid at 450° C for 150 sec. This treatment produced a very good polish over the major part of the surface but did not attack some small regions as rapidly, and thus the surface was covered with a number of hillocks. It was noticed that a crystal polished twice for 150 sec using fresh solutions was less likely to develop hillocks than one polished for 300 sec.

(*b*) Immersion in a $3\frac{1}{2}$:1 mixture of $KHSO_4$ and cryolite at 850° C for 120 sec. This treatment produced a good polish but often removed insufficient material, leaving previously produced etch pits and scratch marks still visible.

(*c*) Immersion in cryolite at 1000° C for 30 to 45 sec removed more material but left the surface with a matt appearance. A good polish could then be obtained by subsequently applying (*b*).

The prism planes were etched with fused $KHSO_4$ at 750° C for 120 sec. The shape of the pits formed often varied from region to region on the same face of a crystal. Figs. 8a and 8b show pits formed on a $\{1\bar{1}00\}$ plane, and fig. 9 shows pits formed on a $\{1\bar{1}20\}$ plane.

These planes were also etched and photographed at successive depths, and again there was little movement of the pit pattern through the crystal, indicating that the dislocations emerged normal to the surface. Sometimes, however, pits would change from one shape to another, slightly different shape, as layers were removed (figs. 8a and 8b).

Often etching revealed needle-shaped depressions on these surfaces, usually with one pointed end and sharp bottoms. They were always parallel to the basal plane and about 0.5 to 1.0 mm long.

Under certain conditions, etch hillocks were formed on the prism planes. For example, crystals heated for 60 sec in an equal mixture of concentrated nitric acid and concentrated orthophosphoric acid at 400° C developed very well-defined hillocks. In shape they were usually rounded polygons with alternate long and short sides, but with no obvious orientation.

4. Conclusions

The experimental results indicate that there is a marked difference in the ease with which the various planes are attacked chemically. The basal planes are the most readily attacked and the rhombohedral planes the least.

There did not appear to be any difference in the conditions for etching and polishing ruby as compared with sapphire, nor between fluxed-melt as compared with flame-fusion material. The shapes of the pits produced on fluxed-melt and Verneuil material were similar, but their densities varied considerably: for the fluxed-melt crystals the figure was 10^2 to $10^4/cm^2$ and for flame-fusion crystals 10^6 to $10^8/cm^2$. These figures agree with those of other workers (e.g. Stephens and Alford [5], White and Brightwell [10]). Comparing ruby with sapphire crystals grown under similar conditions, there was no apparent difference either in the shape of the pits or in their densities.

With flux-grown corundum crystals, it was observed that the density of the pits was extremely uniform from one crystal to another from the same growth batch, but that it varied appreciably (within the range 10^2 to $10^4/cm^2$) from one batch to another. There was, however, a marked decrease in the density of the pits as the fluxed-melt growth technique was improved. More uniform temperature conditions, larger melts, etc., as might be expected, resulted in the production of crystals with fewer imperfections.

On any one, particular face of flux-grown crystals, the pits generally occurred in a number of clusters: fig. 1 shows one such cluster on a {0001} face. On $\{10\bar{1}2\}$ faces, however, only a few clusters of pits (fig. 5 shows an example) were observed, and comparatively large areas were completely free of pits.

The triangular pits formed on the {0001} planes, with edges parallel to $\langle 11\bar{2}0\rangle$ directions, are similar to those reported by other workers. With potassium hydroxide, truncated triangular pits were formed, i.e. hexagons with alternate long and short sides parallel to $\langle 11\bar{2}0\rangle$ directions. These compare with the, admittedly, much smaller, but regular, hexagonal pits with edges parallel to $\langle 10\bar{1}0\rangle$ found by Barber and Tighe [7].

The orientations of the pits produced on {0001}, $\{10\bar{1}1\}$, and $\{10\bar{1}2\}$ faces are also

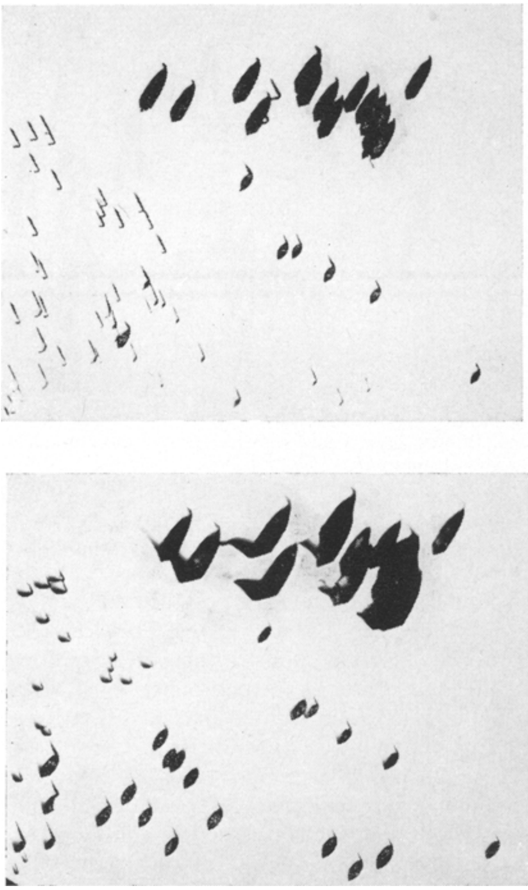

Figure 8 (a) shows pits on {1100} plane and (b) shows same area after chemical polishing and re-etching. [0001] direction lies along length of pits from bottom left to top right (×175).

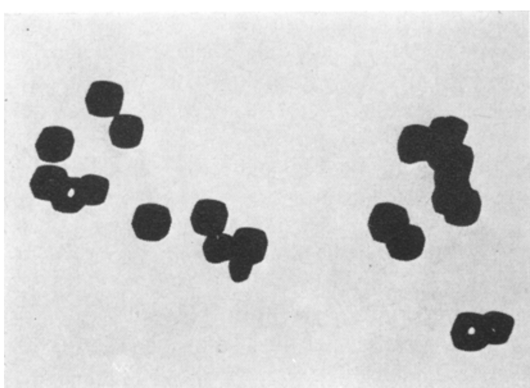

Figure 9 Etch pits on {1 12 0} plane of a flux-melt ruby. [0001] direction horizontal (×140).

shown in fig. 10.

The experiments in which successive layers were removed parallel to the basal and prismatic planes indicate that dislocations probably emerge normally at these surfaces. The observed correspondence between pits on opposite {0001} faces supports this view. These points also strongly support the belief that etch pits are formed at the ends of dislocations and not only at point impurities or imperfections. Inconclusive evidence on these points was obtained for the rhombohedral planes.

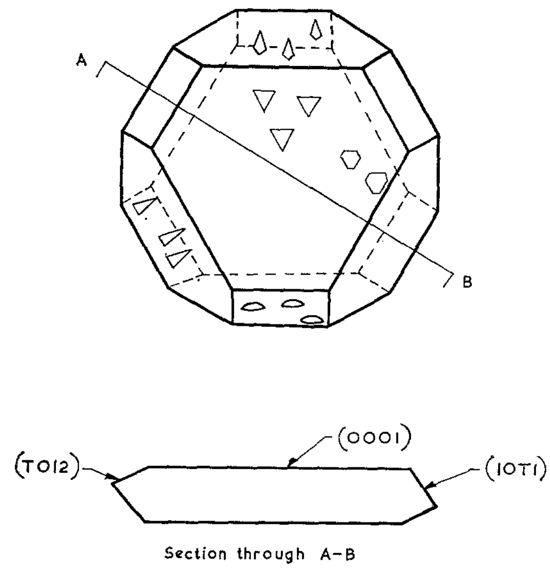

Figure 10 Diagram showing growth habit of fluxed-melt corundum (after White and Brightwell [10]) with orientation of etch pits produced on {0001}, {101̄1}, and {101̄2} faces indicated.

The shape of the pits formed on {101̄1} faces could be related to oblique sections of triangular or rhomboid pyramids or prisms, which forms are derivable from the crystal structure of corundum. The same is true for the pits on {101̄2} planes, if they are regarded as rounded, obtuse-angled, isosceles triangles.

Acknowledgement

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