Fractrue mechanism in sapphire whiskers

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Summary
Previous work on the strength properties of sapphire whiskers both at 20° C and at elevated temperatures (up to 2030° C) is reviewed. In particular size-strength effects at 20° C and the strength temperature variation in the range 20 – 1000° C are examined and from these results deductions are made regarding fracture mechanisms in whiskers of different crystallographic orientations. These deductions are examined in the light of optical and electron microscope evidence of fracture mechanisms obtained by the authors. Two non-basal slip systems are reported. The relevance of these results to the use of sapphire whiskers as reinforcing agents in a composite material and to the deformation behaviour of bulk single crystals and polycrystalline alumina is discussed.

Introduction

The unusually high strengths exhibited by whiskers were first noted by Herring and Galt [1] in 1952. Since then, and particularly during the last decade, whiskers have been the subject of many investigations. The reasons behind this interest are partly academic but mainly connected with the demand for materials of higher specific strength. The academic interest in whiskers lies in the fact that they are almost perfect single crystals so that, for instance, macroscopic observation of some dislocation phenomena such as the 'Eshelby twist' [2, 3] is possible. In addition the high tensile strains attainable enable otherwise negligible effects such as departures from Hooke's Law to be detected directly [4, 5]. With regard to the demand for materials of high specific strength, whiskers have strengths approaching the theoretical value for ideal materials and are thus of some interest in themselves but the main potential application for them is as reinforcing elements in a suitable matrix.

Sapphire whiskers have the greatest potential for high temperature (~1000 °C) applications owing to their chemical stability compared with other ceramic whiskers such as silicon nitride and silicon carbide [6] when embedded in a metal matrix.

Size-strength and surface perfection effects in sapphire whiskers

Size-strength effects in whiskers were first reported by Gyulai [7] for sodium chloride, where the fracture strength, σ_f, of 2-15μ diameter whiskers varied inversely with diameter. Similarly Regester *et al.* [8] found that for sapphire whiskers σ_f varied inversely as the square root of the cross-sectional area, A_c, of the whiskers. This relationship held for whiskers of all cross-sectional shapes and crystallographic orientations

provided they were free from large overgrowths and other gross imperfections.

Brenner [9] tested ⟨0001⟩ sapphire whiskers and obtained a linear relationship between σ_f and diameter. The size effect was present at 25 °C and at 1060-1100 °C but absent at 1550 °C and above.

Soltis [10] found that both ⟨0001⟩ and ⟨11$\bar{2}$0⟩ sapphire whiskers had strengths proportional to $A_c^{-0.33}$. He also mentions that part of a long fractured whisker had a higher fracture stress than the original whole whisker, indicating a possible gauge length effect.

Kelsey and Krock [11] found a rather similar result for sapphire whiskers of all orientations, the strength being proportional to $A_c^{-0.265}$ while Mehan, Feingold and Gatti [12] obtained strengths proportional to $A^{-0.17}$, again for sapphire whiskers of all orientations.

The present authors carried out over seventy tensile tests on sapphire whiskers and fitted the experimental data to empirical equations of the form

$$\sigma_f = K d^m l^n$$

where $d = \sqrt{(A_c)}$, l is whisker gauge length and K, m and n are constants. The details of this work are reported elsewhere [13] and only the results and conclusions will be presented here. It was found that the strength of C-type (⟨0001⟩) whiskers depended only on diameter while that of A-type (⟨$hk.o$⟩) whiskers depended on surface area, A_s. The actual dependencies were

$$\text{C-type: } \sigma_f = 1460\ d^{-0.64}$$

$$\text{A-type: } \sigma_f = 720\ d^{-0.56}\ l^{-0.39}$$

σ_f being in Kgm/mm^2, d in microns and l in mm. From these results it was concluded that fracture in C-type whiskers might be due to dislocation activity (e.g. a pile up or interaction mechanism) while in A-type whiskers it might be due to a Griffith process.

Experimental work on chemical polishing of whiskers [14] showed that the strength of A-type whiskers was dependent on their surface condition while that of C-type whiskers which were small enough to exceed a certain strength (~800 Kgm/mm^2) was not affected by chemical polishing. The strength of large C-type whiskers was increased by chemical polishing. In addition extrapolation of the size-strength equations for polished A- and C-type whiskers predicted a tensile strength of $\sim \frac{E}{10}$ at unit cell dimensions and strengths which agreed with those of flame polished macroscopic sapphire crystals ($d \sim 1$ mm) [15]. The data is summarised in Fig. 1.

The following model is based on these results. It is suggested that unpolished A-type whiskers with strengths of less than ~1000 Kgm/mm² at 20 °C fail by a Griffith mechanism while unpolished C-type whiskers with strengths of less than ~800 Kgm/mm² at 20 °C also fail by such a mechanism. All chemically polished whiskers and also those unpolished ones which are small enough to have strengths above the quoted limits fail by a dislocation activity such as a pile up or interaction mechanism.

The variation of whisker strength with temperature

Recent work on the effect of temperature (in the range 20-1810 °C) on the tensile strength of sapphire whiskers [16] confirms the above model to some extent. The basis of this confirmation rests on the fact that it is possible, for sapphire, to calculate the variation of Griffith fracture stress with temperature. The Griffith equation states that a material having a flaw of length c, Young's modulus of elasticity E, and surface energy (for the surfaces of the flaw) γ will fracture by propagation of this flaw under a stress σ if $\sigma > \sqrt{(2E/\pi c)\gamma}$*. Thus the temperature dependence of σ is determined by those of E and γ as $\sigma_T = \text{const}\sqrt{(E_T \gamma_T)}$.

The variation of E with temperature for sapphire has been accurately determined by Wachtman *et al.* [18] while that of γ has been calculated from sublimation energies by Bruce [19] although direct experimental data is limited. The variation of $\sqrt{(E_T \gamma_T)}$ with temperature is very nearly linear between 20 and 1000 °C such that for C-type whiskers

$$\frac{\sigma_{1000}}{\sigma_{20}} = 0{\cdot}857$$

while for A-type whiskers

$$\frac{\sigma_{1000}}{\sigma_{20}} = 0{\cdot}842$$

Fig. 2 shows the experimental data, the calculated Griffith curves for different flaw lengths and the limits of Brenner's data [9] for C-type chemically polished sapphire whiskers. The strength-temperature variation of unpolished A-type sapphire whiskers coincides with a Griffith mechanism slope with a flaw length of about 100 Å. The strength-temperature variations of chemically polished A-type whiskers and of chemically polished C-type whiskers grown by a chloride oxidation process are much greater than those predicted by the Griffith equation and it is suggested that whiskers in these categories fail by a mechanism involving dislocation activity.

* This is a simplified form – for a fuller discussion see Kelly [17]. More precise forms differ only in the value of the numerical factor.

It is of interest to consider the variation of Griffith stress with temperature for sapphire in more detail. This has been calculated by Brenner [9] for sapphire whiskers but experimental data on the variation of γ with temperature was very limited at that time. Brenner therefore assumed that γ varied linearly with absolute temperature such that $\gamma = 1200 - 0{\cdot}19T$. The first constant was chosen to give the correct order of magnitude while the second was chosen so that γ varied to the same extent as Young's modulus, E. Earlier data of Wachtman and Maxwell [20] on the variation of E with temperature was available at the time.

Since Brenner's calculation further experimental data has become available on the variation of E and γ with temperature. Wachtman *et al.* [18] suggest an expression of the form

$$E_T = E_0 - bT\, e^{-(T_0/T)}$$

where E_0, b and T_0 are constants whose values depend on crystallographic orientation.

A number of authors have measured surface energies of sapphire but one must distinguish between intrinsic surface energy as measured for instance in a liquid drop weight experiment [21] and effective surface energy during fracture as measured for example during controlled fracture experiments [22]. The latter quantity is the sum of the intrinsic surface energy and another whose magnitude will depend on a number of variables such as fracture stress, strain rate, dislocation density prior to testing, purity, grain size etc. Fig. 3 shows data on the variation of intrinsic surface energy of alumina with temperature. The authors believe that during the fracture of sapphire whiskers by a Griffith mechanism the intrinsic surface energy is the relevant quantity.

The reason for believing this is that no class of whisker shows a strength-temperature variation smaller than that predicted by the Griffith mechanism using intrinsic surface energy as the energy term. On the other hand the structure-sensitive term in apparent surface energy should increase with increasing temperature as dislocation motion becomes possible at the prevailing stresses. Therefore, assuming that other factors involved in the structure sensitive term do not decrease with increasing temperature, one would expect the apparent surface energy to show a smaller temperature dependence than does the intrinsic surface energy. Thus the Griffith stress would also show a smaller temperature dependence. This has been demonstrated by Congleton *et al.* [23] for Lucalox polycrystalline alumina. They found a rapid increase in apparent surface energy above 300 °C which they attribute to plastic work due to dislocation movement during fracture propagation. It is thought that in the present work the low dislocation density in whiskers may suppress plastic work

during fracture propagation. Alternatively the large stresses needed to initiate fracture may lead to such rapid propagation of the fracture that there is insufficient time available during fracture propagation for plastic deformation to occur. The small dimensions of whisker specimens will also reduce the total duration of the fracture propagation process.

Microscopic evidence of fracture mechanisms in sapphire whiskers

Previous work

Brenner [4] reported that *C*-type sapphire whiskers exhibited jagged fracture surfaces below 1100 °C and smooth fracture surfaces perpendicular to the whisker axis at temperatures of around 2000 °C. At 1550 °C the fracture surface was jagged for short term tests but smooth for long duration tests.

Soltis [10] has reported optical observations of a number of deformation features associated with the fracture zone of sapphire whiskers both at 20 °C and at 900 °C. At 20 °C he observed basal slip in *C*-type whiskers and also intersecting basal and prismatic slip. A few examples of basal and prismatic slip were noted in *A*-type whiskers but fracture was usually unaccompanied by any evidence of gross plasticity. At 900 °C *C*-type whiskers exhibited considerable basal slip and some necking which was attributed to prismatic slip. *A*-type whiskers did not exhibit necking but prismatic slip was observed on planes normal to the tensile axis.

The present authors have observed a number of deformation mechanisms in fractured sapphire whiskers, both optically and by transmission electron microscopy. No detectable elongation has been encountered during tensile tests at 20 °C using a Marsh tensile testing machine [24] but some has occasionally been detected at elevated temperatures (> 1000 °C).

Optically observed deformation mechansims

The following deformation mechanisms * have been observed:

(i) Intersecting $(10\bar{1}2)$ $\langle 10\bar{1}1\rangle$ slip bands in $\langle 0001\rangle$ whiskers fractured in tension at 1200 °C under a tensile stress of ~90 Kgm/mm² [25]. This is the first report of non basal slip in sapphire but is supported by electron microscope evidence of the existence of dislocations of vector $\langle 10\bar{1}1\rangle$ which has been reported by several authors [26-28].

(ii) Intersecting twins on $(10\bar{1}2)$ in $\langle 10\bar{1}0\rangle$ whiskers fractured in tension at 1200 °C under a tensile stress of ~120 Kgm/mm². See Fig. 5. Rhombohedral twinning of sapphire has been investigated by Heuer [29] and by Conrad [30] in both single crystal and polycrystalline material.

* In this paper the morphological unit cell with $c/a = 1{\cdot}365$ will be used. Some authors use the structural unit cell with $c/a = 2{\cdot}73$. See Kronberg [31] for a discussion of the two conventions.

(iii) An isolated $(10\bar{1}2)$ twin in a $\langle 0001 \rangle$ whisker tensile tested at 1200 °C and a tensile stress of 47 Kgm/mm². See Fig. 6.

(iv) Intersecting slip bands which appear to be $(20\bar{2}1)$ in a $\langle 10\bar{1}0 \rangle$ whisker which fractured after 2·0 hours at 1150 °C under a tensile stress of 70 Kgm/mm². This slip plane has not previously been reported and has only been observed twice by the authors. Nevertheless a two surface stereographic analysis shows that it is within 1 ° of $(20\bar{2}1)$ in the two cases where it has been observed. See Fig. 7.

Transmission electron microscopy of fractured whiskers

It was found that usually only specimens which had been tested after thinning showed any significant substructure. Strong preferential attack during thinning probably destroys evidence of dislocation activity in the case of whiskers tested before thinning (see below). The following deformation mechanisms have been observed:—

(i) Intersecting basal and prismatic slip bands leading to nucleation of a crack in a $\langle 20\bar{2}1 \rangle$ whisker which fractured at 1380 °C under a tensile stress of ~160 Kgm/mm². Fig. 8 shows one half of the fractured whisker. It seems likely that fracture occurred at a slip band intersection in the same way that a small crack can be seen at the intersection of the two slip bands in the micrograph. The other half of the fractured whisker was lost as a result of double fracture i.e. the shock of unloading due to the first fracture led to a second fracture near one grip.

(ii) Transmission electron microscopy of $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ whiskers which had been fractured at 20 °C and 1060 °C after thinning showed absolutely no evidence of dislocation activity.

(iii) A whisker of $\langle 10\bar{1}0 \rangle$ axis tensile tested at 1740 °C and fracturing at a stress of 77 Kgm/mm² showed a clear row of etch pits on subsequent thinning. Transmission electron microscopy revealed that each pit was centred on one or more dislocations. See Fig. 9. It was not possible to determine the Burger's vectors of these dislocations but they would seem to have moved on a $(10\bar{1}\,1)$ type of plane. It is interesting to note the increase in etch pit and presumably dislocation density towards the centre part of the specimen. This may be due to the escape of dislocations at the specimen edges.

Summary of deformation observations

$\langle 0001 \rangle$ whiskers have been observed to deform by a non basal slip system $(10\bar{1}2)$ $\langle 10\bar{1}1 \rangle$ at 1380 °C and by rhombohedral twinning at 1200 °C.

$\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ whiskers fractured at 20 °C and at 1060 °C show no sign of dislocation activity associated with the fracture. At 1200 °C fracture has been observed due to the intersection of rhombohedral

$(\{10\bar{1}2\})$ twins while at 1150 °C intersecting slip bands have been observed to cause fracture under long term loading (2 hours). At 1740 °C a $10\bar{1}0\rangle$ whisker exhibited slip on a $(10\bar{1}\,1)$ type of plane.

The above information indicates that for $\langle 10\bar{1}0 \rangle$ whiskers fracture below about 1100 °C is purely brittle while above this temperature it is associated with a variety of plastic deformation mechanisms. This is consistent with the hypothesis based on the effects of size, surface perfection and temperature on strength of these whiskers. In the case of $\langle 000\bar{1} \rangle$ whiskers the available information is very sparse due to the difficulty of preparing electron microscope specimens from these hexagonal cross section whiskers. Existing information is consistent with the previously proposed model based on size-surface perfection-temperature effects on strength but the hypothesis of fracture at 20 °C being due to dislocation activity cannot be tested at present.

Implications of whisker research

The results of sapphire whisker investigations may not be directly applicable to other forms of sapphire e.g. large Verneuil grown single crystals and polycrystalline material. The two outstanding differences between whisker testing conditions and those for other forms of the same material are

(i) The level of stress applied to the specimen and

(ii) the substructure encountered by the propagating crack.

In the case of sapphire whiskers the stress may be in the range 500-1000 Kgm/mm² at 20 °C and 100-250 Kgm/mm² at 1200 °C which is a factor of five to ten higher than values usually attained on large single crystals and a factor of nearer twenty times higher than for polycrystalline alumina. It is, therefore, likely that many stress induced phenomena such as dislocation nucleation, unpinning, intersection, piling up or even simple movement by overcoming the Peierls-Nabarro stress may not occur in the case of low strength forms of alumina or may at least be confined to the region of high stress near a crack tip rather than occurring spontaneously throughout the specimen due to a high overall applied stress. The high general stress level in the case of whiskers may also account for the observation of novel slip systems not found in bulk material.

A second difference between whisker and other material is in the substructure. Whiskers have a simple substructure being almost dislocation free although not of particularly high purity (silicon is a major impurity in sapphire whiskers being present in a concentration of up to $6^{w}/0$ depending upon the growth process) [16]. On the other hand large sapphire crystals contain sub boundaries and dislocation densities of $\sim 10^{6}$ cm^{-2} [30] while polycrystalline alumina represents the opposite extreme of

substructure. It is likely that a simple substructure will discourage complex dislocation interactions and hence lead to a low fracture energy, the fracture process being due to a relatively simple mechanism e.g. a pure Griffith or a dislocation pile up process. On the other hand a complex microstructure will introduce the possibility of complicated interactions between dislocations and between dislocations and grain boundaries.

It is, therefore, to be expected that whiskers will fail by simple mechanisms, possibly involving slip systems not found in bulk material, having fracture energies close to the intrinsic value for sapphire. On the other hand bulk alumina will tend to fail by mechanisms involving dislocation activity of considerable complexity but based only on the more commonly found slip systems provided that it is sufficiently strong so that suitable stresses are generated. In the case of weakly sintered polycrystalline alumina there may be negligible dislocation activity during fracture at 20 °C although the fracture energy may be higher than the intrinsic value due to the occurrence of multiple, non planar fracture paths. The fracture energy for bulk alumina, either single crystal or polycrystalline should therefore be higher than the intrinsic value appropriate to sapphire whiskers.

With regard to the use of sapphire whiskers as reinforcing elements in a composite material the present work confirms to some extent the results of Brenner [4] on the variation of tensile strength with temperature at least in the range 20-1000 °C. At higher temperatures the authors' results tend to be rather lower than those of Brenner – See Fig. 2 – but at least the range of tensile strengths of sapphire whiskers is reasonably defined. In addition the stress rupture properties of sapphire whiskers have been determined to some extent [4, 32]. Investigations of the fracture properties of sapphire whiskers show that the elastic elongations which can be attained are large, averaging 1% strain at 20 °C but plastic strain is negligibly small, being very difficult to detect at any temperature. In considering the fracture mechanics of a composite containing sapphire whiskers therefore one is dealing with an almost ideally brittle fibrous phase at any temperature between 20 and 1800 °C.

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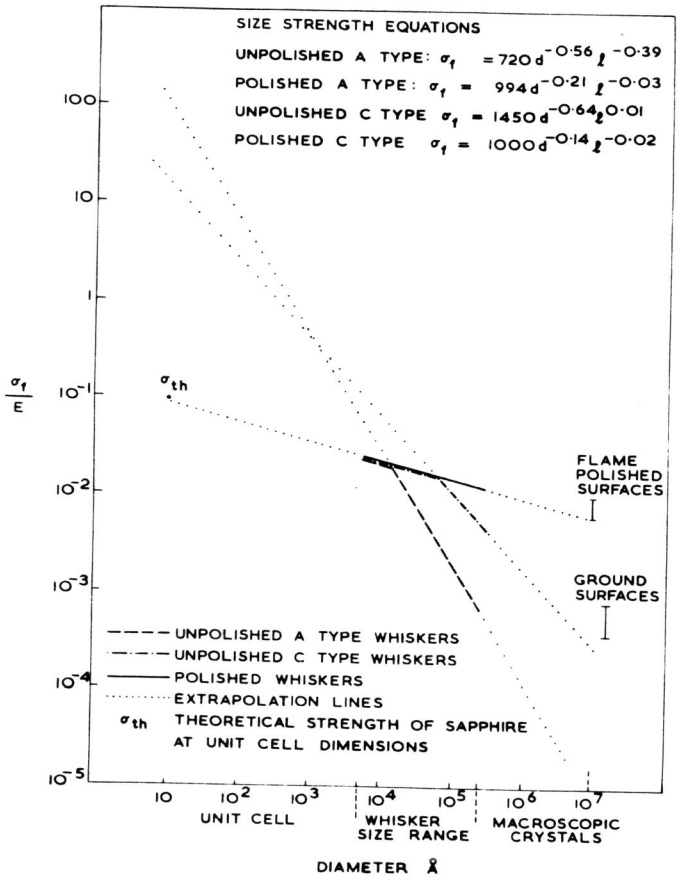


Fig. 1. A diagram indicating the relationships between the strengths of polished and unpolished whiskers, the theoretical crystal strength, and the measured strength of large sapphire crystals. (—— unpolished, *A*-type whiskers; – – unpolished, *C*-type whiskers; —— polished whiskers; ..... extrapolation lines; σ_{th} ,theoretical strength of sapphire at unit-cell dimensions.) The size-strength equations are:

Unpolished *A*-type σ_f	$720\, d^{-0.56}\, l^{-0.39 f}$
Polished, *A*-type σ_f	$994\, d^{-0.21}\, l^{-0.03}$
Unpolished, *C*-type σ_f	$1450\, d^{-0.64}\, l^{-0.01}$
Polished, *C*-type σ_f	$1000\, d^{-0.14}\, l^{-0.02}$

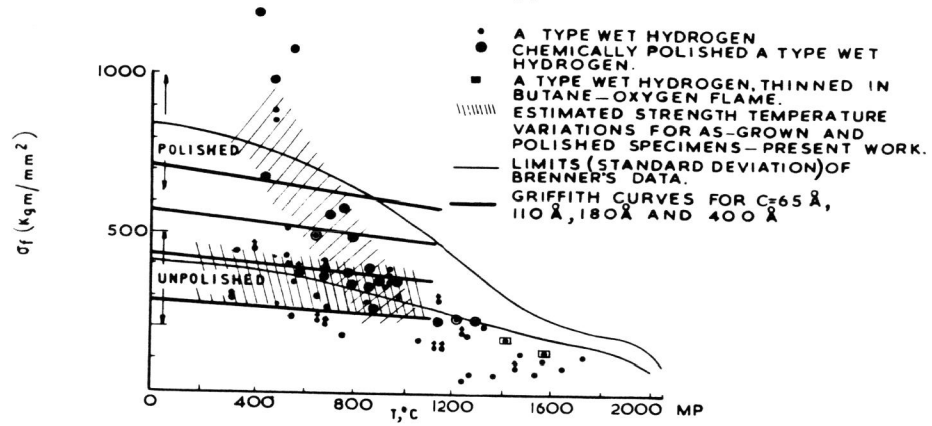


FIGURE 2a

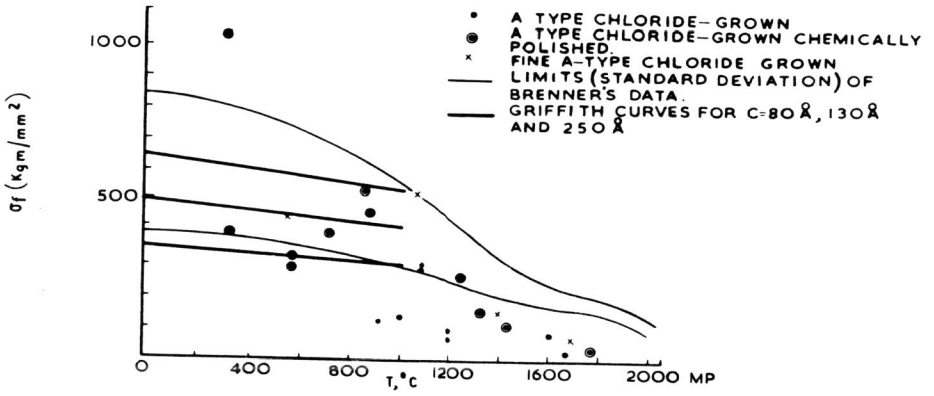


FIGURE 2b

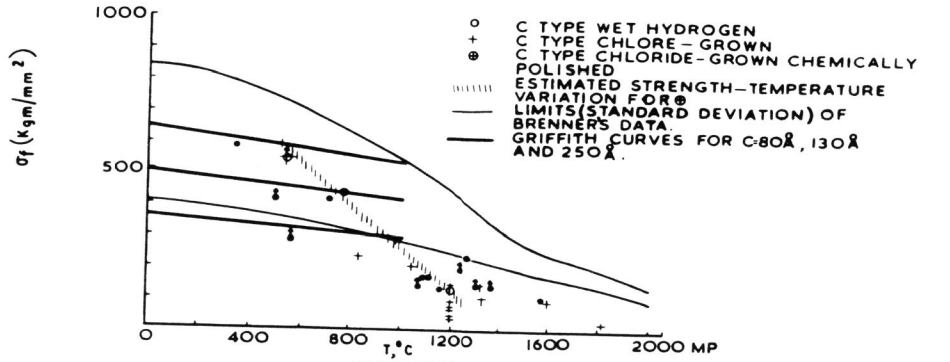


FIGURE 2c

Fig. 2. The effect of temperature on tensile strength of sapphire whiskers.

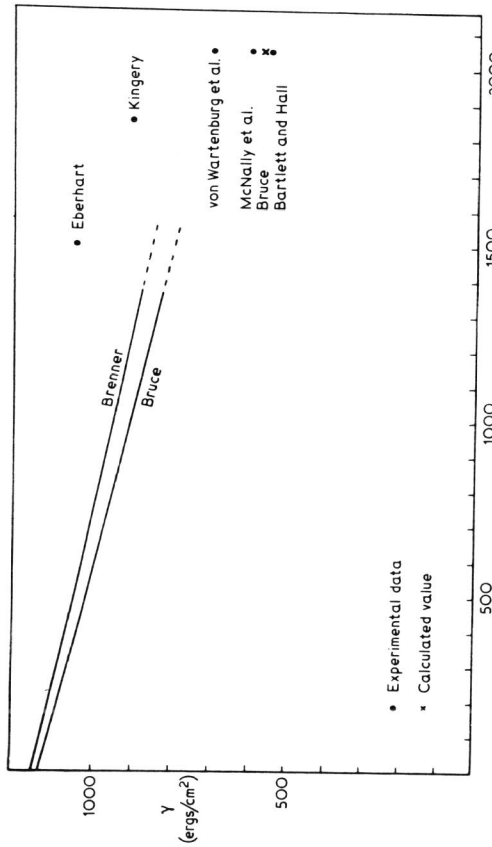


Fig. 3. The effect of temperature on the intrinsic surface energy of alumina.
• Experimental data
× Calculated value

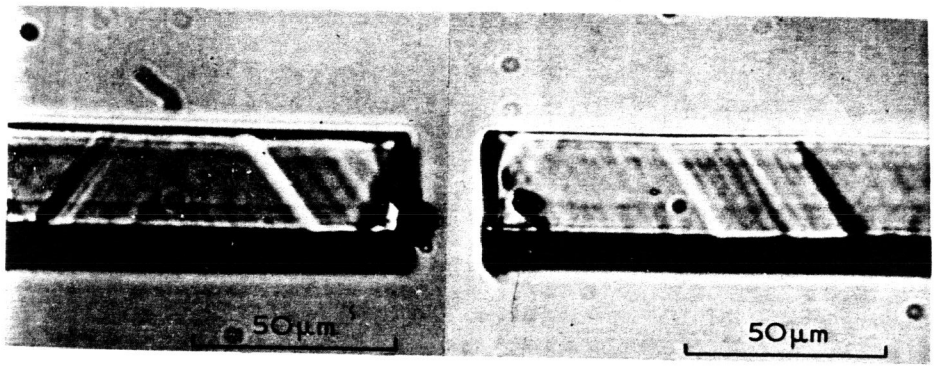


Fig. 4. Optical micrograph of $\{\bar{1}012\}$ $\langle 10\bar{1}1\rangle$ slip bands in an $\langle 0001\rangle$ whisker fractured at 1200° C under a tensile stress of ~90 Kgm/mm².

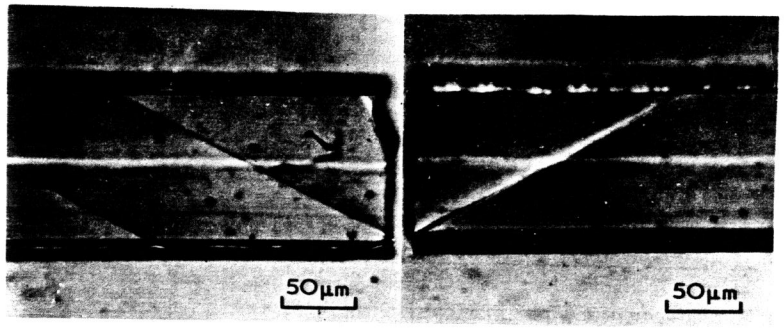


Fig. 5. Optical micrograph of intersecting $\{10\bar{1}2\}$ twins in a $\langle 10\bar{1}0\rangle$ whisker fractured at 1200° C under a tensile stress of ~120 Kgm/mm².

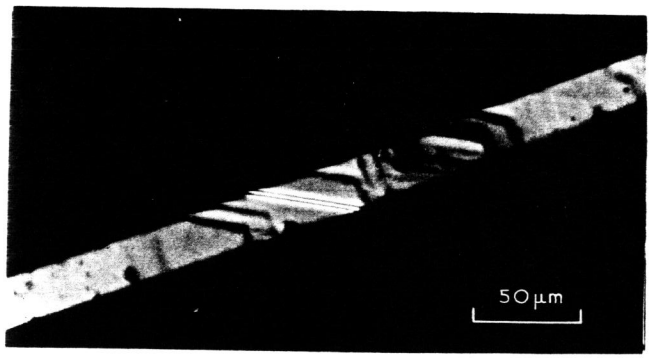


Fig. 6. Optical micrograph of a $\langle 0001\rangle$ whisker containing a $(10\bar{1}2)$ twin formed at 1200° C under a tensile stress of ~90 Kgm/mm².

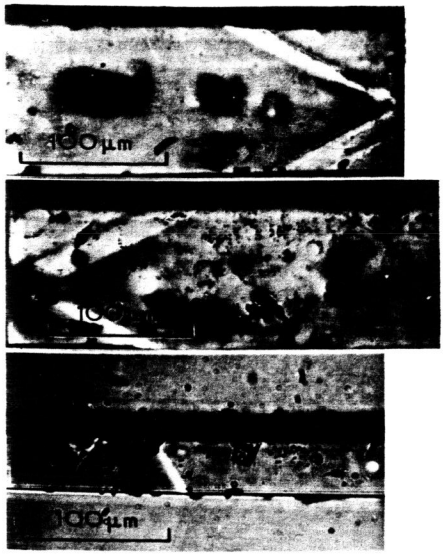
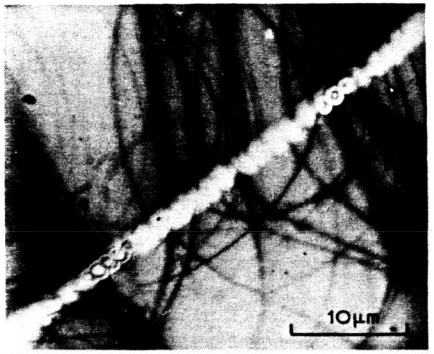


Fig. 7. Optical micrographs of intersecting $(20\bar{2}1)$ slip bands in a $\langle 10\bar{1}0\rangle$ whisker fractured after prolonged loading at 1150° C and a tensile stress of 70 Kgm/mm².



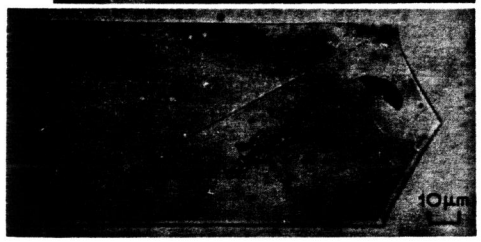


Fig. 9. Micrographs of a series of etch pits produced in a $\langle 10\bar{1}0\rangle$ whisker fractured at 1740° C under a tensile stress of 77 Kgm/mm².

Fig. 8. Electron micrograph of intersecting basal and prismatic slip bands in a $\langle 20\bar{2}1\rangle$ whisker formed at 1380° C under a tensile stress of 160 Kgm/mm².