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The Effects of Chemical Polishing on the Strength of Sapphire Whiskers

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Tensile tests at 20° C have been carried out on forty-four sapphire whiskers after chemical polishing in hot orthophosphoric acid. The orientations tested were $<0001>$, $<11\bar{2}0>$, $<10\bar{1}0>$, and $<10\bar{1}1>$. The results show that chemical polishing increases the strength of large whiskers by a factor of up to 10, but not the strength of small ones. Good correlation is obtained between fracture strength, σ_f, and whisker diameter, d. The relevant size-strength equations, $\sigma_f = Kd^m l^n$ (where l is gauge length, and K, m, and n are constants depending on whisker orientation), predict strengths in good agreement with the theoretical strength of sapphire at unit-cell dimensions and with the measured strengths of macroscopic flame-polished crystals.

The observations are contrasted with those for unpolished sapphire whiskers [1]. They show a transition in the fracture nucleation mechanism of unpolished whiskers at a certain stress.

In unpolished, A-type ($<11\bar{2}0>$ and $<10\bar{1}0>$) whiskers, with $\sigma_f < 1000$ kg/mm^2, fracture initiates at surface flaws, and strength is dependent on surface area. But, for whiskers with $\sigma_f > 1000$ kg/mm$_2$, and for all polished whiskers (both A and C type), fracture is due to dislocation pile-ups or interactions, and strength is dependent only upon diameter. In unpolished, C-type ($<0001>$) whiskers, however, with $\sigma_f < 800$ kg/mm$_2$, fracture initiates at surface flaws which are related to whisker diameter; while, for $\sigma_f >$ 800 kg/mm^2, it occurs at dislocation pile-ups or interactions and is again related to diameter. In contrast, therefore, to A-type whiskers, the strength of C-type whiskers is always diameter-dependent, although there is a clear transition in the size-strength curve at $\sigma_f' \sim 800$ kg/mm^2.

1. Introduction

In a previous paper [1], the room-temperature tensile strength of sapphire whiskers was discussed and the different behaviour of $<0001>$, $<10\bar{1}0>$, $<11\bar{2}0>$, and $<10\bar{1}1>$ whiskers was examined. In particular, the size-strength effect was investigated closely and it was shown that, whereas $<0001>$ whiskers have strengths which depend only on diameter, the other orientations have strengths which depend on their surface area. In the present work, the effect of surface perfection on tensile strength has been examined for the various orientations by comparing chemically polished whiskers with unpolished whiskers.

2. Survey of Relevant Work

The effect of surface perfection on mechanical properties was first demonstrated by Griffith [2] for glass fibres. Many investigations have since been reported on such fibres. The first demonstration on a large piece of material was due to Dash [3], who showed that chemically polished silicon can withstand an elastic strain of over 2%. Quantitative photoelastic work by Marsh [4] on the effect of growth steps as stress concentrators has shown that they can be almost as effective as cracks in this respect. The size-strength effect in whiskers has been explained on the basis that large whiskers will tend to contain larger steps owing to the coalescence of small steps during growth. Mallinder and Proctor [5] have shown that large, flame-polished, sapphire crystals can exhibit strengths comparable with those of whiskers, while King [6] has shown that ground, polycrystalline alumina is strengthened by about 30% by chemical polishing. Brenner [7] describes experiments where iron whiskers were etched while under a tensile stress; their strength was not reduced by the etching process. However, the authors were not aware of any successful attempt to improve the strength of ceramic whiskers by chemical polishing and accordingly undertook the present programme.

3. Experimental Work

Sapphire whiskers from three sources, as used in earlier work [1] (viz: (i) Thermokinetic Fibres Inc, New Jersey, USA; (ii) General Electric Co, Pennsylvania, USA; (iii) AWRE, Aldermaston), were chemically polished and then tensile-tested using standard techniques developed earlier [8]. The chemical polishing was carried out in orthophosphoric acid in the temperature range 210 to 400° C. The temperature was not found to be critical provided that the time of immersion was adjusted accordingly – about 30 min at 210° C and 2 min at 400° C. The acid was changed frequently – every three or four whiskers – in order to avoid the deposition of a visible surface film which otherwise occurred. After polishing, the whisker was rinsed in water, then in alcohol, and was mounted for tensile-testing.

4. Experimental Results

Four growth directions were found, as in previous work [1]. They were $<0001>$, $<11\bar{2}0>$, $<10\bar{1}0>$, and $<10\bar{1}1>$. To conform with usual practice, the following notation is used – $<0001>$, $<hk.0>$, and $<hk.1>$ are referred to as C, A, and A-C types, respectively.

The tensile-test results were analysed by the technique described previously [1] and the equations thus obtained were:

$$\begin{array}{ll} \text{Polished, A-type} & \sigma_f = 994\, d^{-0.21}\, l^{-0.03} \\ \text{Polished, C-type} & \sigma_f = 1000\, d^{-0.14}\, l^{-0.02} \\ \text{Polished, A-C type} & \sigma_f = 10\,700\, d^{-2.47}\, l^{-0.16} \end{array}$$

where σ_f is in kilogrammes per square millimetre, d is in microns, and l is in millimetres; $d = \sqrt{A_c}$, where A_c is the cross-sectional area.*

Strengths were in the range 500 to 1400 kg/mm^2. Fig. 1 shows the strengths of polished, and unpolished, sapphire whiskers of the three orientations as a function of size. The different groups of whisker have strengths which correlate best with different size parameters, but for comparison all have been plotted against volume. Some fractured portions were retested and the points representing them in fig. 1 are joined by solid lines.

5. Discussion

5.1. Present Observations

Fig. 1a gives an indication of the effect of chemical polishing on the strength of A-type whiskers. There is, in general, an increase in strength but a decrease in the size-strength effect such that, below a certain size, polished and unpolished whiskers are approximately equal in strength. This effect can be studied in more detail by considering the size-strength equations, which are:

$$\begin{array}{ll} \text{Polished} & \sigma_f = 994\, d^{-0.21}\, l^{-0.03} \\ \text{Unpolished [1]} & \sigma_f = 720\, d^{-0.56}\, l^{-0.39} \end{array}$$

The dimensions at which polishing causes no strength increase can be found by equating the two expressions. At $l = 1$ mm, the strengths will be equal for $d \sim 0.4$ μm; while, for $d = 1$ μm, they will be equal at $l \sim 0.4$ mm.

Extrapolation of the two equations to unit-cell dimensions ($l = 5$ Å, $d = 10$ Å) gives strengths of $\sim$4300 kg/mm^2 (polished) and 7×10^6 kg/mm^2 (unpolished). The former corresponds to $\sim E/10$ and the latter to $\sim 170E$. Estimates of the theoretical strength of sapphire [7, 9] are usually $\sim E/10$. (In all cases, Young's modulus, E, for sapphire has been taken to be 4.2×10^4 kg/mm^2 – a mean value based on Wachtman's data [10] for single crystals of sapphire.)

These extrapolations suggest that there is no change in the fracture mechanism of polished, A-type, sapphire whiskers with decreasing size down to unit-cell dimensions. By contrast, the fracture mechanism of unpolished whiskers must change with increasing fracture stress, such that a discontinuity occurs in the size-strength curve to predict a reasonable strength value at unit-cell dimensions. It is likely that this change of mechanism occurs at the intersection of the polished and unpolished data. Although it is not possible to carry out tensile tests on whiskers much smaller than $d \sim 1$ μm, $l \sim 0.5$ mm, there are signs of

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*The full experimental results are omitted in the interests of brevity but are available on application to the authors.

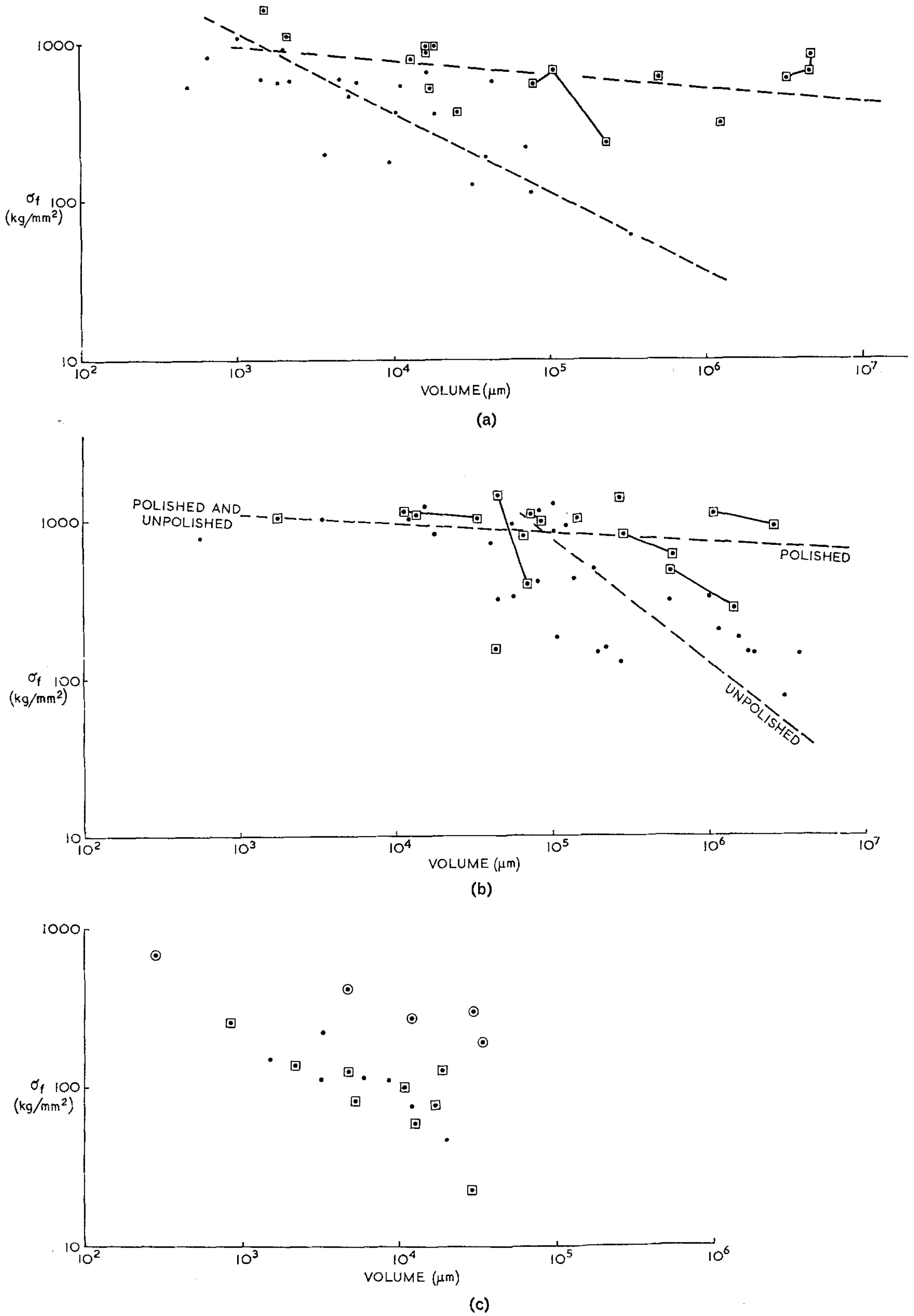

Figure 1 Graphs of tensile strength, σ_f, against volume for polished ⊡ and unpolished • sapphire whiskers of three orientations: (a) A type; (b) C type; (c) A-C type (⊙ A-C type without overgrowths).

such a change in slope for the unpolished, A-type data in fig. 1a.

The implication is that chemically polished, A-type whiskers have such perfect surfaces that the surfaces would play no part in fracture nucleation, even at stresses of $E/10$.

The size-strength equation for these whiskers shows that the strength depends on diameter but not on gauge length. This behaviour suggests fracture nucleation due to dislocation pile-ups or interactions within the whisker rather than fracture due to surface defects.

In the case of C-type whiskers, fig. 1b shows that similar effects exist (i.e. polishing leads to generally increased strengths and a reduced size-strength effect). The equations are:

$$\text{Polished} \quad \sigma_f = 1000\, d^{-0.14}\, l^{-0.02}$$
$$\text{Unpolished} \quad \sigma_f = 1450\, d^{-0.64}\, l^{-0.01}$$

In this case, the intersection of the two sets of data will occur for a wide range of values of l at $d \sim 2$ μm. Extrapolation of the equations to unit-cell dimensions gives strengths of 3500 kg/mm^2 (polished) and 10^5 kg/mm^2 (unpolished) (i.e. $E/12$ and $24E$ respectively). Again, it appears that extrapolation of the equation for polished whiskers to unit-cell dimensions gives a tensile strength close to estimates of the theoretical strength of a perfect crystal. A transition in the unpolished, C-type whisker data can be seen in fig. 1. Whiskers of volume less than 5×10^4 μm^3 have strengths coinciding with the polished data. Unlike the A-type whiskers, the transition occurs at a whisker volume well within the range of experiment.

In order to investigate the nature of the transition in fracture nucleation mechanism in unpolished, C-type whiskers, the results of earlier experiments [1] were divided into those where $\sigma_f > 800$ kg/mm^2 and those where $\sigma_f < 800$ kg/mm^2. The value of 800 kg/mm^2 was chosen so that more results could be included in the former category: if 900 kg/mm^2 were chosen only six results would be in the higher stress group, whereas with a figure of 800 kg/mm^2 ten results could be included. The equations thus calculated were:

Unpolished, C-type, $\sigma_f > 800$ kg/mm^2

$$\sigma_f = 855\, d^{0.11}\, l^{0.005}$$

Unpolished, C-type, $\sigma_f < 800$ kg/mm^2

$$\sigma_f = 815\, d^{-0.44}\, l^{-0.07}$$

There is clearly a difference in size-strength effect for the two sets of data. The high-strength whiskers show a small positive effect (i.e. decreasing strength with decreasing size), while the low-strength whiskers show the normal negative effect (i.e. increasing strength with decreasing size). In both cases, the strength is diameter-dependent; gauge length plays very little part. It is felt, however, that the result obtained for $\sigma_f > 800$ kg/mm^2 may not be very reliable, as only ten tensile tests are involved. The results, therefore, are taken to indicate that there is a definite change in the size-strength effect without being absolute in quantitative terms.

The same implications apply to both A- and C-type, polished whiskers – their surfaces are sufficiently perfect that they would play no part in the fracture nucleation process, probably not even at stresses of $\sim E/10$. In addition, it seems likely that unpolished whiskers, below a certain size, have sufficiently perfect surfaces for fracture nucleation to be due to internal features rather than surface defects.

Extrapolation of the equations for polished, A- and C-type whiskers to the dimensions of Mallinder and Proctor's [5] flame-polished specimens gives predicted tensile strengths of 240 kg/mm^2 and 380 kg/mm^2 respectively. No direct comparison with their results is possible, as their specimens were of a different orientation and were tested in bending. However, an average bend strength of 600 kg/mm^2, which would correspond to $\sim$450 kg/mm^2 in a tensile test, was observed and agrees well with the value predicted by the size-strength equations. (Applying a Weibull theory of fracture [11], tensile strength $\simeq 0.735 \times$ bend strength, for a rectangular cross-section specimen of alumina.)

In a similar manner, the size-strength equations for unpolished whiskers can be extrapolated to macroscopic dimensions and compared with tensile strengths of sapphire crystals obtained by Davies [12] for specimens with ground surfaces. The predicted strengths are 7 and 15 kg/mm^2 for A-type and C-type whiskers respectively, whereas Davies obtained values of $\sim$17 and 42 kg/mm^2 for unannealed and annealed specimens of an intermediate crystallographic orientation. The agreement therefore is again reasonable. Fig. 2 summarises the results of extrapolating the size-strength equations for polished and unpolished whiskers. While the equations involve both l and d, a reasonable

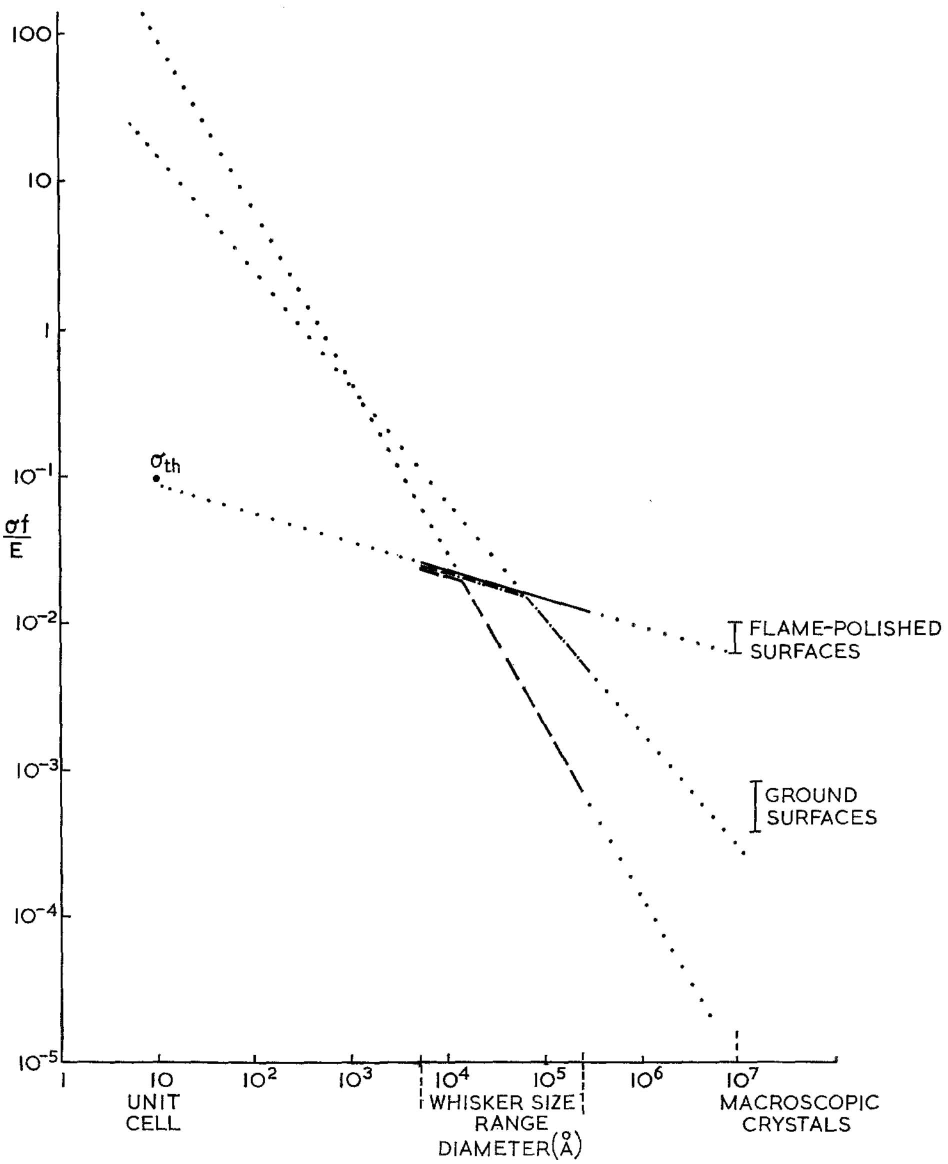

Figure 2 A diagram indicating the relationships between the strengths of polished and unpolished whiskers, the theoretical crystal strength, and the measured strength of large sapphire crystals. (——— unpolished, A-type whiskers; —·—· unpolished, C-type whiskers; ———— polished whiskers; ······ extrapolation lines; σ_{th}, theoretical strength of sapphire at unit-cell dimensions.) The size-strength equations are:

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

indication of their extrapolation behaviour can be obtained by plotting with *d* as abscissa.

Only a few $<10\bar{1}1>$ (A-C) whiskers were tested. Unpolished, A-C-type whiskers with no side growths have similar strengths and size-strength effects to A- and C-type whiskers. Some A-C-type whiskers, however, have pronounced side growths [1]; these were only about one-fifth the strength. Chemical polishing had no noticeable effect on the strength or on the size-strength effect of these whiskers. The data for A-C-type whiskers is given in fig. 1c. The low strengths found in A-C-type whiskers with side growths are due either to notches at the roots of the side growths or to the non-uniform, non-uniaxial stress from the highly variable cross-sectional area. The fact that chemical polishing does not change the strength suggests that it is the latter which is responsible.

5.2. A Fracture Model for Sapphire Whiskers

The following explanation of the tensile-strength properties of sapphire whiskers is consistent with present experimental evidence. It is suggested that sapphire whiskers have surface defects (e.g. growth steps) whose severity decreases with decreasing whisker size. In the case of A-type whiskers, where tensile strength correlates best with surface area, the magnitude of the growth steps is primarily dependent on surface area. This is consistent with the observation of hexagonal overgrowths [8] on A-type whiskers, which suggest that the growth process proceeds by the spreading-out of successive sheets of material across the large faces of the whisker. By contrast, although C-type whiskers are surface-sensitive for $\sigma_f < 800$ kg/mm^2, it appears that the growth steps are more dependent on diameter than surface area.

The fact that unpolished, C-type whiskers of strength > 800 kg/mm^2 behave in a qualitatively similar manner to polished ones suggests that the surfaces of such whiskers play no part in fracture nucleation, which may be due to dislocation movement leading to pile-ups or dislocation interactions. In the case of polished, A-type whiskers, the smoothed surfaces preclude fracture nucleation from surface steps, and, instead, the whiskers will fracture at a higher stress owing to dislocation pile-ups or interactions. Unpolished, A-type whiskers of sufficiently small surface area will have surfaces perfect enough for their fracture stresses to be equal to those of polished ones, and, in this case, the fracture mechanism will change from nucleation at surface steps to nucleation at dislocation interactions or pile-ups.

In an ideally orientated, C-type whisker, neither of the observed slip systems for sapphire ($\{0001\} <11\bar{2}0>$ and $\{11\bar{2}0\} <10\bar{1}0>$) will be active; while, in an ideally orientated, A-type whisker, only slip on the latter system is in principle possible.* In misorientated, A- and C-type whiskers, slip on either, or both, systems will, in principle, be possible. There is indirect evidence that plastic deformation occurs during crack propagation in sapphire [13-15] at room temperature, but there have been no reports of direct observation of room-temperature slip except in the case of whiskers [16]. The unusually high stresses operating in a whisker tensile test may enable dislocation movement to occur at room temperature, even though $\{0001\} <11\bar{2}0>$ slip is not normally observed below 900° C, and $\{11\bar{2}0\} <10\bar{1}0>$ below 1600° C [17], in large specimens.

6. Conclusions

(*a*) Chemically polished sapphire whiskers exhibit smaller size-strength effects than as-grown whiskers, with the tensile strengths (500 to 1400 kg/mm^2) correlating best with whisker diameter for all three orientations tested.

(*b*) Extrapolation of the size-strength equations obtained for polished whiskers leads to a predicted tensile strength of $\sim E/10$ at unit-cell dimensions. This is close to estimates of the theoretical strength of sapphire. Extrapolation to larger dimensions leads to good agreement with measured strengths of flame-polished sapphire crystals of 1 mm diameter and 3 mm length.

(*c*) There is evidence for a transition in fracture nucleation mechanism, at $\sigma_f \sim 1000$ and 800 kg/mm^2 for unpolished, A- and C-type whiskers respectively. Whiskers with fracture stresses above these critical values may fail by crack nucleation induced by dislocation motion; whereas, below such critical values, fracture is nucleated at growth steps with little or no dislocation activity.

(*d*) Polished $<10\bar{1}1>$ whiskers behave in a similar manner to A- or C-type whiskers except for $<10\bar{1}1>$ whiskers with side-growths, whose strengths are not changed by polishing.

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*Since the time of writing, the authors have observed a new slip system – $\{\bar{1}011\} <10\bar{1}2>$ – in C-type whiskers tested at 1200° C with a tensile stress of $\sim$90 kg/mm^2.

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