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Size-Strength Effects in Sapphire and Silicon Nitride Whiskers at 20°C

P. D. BAYER, R. E. COOPER
Metallurgy Division, Atomic Weapons Research Establishment, Aldermaston, Berks, UK

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Tensile tests at 20° C have been carried out on seventy-three sapphire whiskers and on seventeen silicon nitride whiskers. The sapphire whiskers were of $<0001>$, $<1\bar{1}20>$, $<10\bar{1}0>$, and $<10\bar{1}1>$ orientations, while the silicon nitride whiskers were $<0001>$, $<11\bar{2}0>$, and $<10\bar{1}3>$. Tensile strengths were in the range 45 to 1500 kg/mm^2, and deformation was found to be purely elastic. The tensile strength data have been analysed and fitted to empirical equations describing the effect of size on strength for different orientations. These empirical equations have been used to deduce possible fracture nucleation mechanisms. It is concluded that, in the case of $<0001>$ sapphire whiskers, fracture nucleation may be due to dislocation pile-ups or interactions, while in the other cases a Griffith flaw mechanism is probably applicable.

1. Introduction

The mechanical properties of whiskers are undoubtedly their most striking and potentially useful attributes at present. The strength of sapphire whiskers, for instance, can be as high as $E/30$ [1] (E = Young's modulus of elasticity), which is not far short of estimates of theoretical strength based on the cohesive forces between atoms. The existence of a correlation between whisker strength and size is well established – larger whiskers tending to be weaker than smaller ones – but the phenomenon has not been closely studied. The present work describes an investigation of the size-strength effect in sapphire and silicon nitride whiskers.

2. Survey of Relevant Work

Size-strength effects in whiskers were first reported by Gyulai [2] for sodium chloride, where the fracture strength, σ_f, of whiskers of 2 to 15 μm diameter varied inversely with diameter. Similarly, Regester *et al* [3] 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 [4] 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 to 1100° C but absent at 1550° C and above.

Soltis [5] 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 [6] 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 [7] obtained strengths proportional to $A_c^{-0.17}$, again for sapphire whiskers of all orientations.

3. Experimental Work

Sapphire whiskers were obtained from three sources: (i) Thermokinetic Fibers Inc, New Jersey, USA; (ii) General Electric Co, Pennsylvania, USA; (iii) AWRE, Aldermaston, UK. All were produced nominally by the same process, viz. the wet hydrogen process [8]. The Thermokinetic Fiber whiskers had been subjected to a classification process to remove debris and very large whiskers. The GE sample consisted of selected long (~10 mm) whiskers.

The AWRE whiskers were selected directly from the boats in which they were grown and were of a wide variety of sizes and shapes.

The procedure used for the examination and testing of whiskers has been described elsewhere [9]. Four growth directions, viz. $\langle 0001\rangle$, $\langle 11\bar{2}0\rangle$, $\langle 10\bar{1}0\rangle$, and $\langle 10\bar{1}1\rangle$, were observed; of which the first two were the most common. No whiskers of direction $\langle 11\bar{2}3\rangle$ [3] were found. Growth axes of $\langle 00.l\rangle$, $\langle hk.0\rangle$, and $\langle hk.1\rangle$ are usually referred to as C, A, and A-C types, respectively. Whiskers from all the three sources showed similar tensile properties. Some silicon nitride whiskers grown by the Gordon process [10] were also examined. $\langle 0001\rangle$, $\langle 11\bar{2}0\rangle$, and $\langle 10\bar{1}3\rangle$ directions were found.

4. Experimental Results

Seventy-three sapphire whiskers were tested in all, with cross-sectional dimensions of 0.9 to 800 μm and gauge lengths of 0.3 to 5 mm. Fracture stresses varied from $\sim$45 to 1300 kg/mm^2 (6×10^4 to 1.8×10^6 lb/in.^{2}).* No evidence of plastic deformation was found. One whisker, a wide, thin, A-type whisker, was damaged by pinching between tweezers so as to produce two, fairly long cracks – see fig. 1. Its strength was reduced by about an order of magnitude by the presence of these cracks. A-type whiskers were of rectangular cross-section; while C-type whiskers were usually hexagonal, but occasionally of parallelogram cross-section. A-C whiskers often had pronounced side growths parallel to $\langle 0001\rangle$ (see fig. 2), and in cross-section were shaped like a flattened hexagon.

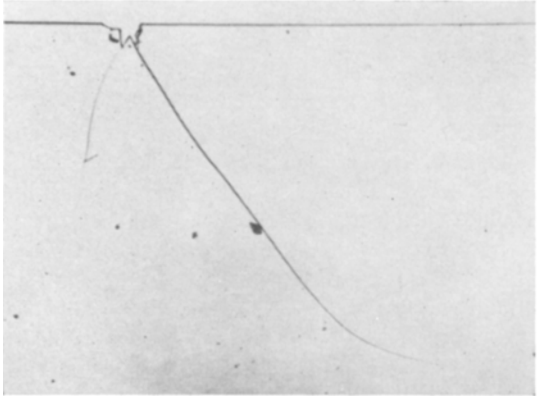

Figure 1 Part of a large, A-type sapphire whisker showing two long cracks produced prior to tensile testing. (×95)

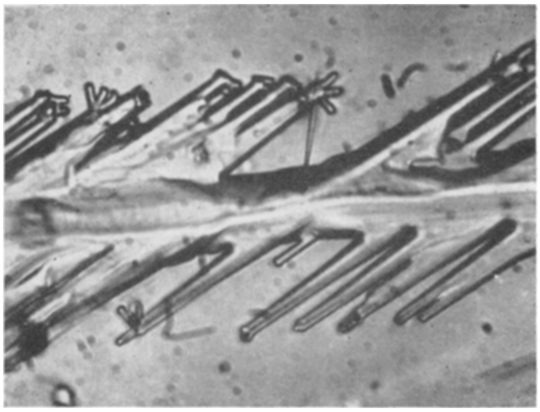

Figure 2 $\langle 10\bar{1}1\rangle$ sapphire whisker showing many pronounced side growths parallel to $\langle 0001\rangle$. (×250)

Seventeen silicon nitride whiskers were tested with cross-sectional dimensions in the range 0.3 to 180 μm and gauge lengths of 0.4 to 4.0 mm. Fracture stresses varied from 64 to 1500 kg/mm^2. Again, no evidence of plastic deformation was found.

5. Treatment of Results

Previous workers in the field have described the strength-size effect by various empirical equations, derived by plotting their data in a variety of ways and by looking for a reasonable correlation between strength and a size parameter – see section 2. In the present work, the authors initially plotted fracture stress σ_f against four size parameters, length, cross-sectional area, surface area, and volume (l, A_c, A_s, and V, respectively), using logarithmic scales. The straight line of best fit was then found for each graph (least-squares criterion) and the correlation coefficient, standard error of the slope, and standard deviation were calculated. The results, however, were not conclusive, as there was a good correlation between σ_f and all four size parameters. This was attributed to the existence of correlations between the size parameters – both geometrical correlations, such as that between V and l, and growth correlations, such as that between l and A_c.

The data were therefore treated in the following manner, which enables one to determine which size parameter correlates most closely with

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

fracture stress. The experimental results were analysed by computer to determine the constants K, m, and n in a general equation

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

where $d = \sqrt{A_c}$. The least-squares criterion was used to obtain the equation, and the d and l values were then substituted in order to determine the departure of each value of σ_f from the calculated equation. From the exponent ratio m/n, it can be determined which size parameter correlates most closely with σ_f. For instance, an exponent ratio of 1 would indicate that σ_f correlated most closely with surface area, while a ratio of 2 would indicate that it correlated most closely with volume.

The equations obtained were:

A-type sapphire whiskers

$$\sigma_f = 720\ d^{-0.56}\ l^{-0.39} \qquad (1)$$

C-type sapphire whiskers

$$\sigma_f = 1460\ d^{-0.64}\ l^{0.01} \qquad (2)$$

A-C-type sapphire whiskers

$$\sigma_f = 780\ d^{-0.99}\ l^{-0.17} \qquad (3)$$

Silicon nitride whiskers

$$\sigma_f = 1420\ d^{-1.11}\ l^{-0.81} \qquad (4)$$

where σ_f is in kilogrammes per square millimetre, d is in microns, and l is in millimetres. (Owing to the small number of silicon nitride whiskers tested, both $<11\bar{2}0>$ and $<10\bar{1}3>$ were included in one equation.)

The exponent ratio for (1) is 1.42, i.e. slightly closer to 1 than to 2, indicating that, of the usual size parameters l, A_c, A_s, and V, the closest correlation of σ_f is with A_s. The l exponent in (2) is almost zero, showing that length has no effect on the strength of C-type sapphire whiskers. This does not agree with experimental results on tested and retested whiskers, but the discrepancy will be discussed later. In (3), the exponent ratio is ~6, which has no physical meaning. The morphology of $<10\bar{1}1>$ whiskers is such, however, that size parameters such as surface area will be related in a very complicated way to l and d. No conclusions can be derived from equation 3, which is included simply for completeness. In (4), the exponent ratio is 1.37, indicating again a correlation of σ_f with A_s. The equations can be rewritten:

A-type sapphire

$$\sigma_f = 720\, A_s^{-\alpha} \quad (\text{where } 0.39 \leqslant \alpha \leqslant 0.56) \qquad (5)$$

C-type sapphire

$$\sigma_f = 1460\ d^{-0.64} \qquad (6)$$

Silicon nitride

$$\sigma_f = 1420\, A_s^{-\alpha} \quad (\text{where } 0.81 \leqslant \alpha \leqslant 1.11) \qquad (7)$$

Fig. 3 shows the data for each class of whisker plotted against the most appropriate size parameter. The lines joining some points indicate "tested and retested" whiskers.

6. Discussion of Results

The above method of treating the strength data is sensitive to extreme points. An example was taken from the silicon nitride data, where one point had a measured strength of 308 kg/mm² and a calculated strength by substitution of 1460 kg/mm². On removing this point and recalculating the equation, it became

$$\sigma_f = 2080\ d^{-1.29}\ l^{-0.96}$$

The exponent ratio was hardly changed (1.34), but the factor was changed by nearly 50%. This experimental point was presumably due to a whisker containing a large defect – it is indicated by the letter "W" in fig. 3c. Another example was taken from the work of Mehan *et al* [7] who give sufficient data in their report. Only results due to whiskers of parallelogram cross-section (presumably A or A-C type) and having no special comments regarding experimental behaviour were used. The equation so obtained was

$$\sigma_f = 495\ d^{-0.16}\ l^{-0.12}$$

It was apparent, however, on substituting d and l values into this equation, that four points showed severe departures (factors of 2 to 4) from the equation. On removing these points and recalculating the equation, the result was

$$\sigma_f = 380\ d^{-0.05}\ l^{-0.16}$$

The d exponent changed considerably; but the exponent ratio still indicates a surface-area correlation. Whether or not the exponent ratio is affected by anomalous points will depend on whether the d and l values of the anomalous points are near one or other extreme. An anomalous point with large d and small l or vice versa will have a large effect on the exponent ratio, while, if d and l are both large or both small, the anomaly will have little effect on the exponent ratio.

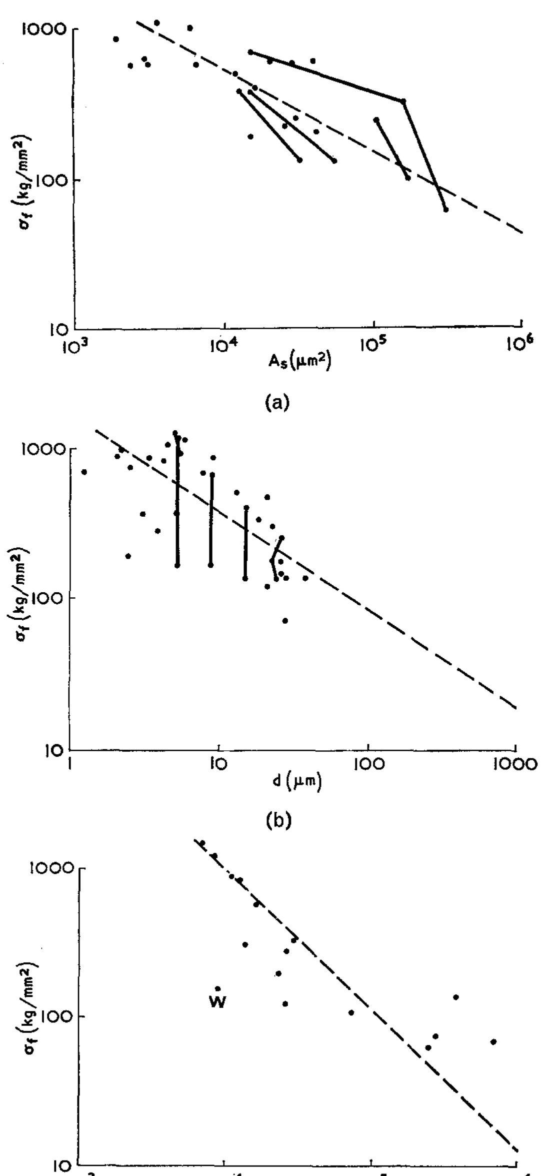

Figure 3 Graphs of tensile strength against the most appropriate size parameter for: (a) A-type sapphire whiskers; (b) C-type sapphire whiskers; (c) silicon nitride whiskers of all orientations. The gradients of the broken lines are calculated from mean values of α (see text).

In fig. 3a, it can be seen that, when whiskers were tested to fracture and then retested, the second test always yielded a higher fracture stress. The increase in stress was reasonably consistent with the general effect of A_s on σ_f, as indicated by the similarity between the slopes of the continuous "tested and retested" lines and the slope of the calculated (broken) line.

Equation 1 can be compared with previous work [3, 5-7] by setting l constant and considering the dependence of σ_f on d: the d exponents become -1, -0.66, -0.53, and -0.34 respectively, compared with -0.56 for the present work on A-type sapphire whiskers, and -0.64 for C-type sapphire whiskers. Brenner's [4] results on C-type sapphire whiskers agree very well with the latter exponent, while the earlier results on A-type whiskers are not inconsistent with equation 1. In Fig. 3b, again the retested whisker always had a higher fracture stress, but it is noticeable that the points representing the original tests lie in a band of low-strength points, while the points due to retested whiskers lie in a band of high strength. It is suggested that the prediction, that C-type sapphire whiskers have strength insensitive to l, applies mainly to small, high-strength whiskers, and that long ones will break at lower stresses and will have strengths dependent on gauge length. On ignoring the low strength results (e.g. $\sigma_f < 200$ kg/mm²) and recalculating the equation, the l index remained very small while the d index was somewhat reduced. The actual values of the constants in the equation depended on the particular criterion of data rejection, but the indices were not affected by rejection of high-strength points.

The classes of whiskers which have been tested fall into one of two groups. A-type sapphire and all silicon nitride whiskers have strengths dependent on surface area, while C-type sapphire whiskers have strengths dependent on diameter. It is suggested that the former types of whisker have strengths dependent on surface flaws, so that a Griffith fracture mechanism may be operative. This suggestion is not new, but the correlation between surface area and strength of whiskers has not previously been demonstrated. A typical whisker, with $\sigma_f = 700$ kg/mm², $E = 4.2 \times 10^4$ kg/mm², and $\gamma + W = 100$ erg/mm² (a plastic work term W being included [11-13]), will have a critical crack-length of $\sim$0.1 μm. This will be optically unresolvable. Two, wide, thin, A-type sapphire whiskers have been chemically thinned and examined by transmission electron microscopy. One was thinned prior to tensile testing and the other after testing. In neither case was there any sign of a dislocation sub-structure in an observable specimen area of about 30 000 μm^2. The surfaces were highly perfect, but this is attributable to the chemical polishing process.

The fact that C-type sapphire whiskers have strengths dependent on diameter suggests that a dislocation pile-up or interaction process may be causing fracture nucleation. There are indications [11-13] that sapphire can deform plastically at 20° C, particularly under very high stresses such as exist near the tip of a moving crack. Similar stresses will be found in a whisker during a tensile test. The two observed slip systems in sapphire are $\{0001\}$ $\langle 11\bar{2}0\rangle$ and $\{11\bar{2}0\}$ $\langle 10\bar{1}0\rangle$. Neither will be active in an ideally oriented C-type whisker, but in the non-ideal case there is a possibility that either may occur.

No tensile-tested C-type sapphire whiskers have been examined by transmission electron microscopy. The hexagaonal cross-section means that such a whisker would need to be thinned to $\sim$2000 Å diameter. Such a specimen would be extremely difficult to tensile-test. Attempts have been made to detect dislocations in whiskers by etching, but so far the results are inconclusive. Even if dislocations were observable it would be difficult to distinguish between those causing fracture nucleation and those caused by the fracture process.

7. Conclusions

A-type sapphire whiskers have tensile strengths in the range 100 to 1000 kg/mm², the size-strength relationship being best expressed by $\sigma_f = \text{const.}\ A_S^{-\alpha_1}$, where $0.3 < \alpha_1 < 0.6$.

A-C-type sapphire whiskers have tensile strengths in the range 45 to 650 kg/mm², the ones with no dendritic side growths being in the range 400 to 600 kg/mm². The size-strength relationship in this case is best expressed by $\sigma_f = \text{const.}\ d^{-1}\ l^{-0.17}$.

C-type sapphire whiskers have tensile strengths in the range 100 to 1300 kg/mm², and the size-strength relationship is best expressed by $\sigma_f = \text{const.}\ d^{-\alpha_2}$, where $\alpha_2 = 0.64$.

Silicon nitride whiskers of $\langle 10\bar{1}3\rangle$ and $\langle 11\bar{2}0\rangle$ orientations have strengths in the range 60 to 1500 kg/mm² and obey a strength-size relationship $\sigma_f = \text{const}\ A_S^{-\alpha_3}$, where $0.8 < \alpha_3 < 1.1$.

It is postulated that, in those cases where there is a correlation between tensile strength and surface area, fracture nucleation occurs at a Griffith flaw. Calculation shows that, in the case of an average sapphire whisker, the critical crack-length will be $\sim$0.1 μm. In the case of C-type sapphire whiskers, it is tentatively suggested that fracture nucleation may be due to dislocation interaction or pile-ups.

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