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The Tensile Strength of Sapphire Whiskers at Elevated Temperatures

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

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Tensile tests have been carried out on 124 sapphire whiskers at temperatures in the range 350 to 1810° C. The effects of crystallographic orientation, growth process, purity and surface perfection have been investigated.

The strength-temperature-dependences of different categories of whisker are compared with that to be expected for a Griffith fracture mechanism, and it is shown that such a mechanism may apply up to ~1000° C to A-type (<hk.o>) whiskers grown by the wet-hydrogen process [1]. Chemically-polished whiskers of this type show a strength-temperature-dependence more consistent with a dislocation-induced fracture mechanism. There is some evidence that chemically-polished C-type (<0001>) whiskers grown by a chloride oxidation process [2] behave in the same manner. For other categories of whisker there are insufficient data to ascribe fracture mechanisms.

1. Introduction

While whiskers have been the subject of many investigations at room temperature, there are few reports of strength measurements at elevated temperatures. Since the main potential use for sapphire whiskers is for reinforcement of metals at elevated temperatures [3] it is important to know as much as possible about their strength under these conditions. The present work was therefore undertaken to supplement existing data [4-6]. Although effort is being made by optical and electron microscopy to determine the operative fracture mechanisms, this work is by no means complete, and the present paper will therefore cover only the mechanical properties of the whiskers.

2. Survey of Relevant Work

The major problem in carrying out tensile tests on whiskers at elevated temperatures is to avoid heating of the grips and consequent slippage due to weakening of the adhesive. Brenner [4] avoided this problem by melting each end of the whisker to form a small sphere, and then gripping this sphere with a claw system. Since this procedure produced a relatively weak interface between the melted and unmelted regions, he found it necessary to thin down part of the whisker to form a gauge length by heating in hydrogen. Brenner used a resistance heater and both hydrogen and oxygen atmospheres around the heating coil and whisker. He found that ⟨0001⟩ whiskers grown by the wet-hydrogen method had strengths of 400 to 450 kg/mm² at 1000° C. Brenner found that a diameter-strength effect was present up to 1060° C, but was absent at 1550° C and above. In his tests a fixed load was applied relatively rapidly, using a solenoid system, and fractures which occurred in less than 10 sec were treated as dynamic tensile strength values. Fractures which occurred after delays of up to 10^4 sec were noted, but will not be discussed here. The most striking feature of Brenner's results is the high strength exhibited close to the melting point (> 63 kg/mm² at 2030° C).

Soltis [5] carried out tensile tests at 900° C on wet-hydrogen-grown whiskers using resistance heating, the whiskers being heated in air. He does not mention any difficulties in gripping the specimen. The tests were of 10 to 20 sec duration, and fracture stresses of > 175 kg/mm² are quoted.

Mehan and Feingold [6] performed bend tests in atmospheres of both air and helium. In order to avoid difficulties due to elastic anisotropy and

the relatively complicated cross-sectional shape of the specimens, they used a technique which gave the high-temperature strength as a fraction of the room-temperature value. The specimen, which was chosen to be free from perceptible taper, was broken at room temperature, and then one part of it was loaded to a known fraction of the room temperature fracture load, and the temperature was increased until failure occurred. The specimens were grown by the wet-hydrogen method, and were coated with titanium and nickel, the nickel being outermost. The results are in agreement with Brenner's, regarding the general form of the strength-temperature curve, but show a slightly greater decrease of strength with increasing temperature. Neither author found any effect of atmosphere on strength.

3. Experimental Technique

The authors considered that a tensile technique was preferable to bend tests, and that the specimen should be tested in the as-grown condition, i.e. there should be no thinned gauge length. In order to test reasonably short whiskers without heating the grips, a very localised heat source is required which does not radiate appreciably parallel to the length of the whisker. These conditions were satisfied by using a small gas-oxygen flame. A burner made of stainless steel hypodermic tubing producing a butane-oxygen flame less than 0.5 mm in length, and diameter was found to be satisfactory, see fig. 1. Temperatures in excess of 1800° C could be attained. The specimen temperature was measured with a very fine thermocouple up to 800° C, and with a specially made optical pyrometer above 800° C. The latter instrument utilises the disappearing filament principle in reverse – the hot whisker is viewed against a background of variable brightness which is matched to it. In order to correct for spectral emissivity some platinum powder or paint must be applied to the whisker hot zone, but there is no evidence that this leads to any chemical reaction. In fig. 1 an excessive amount of platinum powder is visible, this being present in order to increase the contrast for photographic purposes. The temperatures quoted are estimated to be accurate to + 15° C throughout the optical pyrometer range and + 20° C in the thermocouple range, the agreement between the two methods being within the estimated errors at 800° C.

By recording the output from a heated thermocouple with no cover on the Marsh tensile machine [7] it was found that air movements in the laboratory led to temperature fluctuations of several hundred degrees with a periodicity of 0.5 to 5 sec. Accordingly, the ventilation in the laboratory was restricted during tensile tests, and care was taken to seal the tensile machine against external air movements. The metal cover of the tensile machine was replaced by one made of perspex, so that the whisker could be observed during testing.

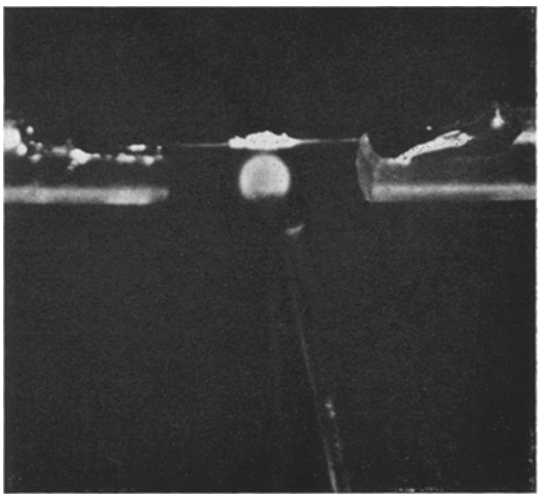

Figure 1 Sapphire whisker heated with an oxy-butane flame in the Marsh tensile testing machine. Whisker length is 4 mm.

The tensile machine was modified, the loading micrometer being driven by a synchronous motor to provide a strain rate of $\sim 10^{-3}$/min, while the null condition of the strain-measuring device was maintained manually, the necessary micrometer movements being recorded automatically.

It was noted that thinning or attack of the whisker could take place at 1600° C, or above under certain conditions. Complete coatings of platinum were partially effective in preventing this, but they tended to flake off. A few whiskers were heated with carbon monoxide instead of butane/oxygen. It was found that if a platinum-coated whisker was initially heated to ~300° C, carbon monoxide would heat the whisker without producing a flame, leading to temperatures in the range 800 to 1300 °C. Presumably the exothermic process $2\ CO + O_2 \rightarrow 2\ CO_2 +$ 41.5 kcal at 1000° C [8] is responsible for the heating. The strengths of whiskers heated in this way did not differ significantly from those

produced by butane/oxygen flame heating. The whiskers tested had cross-sectional areas in the range 1 to 6000 μm^2.

4. Experimental Results

4.1. The Effects of Growth Method, Orientation, and Surface Condition

Specimens were obtained from five sources. (i) AWRE wet-hydrogen process [1]. (ii) AWRE chloride oxidation process [2]. (iii) General Electric (USA) *wet-hydrogen process to be referred to as GE whiskers. (iv) Compagnie Thomson Houston (Paris)† wet-hydrogen process (to be referred to as CTH whiskers). (v) Thermokinetic Fibers Inc (USA)‡ wet-hydrogen process whiskers (to be referred to as TKF whiskers).

The whiskers could be classified into two main growth types – C-type (⟨0001⟩), and A-type (⟨hk.o⟩. In addition, the CTH whiskers included a number of A-C type (⟨10$\bar{1}$2⟩ using morphological indices with $c/a = 1.365$§).

The results are shown in fig. 2, being divided into a number of groups as follows. Fig. 2a shows the effect of temperature and surface perfection on the strength of A-type wet-hydrogen whiskers; similar effects are shown in fig. 2b, for A-type chloride process whiskers. Fig. 2c compares C-type whiskers grown by the two methods with a few results for chemically polished C-type whiskers.

Brenner's results are given on each graph, although his specimens were in yet another category (polished C-type wet-hydrogen). Calculated Griffith curves are also given on each graph (see section 5.2). In the interests of brevity the full results are omitted but are available on application to the authors. Because of the large number of different categories of whisker tested, it was not possible to determine accurately the variation of the size-strength effect with temperature, but the effect appears to be small above 1200° C. The outstandingly high strength points in fig. 2a and 2b in the temperature range 300 to 550° C are all fine whiskers (cross-sectional area < 80 μm^2). The approximate ranges of strength at 20° C are indicated in fig. 2a for unpolished and polished A-type wet-hydrogen. Little room temperature data is available for chloride-grown whiskers.

4.2. The Effects of Purity on Tensile Strength

The major impurity in sapphire whiskers is silicon. Those used by Brenner contained 2 to 3 wt % of silicon. Samples of sapphire whiskers from different sources were analysed with the following results:

AWRE chloride-grown	1.4 wt % silicon
AWRE wet-hydrogen process	6.9 wt % silicon
TKF wet-hydrogen process	0.15 wt %, 0.2 wt % silicon
CTH wet-hydrogen process	1.9 wt % silicon
GE wet-hydrogen process	1.4 wt % silicon

The TKF whiskers had an unusually low silicon content, which was confirmed by a second analysis. Previous work [10] has shown that wet-hydrogen-grown whiskers from different sources have similar strength properties at 20° C, but nothing was known about the effect of silicon content on high-temperature strength. Whilst most TKF whiskers were too short (~ 1 mm) to permit high-temperature testing, a few of sufficient length were found and tested. The strengths were not significantly different from those of other whiskers.

5. Discussions of Results

5.1. The Effect of Temperature on Whisker Strength

The results as presented in fig. 2 show that the strengthening effect of chemical polishing which has been reported at room temperature [11] persists up to ~1000° C in the case of A-type wet-hydrogen, and possibly in the case of A-type chloride-grown whiskers. This suggests that fracture is due to surface flaws below ~1000° C in the case of these whiskers.

Comparing the present results with those of Brenner [4] it can be seen (fig. 2) that the chemically-polished data show somewhat better agreement than the unpolished data, suggesting that Brenner's hydrogen-thinning process, which he used to form a gauge length, also improves the whisker-surface in the same way as does chemical polishing. Above 1200° C there is a

* Address: Valley Forge Space Research Center, King of Prussia, Pennsylvania, USA
† Address: 51 Boulevard de la République, BP 17, 78-Chaton (Yvmes), France.
‡ Address: Nutley, New Jersey, USA
§The morphological unit cell is used in this paper. Some authors use the structural unit cell with $c/a = 2.73$. Kronberg [9] has discussed the relationship between, and the uses of, the two notations.

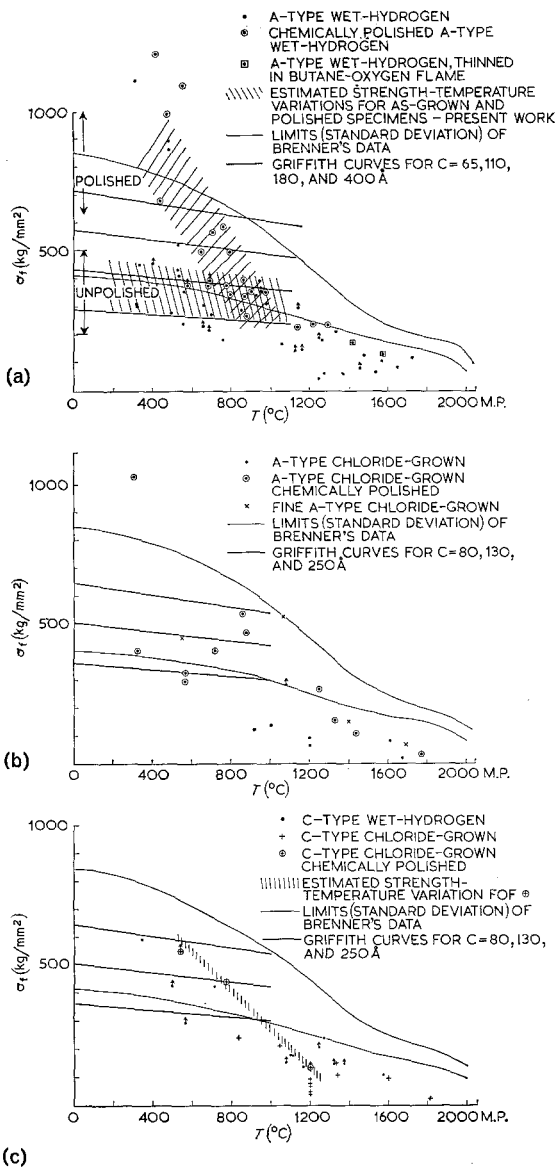

Figure 2 The effect of temperature on tensile strength of sapphire whiskers.

more marked difference between the present data and those of Brenner, and there is no sign of the decrease in the slope of the (σ, T) curve at ~1600° C observed by Brenner. The present data appear to extrapolate to zero strength at the melting point of sapphire for all whisker categories. This is comparable with the behaviour of other materials, and contrasts with Brenner's results which require an extremely rapid decrease of strength with temperature above 2000° C. In Brenner's work the temperature was measured by noting the electrical power required to melt a small amount of an appropriate metal supported on a small sapphire blade in the heating coil or to melt the sapphire blade itself. It was assumed that a sapphire whisker in the same position would attain the same temperature as the metal for a given power input. However, differences of optical emissivity between sapphire and the calibration metals may introduce errors due to the whisker attaining a different temperature from the calibration metals.

5.2. The Applicability of a Griffith Equation to Whisker Strengths

The Griffith criterion for fracture of a brittle material states that in a specimen having Young's modulus of elasticity E, specific surface energy γ, and an elliptical flaw of length c, it is energetically favourable for the flaw to propagate parallel to its length if the applied tensile stress perpendicular to the flaw length exceeds $\sqrt{2E\gamma/\pi c}$, Since one would expect c to depend on the specimen preparation or growth process rather than on temperature, the variation of Griffith fracture stress σ_f with temperature will be of the form $\sigma_f \propto \sqrt{E_T \gamma_T}$. Some data is available on the variation of E and γ with temperature for sapphire. Watchman *et al* [12] suggest an equation of the form $E_T = E_0 - b\,T \exp(-T_0/T)$ where E_0, b, and T_0 are constants which depend on the crystallographic orientation of the specimen. They have determined these constants experimentally. Bruce [13] suggests an average surface energy variation of the form $\gamma_T = \gamma_0 - aT$. In both cases T is the absolute temperature.

Using these equations, the quantity $\sqrt{E_T \gamma_T}$ can be calculated as a function of temperature. The results are given in table I for $\langle 11\bar{2}0 \rangle$ and $\langle 0001 \rangle$ specimen orientations (i.e. A-type and C-type whiskers respectively). The variation of $\sqrt{E_T \gamma_T}$ with temperature is very nearly linear in the temperature interval 20 to 1000° C such that for $\langle 0001 \rangle$ whiskers

$$\sqrt{\frac{E_{1000}\,\gamma_{1000}}{E_{20}\,\gamma_{20}}} = \frac{\sigma_{f_{1000}}}{\sigma_{f_{20}}} = 0.857$$

while for $\langle 11\bar{2}0 \rangle$ whiskers

$$\sqrt{\frac{E_{1000}\,\gamma_{1000}}{E_{20}\,\gamma_{20}}} = \frac{\sigma_{f_{1000}}}{\sigma_{f_{20}}} = 0.842$$

One can thus draw a family of curves for each orientation of whisker, each curve corresponding to a different flaw length, and the whisker strength data can be matched with an appropriate curve if the Griffith mechanism of fracture is

TABLE I Calculated Griffith strength variation with temperature.

		⟨0001⟩			⟨1120⟩	
T (°C)	γ (erg/cm²)	E (10^4 kg/mm²)	$\frac{\sigma_{fT}}{\sigma_{f20}}$	γ (erg/cm²)	E (10^4 kg/mm²)	$\frac{\sigma_{fT}}{\sigma_{f20}}$
20	1132	4.600	1.000	1132	4.317	1.000
200	1090	4.543	0.976	1090	4.238	0.974
400	1044	4.467	0.947	1044	4.131	0.941
600	998	4.387	0.918	998	4.035	0.909
800	952	4.309	0.889	952	3.929	0.876
1000	905	4.220	0.857	905	3.822	0.842

applicable. Fig. 2 shows the appropriate family of Griffith curves superimposed on the whisker strength data. It can be seen that in no case does the whisker data lie on a shallower curve than the Griffith curve. This suggests that the choice of true surface energy γ is appropriate, since, if a term were necessary to account for plastic work at the crack tip, one would expect this term to increase with increasing temperature. The strength data would then lie on a shallower strength-temperature curve than that predicted by a pure Griffith mechanism.

The data for unpolished A-type whiskers fit a Griffith curve fairly well, while those for polished A-type wet-hydrogen whiskers, and for polished chloride-process C-type whiskers, do not fit a Griffith curve, the variation of strength with temperature being too great. At ~1000° C the strength of unpolished A-type wet-hydrogen-process whiskers begins to fall off more rapidly with temperature, and no longer follows the Griffith curve. The tentative conclusions to be drawn from these observations are that unpolished wet-hydrogen A-type whiskers fail by a Griffith mechanism at temperatures between 20 and ~1000° C, while the other categories of whisker fail by some other mechanism which exhibits a stronger temperature-dependence than the Griffith mechanism.

In earlier work based on room temperature data [11], the authors suggested that unpolished A-type whiskers with strengths of less than 1000 kg/mm² at 20° C fail by a Griffith mechanism while unpolished C-type whiskers with strengths of less than 800 kg/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 present observations on the effects of temperature on strength are in agreement with the above fracture model. The transition stress above which the mechanism changes from Griffith to a dislocation process would be expected to be temperature-dependent, as it is probably a dislocation nucleation, multiplication or unpinning stress. However, the present data are insufficient to allow identification of such an effect.

6. Conclusions

(i) The tensile strengths of sapphire whiskers of all categories tested decrease monotonically with increasing temperature, typical strengths for as-grown whiskers being ~200 kg/mm² (2.8×10^5 psi) at 1100° C and ~100 kg/mm² at 1500° C.
(ii) Chemical polishing of A-type whiskers in hot orthophosphoric acid produces a strengthening effect which persists up to ~1000° C. Polished whiskers show fair agreement with previously published data [4] at temperatures up to ~900°C, but there is an increasing discrepancy at higher temperatures. At 1100° C the strength of polished whiskers is ~250 kg/mm² (3.5×10^5psi). The present data extrapolate to zero strength at the melting point of sapphire.
(iii) Comparison of the strength-temperature data with calculated curves for the Griffith mechanism suggests that unpolished A-type wet-hydrogen whiskers fail by such a mechanism below ~1000° C. Polished A-type wet-hydrogen, and C-type chloride-grown whiskers, do not show such agreement, and it is suggested that these categories of whisker fail by a more strongly temperature-dependent means such as a dislocation interaction or pile-up mechanism. These suggestions are consistent with a fracture model published previously [11] based on size-strength and surface perfection effects at 20° C.
(iv) A variation of silicon-content in the range 0.15 to 6.9 wt % has no discernible effect on the high-temperature strength of sapphire whiskers.

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