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Deformation dynamics of pore-free Ti^{4+}-doped and pure *c*-axis sapphire crystals

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Single crystal alumina filaments undoped and Ti^{4+}-doped, having the *c*-axis within 2° of the filament axis were plastically strained in constant strain-rate tensile experiments. The results of differential strain-rate and differential temperature tests were used to calculate the stress exponents in the strain-rate equation, the activation volumes, and the activation enthalpies. The relatively high values of the stress-exponents (6 to 7), the variations of the activation enthalpy with stress and temperature, and the magnitudes of the strain-independent activation volumes suggest overcoming the Peierls-Nabarro stress as the rate-limiting mechanism for plastic deformation of the alumina crystals. The microscopic observations of the deformed specimens are consistent with slip on the $\{10\bar{1}1\}\langle\bar{1}101\rangle$ pyramidal system as reported in previous investigations of similar materials.

1. Introduction

The plastic deformability of sapphire via basal slip is well established and has been the subject of numerous investigations ([1-3] for summaries). On the other hand, the literature for the deformability of sapphire with the resolved shear stress maximized on the pyramidal planes is much more recent and limited in scope.

Heuer *et al.* [4] deformed 0° Czochralski sapphire† from 1600 to 1800°C in tensile creep at very low stresses. A value for the stress exponent, n, from a relation of the form $\dot{\epsilon} \propto \sigma^n$, was found to be approximately equal to 3, in agreement with pure Nabarro-climb deformation. However, long, straight dislocations were observed lying on $\{\bar{1}012\}$ planes, suggesting rhombohedral slip.‡

Gooch and Groves [5] have performed tensile creep experiments on *c*-axis Tyco filaments. A power law dependence for the effect of stress was found with stress exponent values being approximately equal to six. Apparent activation enthalpies showed a marked stress dependence, ranging from 310 kcal mol^{-1} at a stress of 132 MN m^{-2} to 200 kcal mol^{-1} at 204 MN m^{-2}. The deformation mechanism was not conclusively established.

Tressler and Barber [6] tensile tested the production type *c*-axis Tyco filaments, which contained a characteristic pore structure, from 1760 to 1875°C. It was observed that the flow stress followed a power law dependence with n values increasing from 8.5 at 1775°C to 12.4 at 1875°C. The activation enthalpy calculated from the results of differential strain-rate and differential temperature tests was found to be approximately 80 kcal mol^{-1} which compares with the enthalpy obtained for defect diffusion in single crystal aluminium oxide by Jones *et al.* [7].

In the study reported here, the flow behaviour of the undoped, *c*-axis, pore-free, filaments grown by Haggerty [8] was compared to the undoped, porous filaments tested by Tressler and Barber [6]. The effect of the Ti^{4+} dopant on the

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†0° sapphire or *c*-axis sapphire refers to sapphire samples tested with the applied stress parallel to the *c*-axis.

‡The structural unit cell ($c/a = 2.73$) is used throughout this paper. Morphological rhombohedral planes $\{\bar{1}012\}$ are referred to as "rhombohedral" planes to agree with previous literature although the crystallographically correct rhombohedral planes are the $\{10\bar{1}1\}$ planes.

flow stress and deformation dynamics of *c*-axis sapphire was also investigated.

2. Experimental procedure

Titanium-doped single crystals, having the *c*-axis oriented within 2° of the specimen axis, grown by the Arthur D. Little fibre growth process from feed stock originating with a Linde White Star Sapphire boule, were used for the majority of the tensile testing (a few tests were conducted with undoped samples). The Ti-dopant level was between 0.024 and 0.077 wt % and virtually all of the titanium ions were initially in the trivalent state as determined by Haggerty [8]. The cross-section of a typical filament was essentially circular with a nominal diameter of 0.0275 cm and never varied more than 2 to 3% along the hot-zone section where deformation occurred (see [8] for a complete description).

The pivot bearing, hypodermic needle method for tensile testing and sample gripping described by Tressler and Crane [9] was used. The furnace was an internally wound Pt–40% Rh model adapted from the design of St. Pierre [10] with an i.d. of 1.6 cm and a hot-zone length of $\simeq$ 2.5 cm.

The temperature was measured using a Pt40Rh–Pt20Rh thermocouple which was calibrated periodically using a National Bureau of Standards standard thermocouple of the same type. The temperature was constantly monitored with a Leeds and Northrup precision millivolt potentiometer and controlled to ± 2°C by manually adjusting the power input.

The tensile testing apparatus was a table model Instron equipped with a 50 kg tension load cell. The cross-head speeds used were 0.005, 0.01, 0.02 and 0.05 cm min^{-1}. Both differential strain-rate and differential temperature tests were performed at constant structure from 1800 to 1850°C. Differential strain-rate tests were performed by changing the cross-head speed as the specimen deformed plastically. The differential temperature tests were performed by tensile testing a specimen at a given temperature, removing the load, lowering the temperature 25°C and restressing, a process that took approximately 10 min.

All samples tested at 1825°C and below were prestressed for 30 min at the test temperature at approximately one-third the yield stress to effect plastic deformation. The furnace was held at approximately 1000°C between tests and it took approximately $\frac{1}{2}$ h to heat the sample to the test temperature.

To guarantee that the Ti-ions were all in the Ti^{4+} state the samples were oxidized using the data of Jones *et al.* [7, 11]. To demonstrate that the Ti^{4+} ions were in solution at the test temperatures a specimen was optimally aged at 1300°C for 14 days to produce the Ti-rich precipitates [11]. The specimen was then heated at 1800°C for 1 h with the result that the precipitates were completely dissolved as evidenced by microscopic examination using a petrographic microscope.

Slip traces on deformed crystals were viewed by transmitted light microscopy and scanning electron microscopy. Preliminary transmission electron microscopic examination was performed on specimens thinned by mechanical polishing and ion thinning techniques.

3. Results and discussion

3.1. Sapphire doped with Ti^{4+} ions

Gross plastic deformation was observed in the temperature range 1800 to 1850°C. At 1800°C, approximately 7% plastic deformation took place over a 2.5 cm hot-zone section. Typical stress-elongation curves are shown in Figs. 1

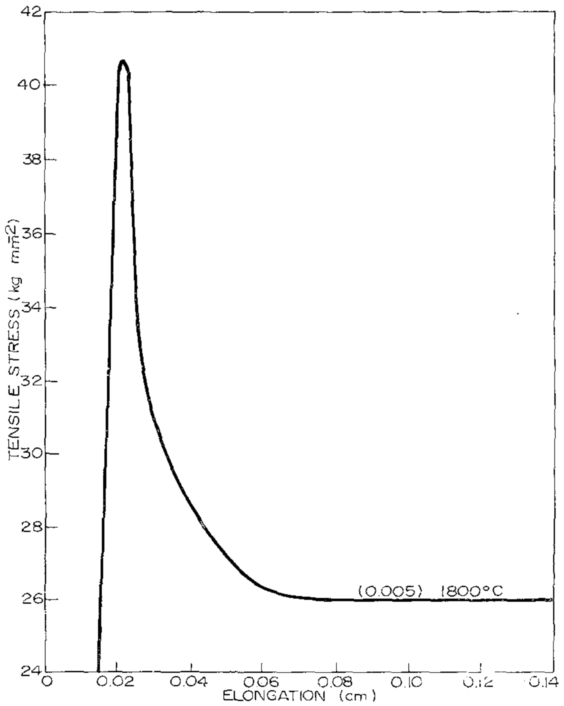

Figure 1 Tensile stress versus elongation curve for a Ti^{4+}-doped *c*-axis sapphire filament tensile tested at a cross-head speed of 0.005 cm min^{-1} at 1800°C.

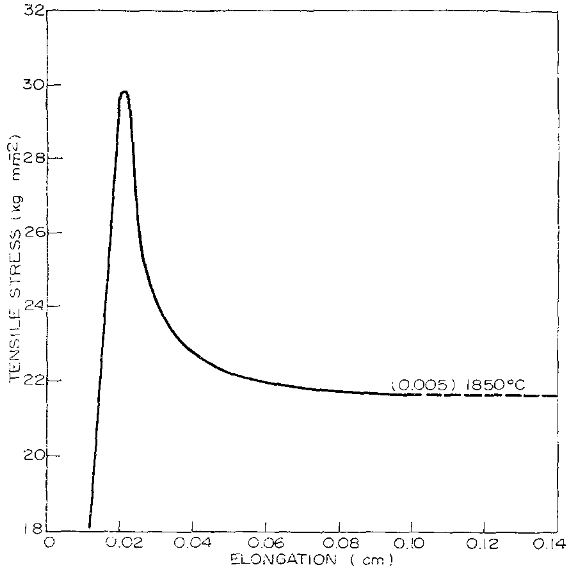

Figure 2 Tensile stress versus elongation curve for a Ti^{4+}-doped *c*-axis sapphire filament tensile tested at a cross-head speed of 0.005 cm min^{-1} at 1850°C.

and 2 for samples tensile tested at 0.005 cm min^{-1} at 1800 and 1850°C.

Interesting features of these curves are a gradual departure from elastic behaviour followed by a sharp yield drop. These features have also been observed for samples deformed via basal slip [2, 12] and also for samples tested with the applied stress parallel to the *c*-axis [6, 13]. In the present study, the yield points were relatively irreproducible due to the various pretest thermo-mechanical treatments. Therefore, the yield behaviour was not as well characterized as the flow behaviour.

Once substantial elongation had occurred, it was evident that remaining deformation occurred at approximately constant stress. Generally, deformation via basal slip has exhibited both an

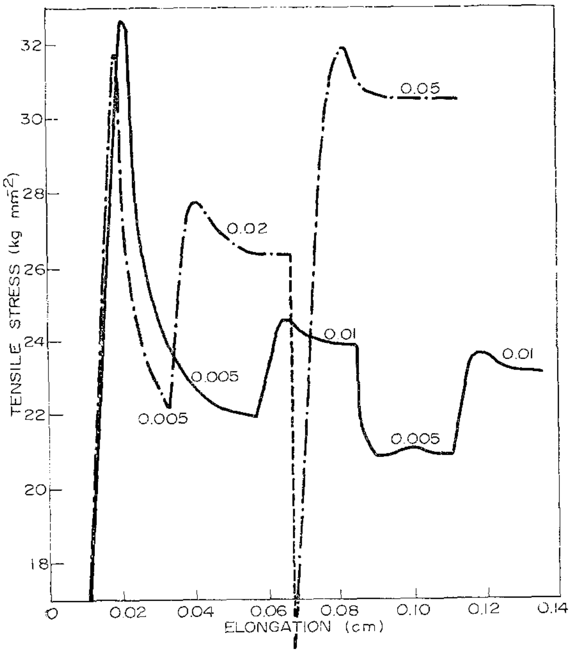

Figure 4 Typical tensile stress versus elongation curves for a differential strain-rate test at 1850°C for a Ti^{4+}-doped *c*-axis sapphire filament. The cross-head speeds are indicated on the figure.

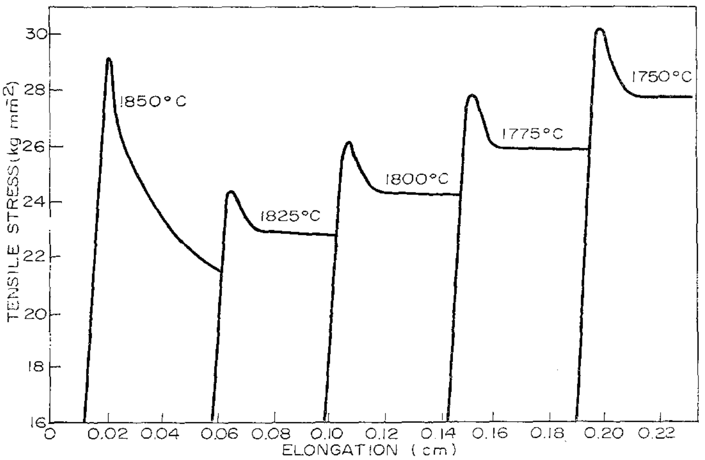

Figure 3 Typical tensile stress versus elongation curve for a differential temperature test at a cross-head speed of 0.005 cm min^{-1} on a Ti^{4+}-doped *c*-axis sapphire filament. The temperatures are given on the figure.

upper and lower yield stress followed by strain hardening. The lack of strain hardening or strain softening has only been observed by Gooch and Groves [13] in bend specimens oriented with the applied stress parallel to the *c*-axis. The *c*-axis Tyco filaments of Tressler and Barber [6] exhibited a gradually decreasing flow stress, indicating that recovery occurred faster in their samples than in those of the present study.

Typical stress-elongation curves for differential temperature and differential strain-rate tests are shown in Figs. 3 and 4. Tests such as these were used to calculate activation parameters to aid in the identification of the deformation mechanism. Generally, the deformation dynamics of sapphire via basal slip have fitted either a relation of the form

$$\dot{\gamma} = \nu \exp\left[\frac{-H(\tau^*)}{RT}\right] \qquad (1)$$

indicative of the overcoming of a Peierls-Nabarro stress as being the rate controlling mechanism, or a relation of the form

$$\dot{\gamma} = \frac{A}{T}(\tau^*)^n \exp - \left(\frac{H_0}{RT}\right) \qquad (2)$$

indicative of dislocation climb as the rate controlling mechanism. ($\dot{\gamma}$ is the shear strain-rate, ν is a constant, $H(\tau^*)$ is the stress dependent activation enthalpy, R is the gas constant, T is the absolute temperature, A is a constant, τ^* is the effective resolved shear stress, n is a constant, and H_0 is the activation enthalpy relatively independent of stress.)

Assuming a deformation equation of the form of Equation 2 and using data from differential strain-rate tests, stress exponent values were calculated using the relation

$$n = \frac{\delta \ln \dot{\epsilon}}{\delta \ln \sigma} \simeq \frac{\Delta \ln \dot{\epsilon}}{\Delta \ln \sigma} \, . \qquad (3)$$

The values generally fell between 6 and 7 and were independent of elongation, stress and temperature as illustrated in Fig. 5.

Gooch and Groves [5] also found stress exponents that were in the range of 6 to 7 for the tensile creep of *c*-axis Tyco filaments at 1600 to 1800° C. Since these values were not calculated directly from differential strain-rate tests, they may not represent constant structure data although they are in good agreement with those of the present study. For the same type of sapphire filaments, Tressler and Barber [6] found higher *n* values, ranging from 8.5 at 1775° C to 12.4 at 1875° C, using differential strain-rate results at several orders of magnitude higher strain-rates than those of Gooch and Groves [5].

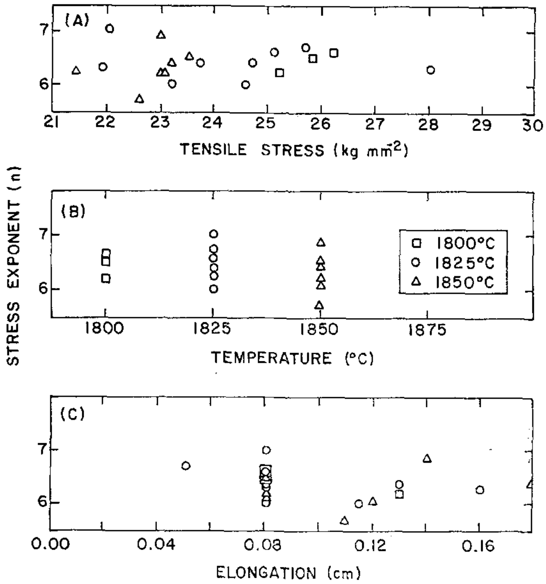

Figure 5 The stress exponent, n, calculated from $n = \Delta \ln \dot{\epsilon} / \Delta \ln \sigma$ assuming a deformation equation of the form of Equation 2, as a function of elongation, tensile flow stress, and temperature.

One can calculate from differential strain-rate data the activation volume V^*, given by the relation

$$V^* = RT \frac{\partial \ln \dot{\gamma}}{\partial \tau} \simeq RT \left(\frac{\Delta \ln \dot{\epsilon}}{\Delta \sigma}\right) \frac{1}{\cos \theta \cos \Phi} \, . \qquad (4)$$

Fig. 6 illustrates that for the present study V^* is a decreasing function of stress. This result is in accord with the results of Conrad *et al.* [2] and Bertolotti and Scott [3] for basal slip, and Tressler and Barber [6] for pyramidal slip. It is also noted that the present activation volumes are considerably smaller than those determined for the deformation of the *c*-axis Tyco filaments (for an equivalent extrapolated stress level) which are plotted in the same figure.

Employing both differential temperature and differential strain-rate tests, activation enthalpies were calculated using the relation

$$\left(\frac{\partial \ln \dot{\epsilon}}{\partial \sigma}\right)_T \left(\frac{\partial \sigma}{\partial T}\right)_{\dot{\epsilon}} = \Delta H / RT^2 \qquad (5)$$

$$\simeq \left(\frac{\Delta \ln \dot{\epsilon}}{\Delta \sigma}\right)_T \left(\frac{\Delta \sigma}{\Delta T}\right)_{\dot{\epsilon}} \, .$$

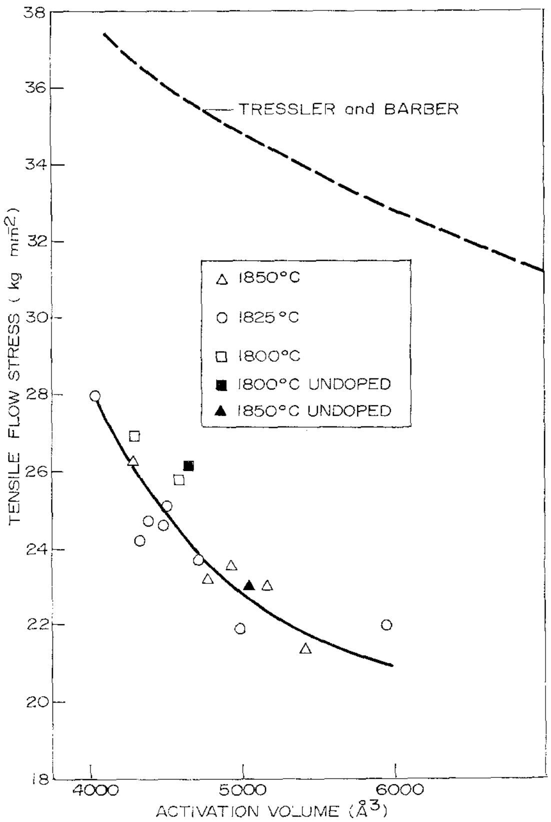

Figure 6 Activation volume (V^*) versus tensile flow stress for Ti^{4+}-doped *c*-axis sapphire filaments.

This equation is only valid when the applied stress is a unique function of strain-rate for a given structure [17]. This situation appears to be the case for the present study since the flow stresses are reproducible. The activation enthalpies calculated ranged from approximately 115 to 170 kcal mol^{-1}.

Taking the low flow stress from a given strain-rate change as the reference stress, activation enthalpies were plotted as a function of stress. As Fig. 7 illustrates, the activation enthalpy appears to be a decreasing function of stress. Using the temperature at which the differential strain-rate test was conducted as the reference temperature, the activation enthalpy was plotted versus temperature and, as shown in Fig. 8 appears to be an increasing function of temperature.

Tressler and Barber [6] obtained activation enthalpies for the deformation of *c*-axis Tyco filaments by performing differential strain-rate and differential temperature tests. Their values of around 80 kcal mol^{-1} are considerably smaller than those obtained here. Because their filaments flowed at a higher stress level for a given temperature and strain-rate than did the Ti^{4+}-doped specimens of the present study, and their activation volumes were substantially higher, an attempt was made to calculate for both sets of data the activation enthalpy at zero effective stress, ΔH_0. This quantity is given by the relation [17]

$$\Delta H_0 = \Delta H + \int_0^{\tau^*} V^* \, \mathrm{d}\tau^* \tag{6}$$

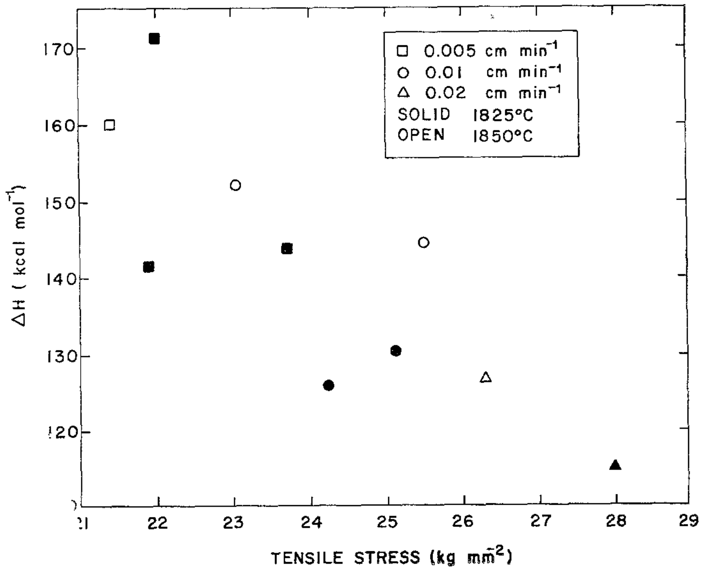

Figure 7 Activation enthalpies versus flow stress for Ti^{4+}-doped *c*-axis sapphire filaments.

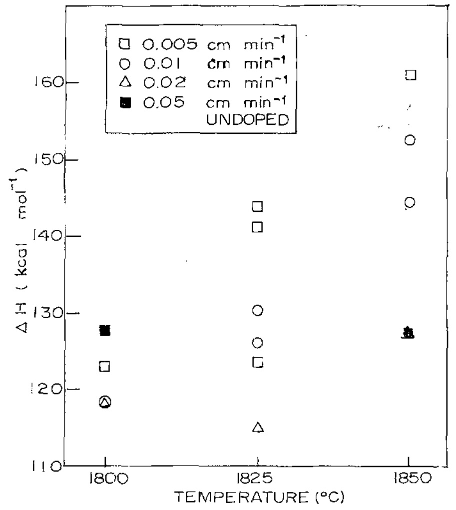

Figure 8 Activation enthalpies versus temperature for Ti^{4+}-doped *c*-axis sapphire filaments.

where ΔH represents the thermal contribution to the total activation enthalpy and the integral quantity represents the mechanical contribution. To evaluate the integral quantity, it was necessary to extrapolate the V^* versus σ curves to zero stress and integrate. Due to the relatively high stress levels and limited stress range over which deformation occurred this integration could only be approximated. The mechanical contributions to the total activation enthalpy obtained for Tressler and Barber's results and for the present study, are 13.8 and 9.3 kcal mol^{-1}, respectively. The lowest activation enthalpy obtained in the present study was approximately 115 kcal mol^{-1} and the highest approximately 170 kcal mol^{-1}. Assuming the same error in both extrapolations, it appears that the ΔH_0 values are distinctly different for the two studies. It is evident that the zero stress activation enthalpy obtained for the present study in this manner is considerably smaller than one would expect from extrapolating Fig. 7 to zero stress. This difference could be an indication of the error involved in the extrapolation or it could indicate that the stress dependence of the activation enthalpy is not, in reality, as great as that indicated in Fig. 7.

3.2. Undoped *c*-axis sapphire

Three undoped samples were available for comparing the results for pure sapphire to those for Ti^{4+}-doped sapphire. Table I summarizes the data for these samples. It is remarkable that these values cannot be distinguished from those for the doped specimens. Likewise, the stress-elongation curves are very similar to those for the doped specimens. The fact that there were no detectable changes in either the flow stresses or activation parameters indicates that Ti^{4+} solid solution strengthening is not operable for sapphire in the concentration, orientation and temperature regime studied.

3.3. Rate-controlling mechanisms

The theories available for both deformation evidenced by pure dislocation climb and by dislocation glide rate limited by climb predict an activation enthalpy for deformation equal to that for self-diffusion [14, 15]. In sapphire this value would presumably be for the larger O^{2-} ion where the activation enthalpy according to Oishi and Kingery [16] is 152 kcal mol^{-1}. With corrections to zero stress and recognition of the considerable scatter in the data, the present activation enthalpies do not rule out the possibility of an O^{2-} diffusion-controlled deformation mechanism.

Nabarro [15] also predicts $n = 3$ for diffusion through the lattice and $n = 5$ for diffusion along dislocation cores, while Weertman [14] predicts $n = 4.5$. The present stress exponent values, ranging from 6 to 7 are not consistent with a diffusion-controlled mechanism. Gooch and Groves [5] found stress exponents in this range. They suggested that overcoming a Peierls-Nabarro stress was the rate-controlling mechanism in the creep deformation of *c*-axis Tyco filaments at low strain-rates via the slip system $\{\bar{1}011\}\langle 0\bar{1}11\rangle$.

TABLE I Flow stresses (at a cross-head speed of 0.005 cm min^{-1}) and activation parameters for the undoped *c*-axis Arthur D. Little sapphire filaments.

Sample	Temperature (°C)	σ_{flow}(kg mm^{-2})	V^* (Å^3)	ΔH(kcal mol^{-1})	n
1	1850	23.0	5056	127.4	6.2
2	1850	21.6	–	–	–
3	1800	26.2	4669	127.6	6.6

Equation 1 has been used to describe deformation when overcoming a Peierls-Nabarro stress is the rate-controlling mechanism. Taking the logarithm of this equation and solving for the activation enthalpy, one obtains

$$H(\tau^*) = RT\ln(\nu/)\,\dot{\gamma}. \qquad (7)$$

Therefore, $H(\tau^*)$ should be an increasing function of T at constant ν and $\dot{\gamma}$. In the present work the activation enthalpy does appear to be an increasing function of T.

In Equation 1 the activation enthalpy is a decreasing function of stress and this appears to be in agreement with the present study. On the other hand, Equation 2, which is indicative of dislocation climb being the rate-controlling mechanism, has an activation enthalpy which is relatively independent of stress.

Evans and Rawlings [17] indicate that for a Peierls-Nabarro rate-controlling mechanism, the activation volume is independent of strain and this is true of the present study. Also, the magnitudes of the present activation volumes are not inconsistent with the overcoming of a Peierls-Nabarro stress as the rate-controlling mechanism. The V^* values obtained here range from approximately 4000 to 6000Å^3. Conrad *et al.* [2] also obtained values in this range for Peierls-Nabarro rate-controlled basal slip deformation.

In the case of the Ti^{4+}-doped sapphire the predominant defects introduced would very likely be cation vacancies [18]. If the rate-controlling mechanism were cation-defect diffusion-controlled climb in the current study, the aluminium vacancies introduced would have greatly increased the strain-rates for a given flow stress (or greatly lowered the flow stress for a given strain-rate) for the doped samples compared to the undoped samples as observed by Hollenberg and Gordon [18] for Ti^{4+}-doped polycrystalline Al_2O_3. The fact that this result was not observed further suggests a Peierls-Nabarro rate-controlling mechanism or O^{2-} controlled climb in the present study.

4. Microscopic observations

Optical examination of the deformed filaments revealed slip traces emerging every 120° around the filament axis in accord with the three-fold symmetry of sapphire about the c-axis. Qualitative examinations revealed no obvious differences between the slip trace morphologies and geometries seen here and those reported by Tressler and Barber [6] who have suggested $\langle 10\bar{1}1\}$ $\langle 01\bar{1}1\rangle$ slip. Thus, it is inferred that the deformation observed in this study occurred via the same slip system.

Very limited examination of ion-thinned undeformed specimens in the transmission electron microscope demonstrated a total absence of dislocations in the as-grown crystals. TEM micrographs of deformed specimens revealed a distinctive dislocation substructure of non-basal dislocations. The elucidation of the characteristics of this dislocation substructure is the subject of a separate study.

5. Summary and conclusions

Significant plastic deformation ($\simeq$ 7% plastic strain) of undoped and Ti^{4+}-doped c-axis single crystal Arthur D. Little sapphire in uniaxial tensile tests at constant strain-rate was observed from 1800 to 1850° C. The stress exponent values calculated from differential strain-rate data ranged from 6 to 7 and were independent of temperature, stress and the amount of plastic deformation. The activation volumes calculated from differential strain-rate data decreased with increasing stress and were independent of the amount of plastic deformation. The activation enthalpies calculated from differential temperature and differential strain-rate tests ranged from approximately 115 to 170 kcal mol^{-1} and appeared to be a decreasing function of stress and an increasing function of temperature.

Comparing the flow stresses and activation parameters of the Ti^{4+}-doped and the undoped c-axis sapphire filaments investigated here, it was found that the Ti^{4+} dopant had no effect on these, ruling out the possibility of a cation defect diffusion rate-controlling deformation mechanism.

The most probable rate-controlling mechanism appears to be the thermally activated overcoming of a Peierls-Nabarro stress since (a) V^* is independent of strain and has magnitudes not inconsistent with such a mechanism, (b) the stress exponent values do not fit a diffusion rate-controlling process model and (c) the activation enthalpies appear to be a decreasing function of stress and an increasing function of temperature. However, an O^{2-} diffusion rate-controlling mechanism cannot be ruled out as the range of activation enthalpies obtained here include the 152 kcal mol^{-1} activation enthalpy for the diffusion of O^{2-} in Al_gO_3.

The estimated zero stress activation enthalpy for the present Arthur D. Little c-axis Ti^{4+}-doped sapphire appears to be distinctly different from that of the porous Tyco *c*-axis sapphire filaments of Tressler and Barber [6] and, along with significant differences in flow stresses and the other activation parameters, suggests different rate-controlling deformation mechanisms for the two materials in the temperature, stress, and strain-rate ranges studied.

Scanning electron and optical microscopic examination of deformed filaments revealed a slip trace morphology apparently identical to that of Tressler and Barber [6] indicating the operation of the $\{10\bar{1}1\}\langle\bar{1}101\rangle$ slip system.

References

1. H. CONRAD, *J. Amer. Ceram. Soc.* **48** (1965) 195.
2. H. CONRAD, G. STONE and K. JANOWSKI, *Trans. Met. Soc. AIME* **233** (1965) 889.
3. B. L. BERTOLOTTI and W. D. SCOTT, *J. Amer. Ceram. Soc.* **54** (1971) 286.
4. A. H. HEUER, R. F. FIRESTONE, J. D. SNOW and J. TULLIS, “Proceedings of the Conference on Ceramics in Severe Environments” (Raleigh, N.C., 1970) pp. 331-340.
5. D. J. GOOCH and G. W. GROVES, *J. Mater. Sci.* **8** (1973) 1238.
6. R. E. TRESSLER and D. J. BARBER, *J. Amer. Ceram. Soc.* **57** (1974) 13.
7. T. P. JONES, R. L. COBLE and C. J. MOGAB, *ibid* **52** (1969) 331.
8. J. S. HAGGERTY, U.S. Air Force Materials Lab. Technical Report AFML-TR-73-2 (1973).
9. R. E. TRESSLER and R. L. CRANE, “Advanced Materials: Composites and Carbon”, A Symposium of the *Amer. Ceram. Soc.* April 1971, Chicago, Ill. pp. 59-65.
10. P. D. S. ST. PIERRE, *Amer. Ceram. Soc. Bull.* **39** (1960) 264.
11. R. J. BRATTON, *J. Appl. Phys.* **42** (1971) 211.
12. M. L. KRONBERG, *J. Amer. Ceram. Soc.* **45** (1962) 274.
13. D. J. GOOCH and G. W. GROVES, *Phil. Mag.* **28** (1973) 623.
14. J. WEERTMAN, *J. Appl. Phys.* **28** (1957) 362.
15. F. R. N. NABARRO, *Phil. Mag.* **16** (1967) 231.
16. Y. OISHI and W. D. KINGERY, *J. Chem. Phys.* **33** (1960) 480.
17. A. G. EVANS and R. D. RAWLINGS, *Phys. Stat. Sol.* **39** (1969) 9.
18. G. W. HOLLENBERG and R. S. GORDON, *J. Amer. Ceram. Soc.* **56** (1973) 140.

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