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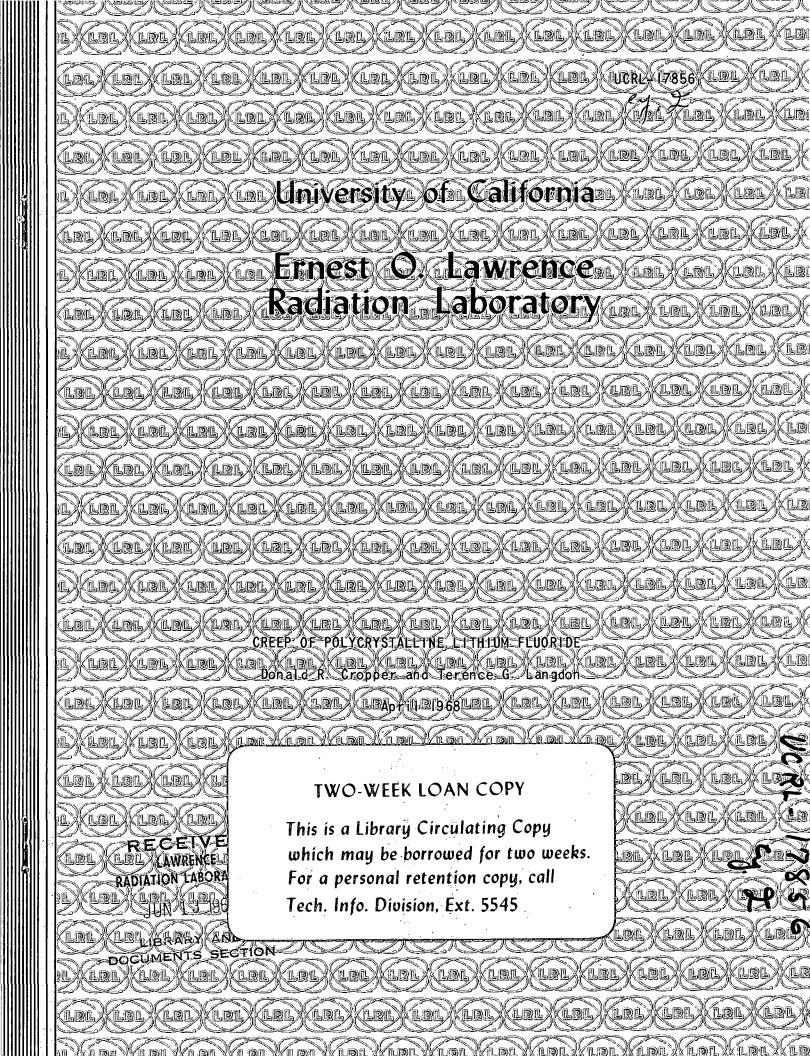
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Authors

Cropper, Donald R. Langdon, Terence G.

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Donald R. Cropper

and

Terence G. Langdon

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Donald R. Cropper and Terence G. Langdon

Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Mineral Technology, College of Engineering,
University of California, Berkeley, California

ABSTRACT

The creep behavior of polycrystalline lithium fluoride under conditions of constant stress was investigated over the temperature range from 300°C to 550°C and found to be essentially similar to that observed in pure metals. The measured activation energy for steady-state creep was of the anticipated magnitude for diffusion of the fluorine ion, and the results suggest that the rate-controlling mechanism is some form of dislocation motion rather than the stress-directed diffusion of vacancies.

^{*} Now at Department of Surface Physics, Cavendish Laboratory, University of Cambridge, Cambridge.

I. INTRODUCTION

Whilst the creep of pure polycrystalline metals is fairly well documented for temperatures greater than \circ 0.5 T_m , where T_m is the melting point in degrees Kelvin, there is at present only limited information on the creep behavior in ionic and covalently bonded materials. Furthermore, many of the results so far published on ceramic polycrystals have tended to indicate a linear relationship between the steady-state creep rate and stress (e.g., Folweiler 1961, Barmore and Vandervoort 1965²), even at high stresses, which suggests that creep in these materials is controlled by the stress-directed diffusion of vacancies either through the lattice (Nabarro 1948, 3 Herring 19504) or along the grain boundaries (Coble 1963⁵). This contrasts with the evidence in metals, where diffusional creep is usually only of importance under conditions of very low stress and at temperatures near the melting point (McLean 1966⁶), although recent evidence (e.g., Bernstein 1967⁷) indicates that in some metals it may also be important for low stress levels at more moderate temperatures.

These results suggest, therefore, that the creep behavior of ionic polycrystals may be markedly different from that of metals. However, in a recent creep study on polycrystalline sodium chloride, Burke and Sherby (1967)⁸ showed that their results were closely similar to those obtained for pure metals, with the creep rate proportional to stress to the fifth power. To further check this apparent anomaly, the present investigation was initiated on polycrystalline lithium fluoride, this material being chosen to extend the observations to a fluoride whilst at the same time retaining the rock salt structure, and also to provide

creep data on a material for which no such information is currently available.

II. MATERIALS AND TECHNIQUES

The polycrystalline lithium fluoride was provided by the Honeywell Research Center (Hopkins, Minnesota) in the form of a rod of 4.65 mm diameter. This rod was produced by the extrusion of a single crystal at 500°C, using a technique essentially similar to that described by Stokes and Li (1963)⁹ for the production of polycrystalline sodium chloride. The rod was transparent and free of any visible porosity under the optical microscope, and the density, determined by weighing in air and water, was in close agreement with that of LiF single crystals. In the extruded condition, the grain size, determined by the linear intercept method, was $\sqrt{7.7}$ grains/mm. The major impurities in ppm, revealed by spectrographic analysis and reported as oxides of the elements indicated, were Mg:10, Ag:5, Cu:5, Al:10, Ca:4 and Si:150.

Specimens were cut to lengths of ~ 6.1 mm using a wire saw with an abrasive of 60 g. boron carbide in 100 ml glycerin and 40 ml water. Each specimen was mounted in a special jig, and the ends polished so that they were accurately perpendicular to the cylinder axis. Prior to testing, specimens were annealed in air for 3 hours at temperatures of either 600°C or 750°C, to produce uniform equi-axed grain sizes of $\sim 160 \mu$ m and $\sim 3000 \mu$ m respectively. Specimens were tested in compression in the temperature range 300-550°C ($\sim 0.50-0.72$ T_m), using a small dead-load testing machine similar to that described by Sherby (1958). The total strain was continuously recorded with a linear variable differential transformer having a sensitivity of $\pm 5 \times 10^{-5}$. Elevated

temperatures, obtained by a small resistance furnace positioned around the specimen, were constant to within ±1°C of the reported values. To maintain conditions of constant stress, additional pre-determined load increments were added at true strain intervals of 0.01, these increments being calculated by assuming constancy of volume and by neglecting any barrelling that may take place.

III. EXPERIMENTAL RESULTS

Preliminary tests showed that the material exhibited the primary and secondary regions of creep usually associated with a metal; this observation confirms that made on polycrystalline sodium chloride (Burke and Sherby 1967). 8

In pure metals, the steady-state creep rate, $\hat{\epsilon}$, may often be expressed by an equation of the form

$$\dot{\hat{\epsilon}} = A \sigma^{n} \exp \left(-Q/RT\right) \tag{1}$$

where σ is the applied stress, Q is the activation energy for creep, R is the gas constant, T is the temperature in degrees Kelvin, and A and n are constants.

A determination of the stress exponent, n, aids in distinguishing between various rate-controlling mechanisms, since diffusional creep requires that n = 1 whereas models based on the movement of dislocations through the lattice require n = 3 or greater (e.g., Weertman 1955, 11 1957 12). To avoid experimental scatter between specimens, n is best determined from one specimen by measuring $\hat{\epsilon}$ for a series of different stresses under isothermal conditions. Tests were therefore carried out

in which the stress was maintained constant until steady-state creep was reached, and then instantaneously changed and maintained constant until the creep rate was again steady. Further changes in stress were later made, at true strain intervals of $\infty.03$, and the steady-state creep rate recorded in each case. With this technique, the value of ε for any given stress was found to be independent of whether this stress was reached by an upwards or downwards change.

The results are shown in Fig. 1, for both the small ($\sim 160 \mu m$) and large ($\sim 3000 \mu m$) grain sizes. Owing to the difficulty of determining the point at which the specimen first passed into the steady-state region, the value of $\dot{\epsilon}$ associated with the initial stress was invariably somewhat higher than anticipated from the subsequent points. For completeness, these points are marked with an asterisk in this, and the subsequent figures, but were discounted in determining the line of best fit from a least squares analysis. The results in Fig. 1 show clearly that a direct relationship exists between $\dot{\epsilon}$ and σ , and, within the limits covered by these experiments, this relationship is independent of temperature and grain size. For both grain sizes, the stress exponent, n, is of the order 7-8.

To determine the activation energy, Q, a series of tests were carried out on the smaller grained material in which rapid changes in temperature, of about 20°C , were made at regular increments of strain. By this procedure, the structure is assumed to remain constant immediately before and after such changes (Tietz and Dorn 1956), 13 and Q is then calculated from the instantaneous creep rates just preceding ($\hat{\epsilon}_1$) and immediately following ($\hat{\epsilon}_2$) an abrupt change in temperature from T_1 to

 T_2 . Thus, from Eq. (1), it follows that

$$Q = \frac{\partial \ln \dot{\varepsilon}}{\partial (-1/RT)} \simeq \frac{\Delta \ln \dot{\varepsilon}}{\Delta (-1/RT)} = \frac{R \ln (\dot{\varepsilon}_2/\dot{\varepsilon}_1)}{(T_2-T_1)/T_1T_2}$$
(2)

Cyclic temperature tests of this type were carried out over the temperature range $400-550^{\circ}\text{C}$, with the initial stress chosen in each case to give $\dot{\epsilon}_1 \sim 2 \times 10^{-6}$ sec $^{-1}$. The results yielded an average value of $Q \sim 50.1$ kcal/mole, with Q apparently independent of temperature in the range covered, and independent of strain up to true strains in excess of ~ 0.30 . As with metals (Dorn 1957), 14 similar values of Q were obtained in both the primary and steady-state regions, and these were independent of whether the temperature was increased or decreased. An isolated test on the larger grained material between 480°C and 500°C yielded similar results.

IV. DISCUSSION

The value obtained for the activation energy for steady state creep corresponds closely to the reported activation energy (Q_D) for diffusion of the fluorine ion in LiF single crystals (~ 50.7 kcal/mole; Eisenstadt 1963), ¹⁵ as shown in Table I. The value is somewhat larger than those reported for diffusion of the lithium ion, thereby suggesting that, whilst both ions must diffuse at the same rate to maintain electrical neutrality, creep is controlled principally by volume anion diffusion. A similar conclusion arises from the results of Chang (1960)¹⁶ for creep of Al₂O₃. However, the value for anion diffusion in LiF refers to the intrinsic region, which is generally taken as temperatures greater than 560° C. In the temperature range used for these tests ($400-550^{\circ}$ C), Q_D

for Li is very much lower, but no value is presently available for the extrinsic diffusion of the fluorine ion. In the absence of such data, the reason for close correlation with the value for the intrinsic region is not clear, but it should be noted that experiments on sodium chloride have shown that, whilst the activation energy for cation self-diffusion changes abruptly at the temperature (~550°C) separating the intrinsic and extrinsic regions, Q_{D} is essentially constant for anion diffusion in the temperature range 300-700°C (Barr et al. 1960, 17 1965 18). It is possible that this trend may also pertain in LiF. Alternatively, the results may be similar to those reported by Christy (1954, 19 195620) for NaBr, NaCl and AgBr, in which the activation energies for creep were found to be higher than the known values for self-diffusion. This difference was ascribed (Christy 1959)²¹ to the energy required for the formation of vacancies, which, it was suggested, was significant in ionic crystals but not in metals. In either case, the magnitude of Q obtained experimentally (∿50.1 kcal/mole) suggests that creep is controlled by lattice diffusion of the fluorine ion.

The slope of the lines shown in Fig. 1 strongly suggests that the creep of polycrystalline LiF is similar to that observed in pure polycrystalline metals. However, whilst Fig. 1 gives an indication of the value of n, a better approach is to plot the ratios of the strain rates and stresses before and after the change in stress. If n is independent of temperature and grain size, as suggested in Fig. 1, it follows that such a plot should reduce all points to a single line. As shown in Fig. 2, this plot has the additional advantage of reducing the spread on the data, and does not strictly require that creep be within the steady-

state region. From Fig. 2., a least squares analysis yielded n = 7.6, which suggests that creep is controlled by some form of dislocation motion, either by the climb of dislocations over barriers (Weertman 1955, 11 1957¹²) or by the non-conservative motion of jogged screw dislocations (Barrett and Nix 1965²²).

The results in Fig. 2 clearly deviate from the predictions arising from Nabarro-Herring diffusional creep, as indicated by the line of slope n = 1. Two other factors serve to negate the possibility of diffusional creep. Firstly, whilst theories for creep based on dislocation motion predict that $\dot{\epsilon}$ is independent of the average grain diameter, d, the theories of diffusional creep suggest that $\dot{\epsilon}$ is inversely proportional to d^2 or d^3 for lattice diffusion or grain boundary diffusion respectively. Thus the stress-directed diffusion of vacancies requires that ε increases with decreasing grain size, but an examination of Fig. 1 shows clearly that this is not realized in the present investigation. With a difference in grain size of greater than an order of magnitude, there is no significant difference in the creep rates for the tests at 400°C and 450°C. Furthermore, at 550°C the situation is reversed since $\dot{\epsilon}$ for the larger grain size is slightly faster than that for the smaller grain size; this difference may be due to the use of specimens having only a small number of grains in the cross-section.

Secondly, it is possible to calculate the anticipated creep rate if diffusional creep is the operative mechanism. Considering lattice diffusion, since this has the weaker grain size dependence, Herring (1950) has shown that the creep rate is given by

$$\stackrel{\bullet}{\varepsilon} = \frac{B}{d^2} \frac{\Omega \sigma}{kT}$$
 (3)

where B is a constant ($^{\circ}10$ for equiaxed polycrystals), $^{\Omega}$ is the volume of a vacancy, D is the lattice self-diffusion coefficient and k is Boltzmann's constant. Using this relationship, the values calculated for $^{\circ}$ are some orders of magnitude slower than those observed experimentally, even for the smaller grain size (e.g., for the small grain size, taking $^{\Omega}$ = 1.65 x 10 cm³, T = 723°K, and D for the slower moving ion, the calculated creep rate is $^{\circ}$ $^{\circ}$ x 10 sec⁻¹ at a stress of 2000 p.s.i., in contrast to the observed rate of $^{\circ}10^{-5}$ sec⁻¹).

McLean and Hale (1961)²³ and Sherby (1962)²⁴ have shown that the steady-state creep data for a number of metals obey the relationship

$$\dot{\hat{\epsilon}} = A \left(\frac{\sigma}{R}\right)^n \exp\left(-Q/RT\right) \tag{4}$$

where A is a constant related to the stacking-fault energy of the material (Barrett and Sherby 1965) 25 , and the stress is normalized by dividing by Young's modulus E. For a number of materials, all tested at high temperatures and low stresses, this yields a series of straight lines lying in a narrow band. To test the applicability of Eq. (4) to LiF, $^{\epsilon}$ /D was plotted against σ /E, as shown in Fig.3, where the self-diffusion coefficient D = D exp (-Q/RT). The value of E at room temperature was calculated from the single crystal data of Briscoe and Squire (1957) 26 by taking the average of the values obtained for polycrystals by the methods of Voigt and Reuss; the variation of E with temprature

was calculated by extrapolating their data to the temperature range used in this investigation. Since the measured activation energy for steady-state creep was similar to that for the intrinsic diffusion of the fluorine ion, D was calculated by extrapolating the intrinsic fluorine data of Eisenstadt (1963)¹⁵ to the present temperature range.

As shown in Fig. 3, Eq. (3) is well satisfied at the higher temperatures, and all results for both grain sizes then fall on a straight line. At the lower temperatures, at values of $\dot{\epsilon}/D$ greater than $\sim 10^9$ cm⁻², there is an apparent discontinuity in the data, and the points no longer fall on a straight line. This trend is identical to that reported for NaCl (Burke and Sherby 1967)⁸ and for a number of pure metals (e.g., Barrett et al. 1964)²⁷, with the deviation from linearity occurring at approximately the same value of $\dot{\epsilon}/D$ ($\sim 10^9$ cm⁻²) for each material. Furthermore, the line falls within the band obtained for a number of pure metals by Sherby (1962),²⁴ although the slope of the linear portion (n ~ 6.1 for $\dot{\epsilon}/D < 10^9$ cm⁻²) is slightly greater than for most metals (n ~ 5).

Whilst this approach permits a direct comparison with the published data for metals, the analysis is not strictly correct since the model of creep by dislocation climb (Weertman 1957)¹² indicates that it is probably more accurate to write Eq. (4) in the form

$$\dot{\hat{\epsilon}} = \frac{A''}{T} \frac{\sigma^n}{\sigma^{n-1}} \exp \left(-Q/RT\right)$$
 (5)

where A'' is a constant and G is the shear modulus. From Eq. (5) it follows that

$$\frac{\dot{\varepsilon}T}{G} = A'' \left(\frac{\sigma}{G}\right)^n \exp\left(-Q/RT\right) \tag{6}$$

To check this relationship, and to permit a calculation of Q using the dislocation climb model, $\epsilon T/G$ was plotted against σ/G , using values of G calculated from the data of Briscoe and Squire (1957)²⁶ from the average of the Voigt and Reuss approximations. The result is shown in Fig. 4 for the small-grained material. The activation energy was then determined from this figure, since it follows from Eq. (6) that, at a constant value of σ/G and two temperatures T_1 and T_2 ,

$$Q \simeq \frac{\frac{(\mathring{\epsilon}T/G)_2}{(\mathring{\epsilon}T/G)_1}}{\frac{(\mathring{\epsilon}T/G)_1}{(T_2-T_1)/T_1T_2}}$$
(7)

Disregarding the data at the two lower temperatures, since the scatter is then so great that the lines are not well defined, and taking $T_1 = 723^{\circ}K$ and $T_2 = 823^{\circ}K$, Q was estimated as ~ 48.5 kcal/mole in good agreement with the direct experimental value. Since the lines are parallel, it follows that Q is not a function of stress over the limited range studied.

To determine the stress exponent in Eq. (6), ε T exp (Q/RT)/G was plotted against σ/G as shown in Fig. 5, taking the experimental value of 50.1 kcal/mole for Q. As with Fig. 3, there is a marked discontinuity in the data at the lowest temperature (ε T exp (Q/RT)/G greater than 10^3 °K cm² dyne⁻¹ sec⁻¹), and the points at 300°C were therefore excluded in determining the slope of the line as n = 6.6. Whilst this

stress exponent is higher than that predicted theoretically for pure metals, for which n = 4.5, even higher values have been reported in metals in some instances (e.g., Davies 1963), and the value does not preclude dislocation climb as a possible rate-controlling mechanism.

V. CONCLUSIONS

- 1. The creep behavior of polycrystalline lithium fluoride in compression is similar to that observed for pure metals, with the creep curves exhibiting both primary and secondary regions.
- 2. The activation energy for creep in the temperature range 400-550°C is ∿50.1 kcal/mole, which suggests that creep is controlled by lattice diffusion of the fluorine ion.
- 3. At the higher temperatures (>300°C), the steady-state creep rate obeys the relationship $\dot{\epsilon} = A'' \sigma^n \exp{(-Q/RT)/TG^{n-1}}$ where n = 6.6. This relationship appears to break down at values of $\dot{\epsilon}T$ exp (-Q/RT)/G greater than $\sim 10^3$ °K cm² dyne⁻¹ sec⁻¹.
- 4. The results suggest that creep is controlled by a dislocation mechanism, such as the climb of dislocations over barriers, rather than by the stress-directed diffusion of vacancies.

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Table I. Activation Energies for Diffusion in Lithium Fluoride

Intrinsic Region (>560°C)	Extrinsic Region (<560°C)	Reference
$Q_{\overline{D}}(Li^{+})$ $Q_{\overline{D}}(F^{-})$	Q_(Li ⁺) Q_(F ⁻)	
41.7 kcal/mole 50.7 kcal/mole	16.3 kcal/mole -	Eisenstadt 1963 ¹⁵
45.7 kcal/mole -	14.9 kcal/mole -	Haven 1950 ²⁹
43.0 kcal/mole -	15.2 kcal/mole -	Stoebe and Huggins 1966 ³⁰

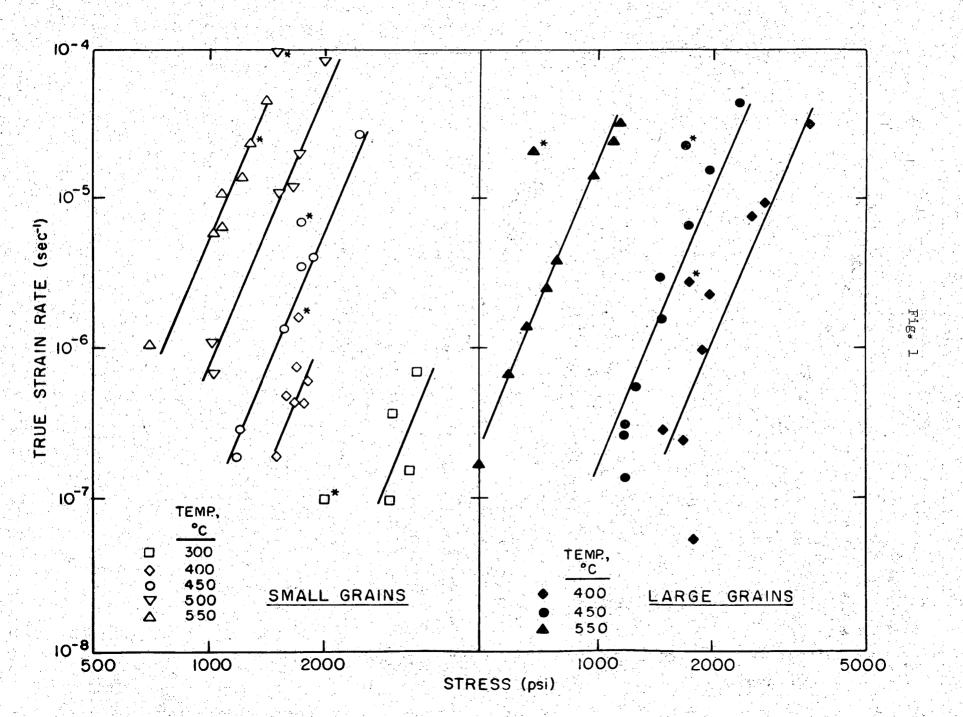
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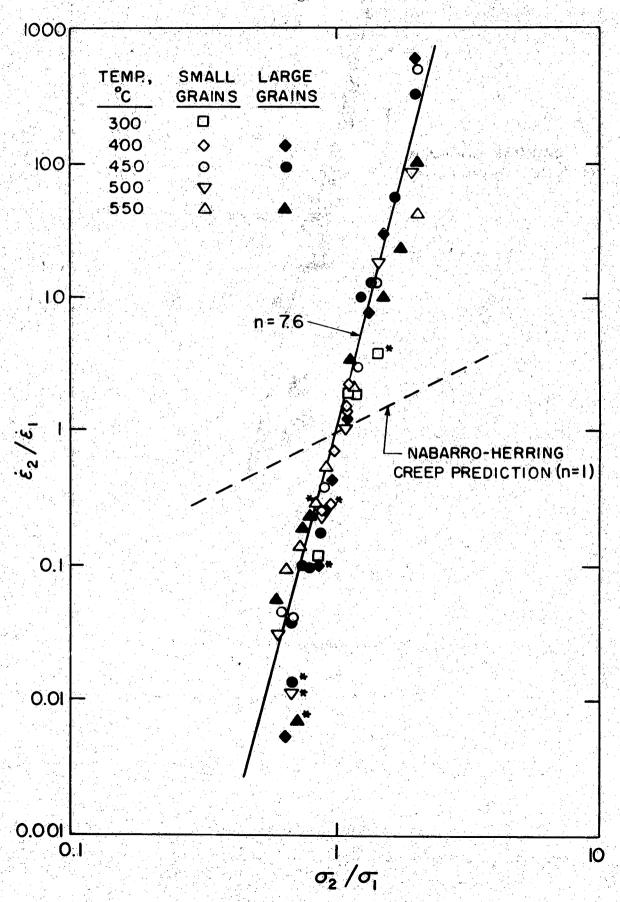
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FIGURE CAPTIONS

- Fig. 1. Creep rate vs. stress for specimens of two different grain sizes ($\sim 160 \mu m$ and $\sim 3000 \mu m$ respectively).
- Fig. 2. Creep rate ratios vs. stress ratios obtained by instantaneous changes in the stress at constant temperature. The prediction arising from Nabarro-Herring diffusional creep is also shown.
- Fig. 3. Diffusion compensated creep rate $(\hat{\epsilon}/D)$ plotted as a function of the normalized stress (σ/E) .
- Fig. 4. Normalized (creep rate x temperature) vs. normalized stress for specimens of the smaller (~160µm) grain size.
- Fig. 5. Temperature-compensated creep rate plotted as a function of the normalized stress to test the applicability of the dislocation climb model of creep.







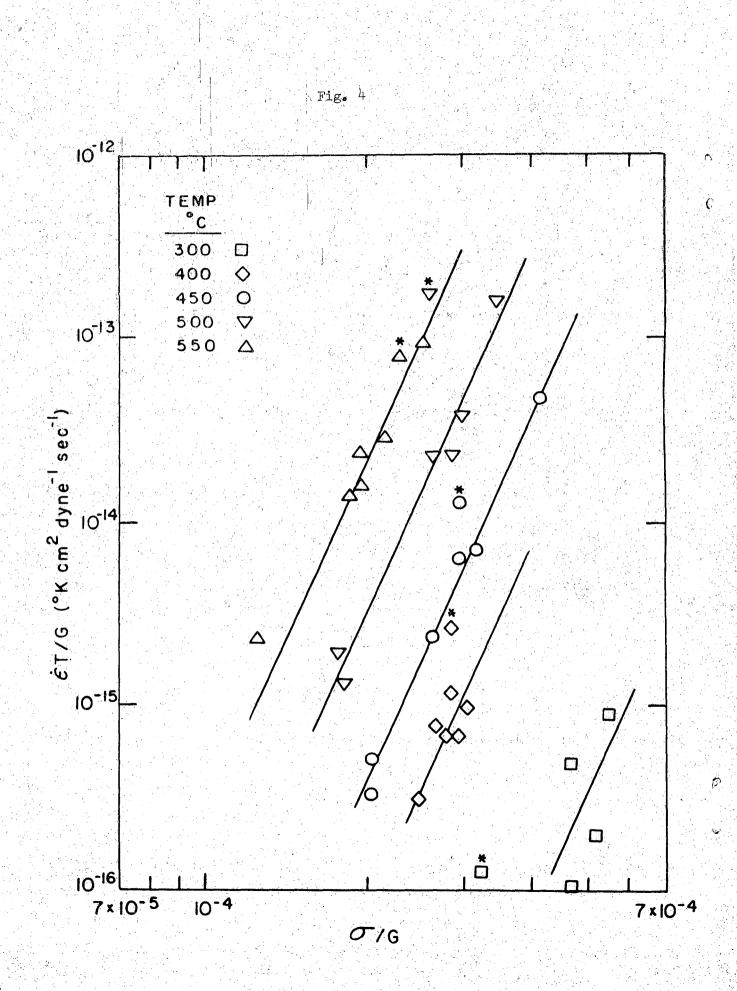
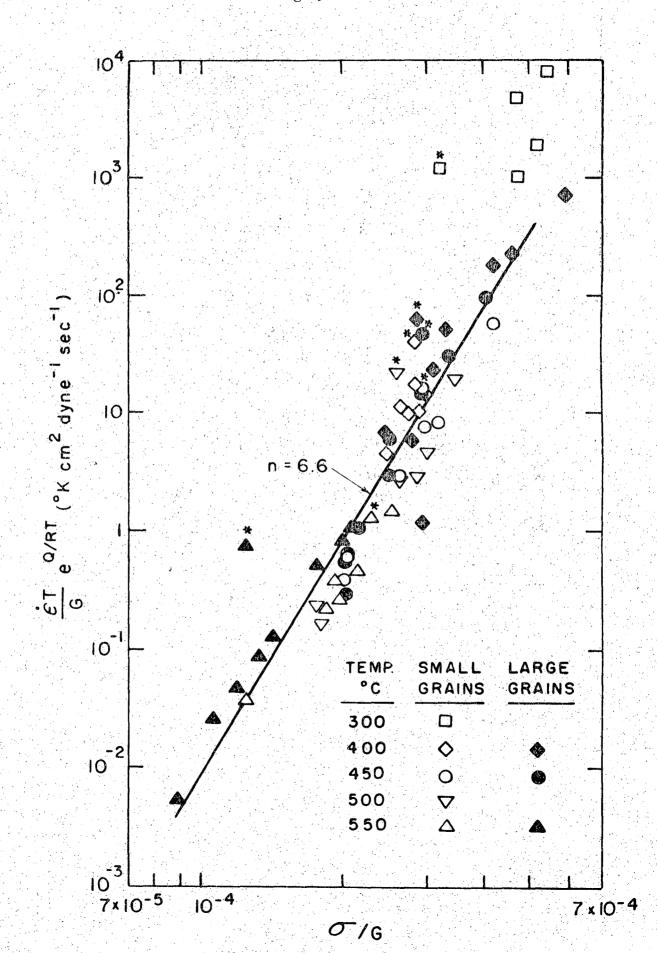


Fig. 5



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