JOURNAL OF MATERIALS SCIENCE 11 (1976) 283–290

Plastic deformation of polycrystalline zirconium carbide

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The compressive yield strength of arc melted, polycrystalline zirconium carbide has been found to vary from 77 kg mm^2 at 1200°C to 19 kg mm^2 at 1800°C. Yield drops were observed with plastic strain-rates greater than 3×10^{-3} sec^{-1} but not with slower strain-rates. Strain-rate change experiments yielded values for the strain-rate sensitivity parameter m which range from 6.5 to 1500°C to 3.8 at 1800°C, and the product $m^*(T)$ was found to decrease linearly with increasing temperature. The deformation rate results are consistent with the Kelly–Rowcliffe model in which the diffusion of carbon assists the motion of dislocations.

1. Introduction

The deformation behaviour and the rate-controlling mechanisms in the transition metal carbides are not well defined, and published data for the polycrystalline forms of the carbides are frequently contradictory. The discrepancies are generally attributed to the use of impure, inhomogeneous, and poorly defined hot-pressed and sintered samples. A major experimental difficulty has been the preparation of gas and pore-free carbides having a well controlled and uniform stoichiometry. Dissolved gases, particularly oxygen, affect noticeably the physical and chemical properties of carbides; likewise the presence of any significant porosity can generally be expected to influence strongly the mechanical properties in that it provides internal discontinuities and crack nuclei.

The use of an arc melting technique to prepare bulk carbides offers a means of overcoming the above problems if the resulting as-cast microstructure can be disrupted by subsequent homogenization treatments. Oxygen contamination can be minimized or even reduced by the careful design of the melting and homogenization procedures.

The present work is concerned with the determination of the compressive yield strength of polycrystalline ZrC in the temperature range 1200 to 1800° C. Also, the variation of the yield strength with plastic strain-rate is examined in this temperature range. The results are discussed in terms of a carbon diffusion model of the deformation mechanism proposed by Kelly and Rowcliffe [1].

2. Experimental

The polycrystalline specimens used for compression testing were diamond saw cut from carbide buttons. The production of the buttons, described in detail elsewhere [2], consisted of the arc melting of powder compacts followed by a homogenization treatment. The samples used in the present work had a C/Zr ratio of 0.94 and contained approximately 400 ppm oxygen. Metallographic examinations of random sections of homogenized buttons revealed negligible porosity and equi-axed grains having a mean diameter of 0.25 mm. The saw-cut specimens having the nominal dimensions 2 × 2 × 2.7 mm were ground on diamond wheels in order to obtain flat and parallel faces. Grinding was followed by polishing with 3 and 1 μm diamond paste.

The samples were tested in vacuum with an Instron unit equipped with a tungsten mesh furnace. Motion was transmitted by tungsten

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rods welded to stainless steel bellows attached at each end of the loading fixture. A sample was sandwiched between two tantalum carbide discs; these discs were harder than the zirconium carbide samples at all temperatures and showed no depressions on them after the testing. Pyrolytic graphite pads were placed between the TaC discs and the tungsten rods to reduce excessive heat conduction to the tungsten rods. A spherically seated loading block made of high strength graphite was used below the lower graphite pad to minimize load eccentricity. The temperatures were measured and controlled to within 10°C with a 97W–3Re versus 75W–25Re thermocouple placed near a sample. A specimen was soaked at the temperature of the experiment for 1 h before the start of a test; during the soaking, the vacuum was stabilized at 10^{-5} mm Hg or lower.

The Instron machine records the load versus cross-head displacement curves from which stress versus strain curves were obtained by using appropriate conversions. Blank tests (without samples) were run at each temperature in order to determine the elastic deflection of the machine fixtures and the TaC and graphite discs; from these experiments, the elastic deflection of the machine and the pads was calculated for all the temperatures used in the investigation. These tests revealed no deviation from linearity in the load versus elongation curves up to the maximum loads used in this investigation, indicating that there was no indicated plastic deformation of the TaC and graphite discs.

The true plastic strain-rates were determined graphically by the method described by Williams [3]. As discussed below, yield drops were observed at strain-rates greater than $3 \times 10^{-3}\,\text{sec}^{-1}$; most of the testing was conducted at lower strain-rates where the yield stresses were taken at a 0.2% plastic strain offset.

The variation of the yield stress with strain-rate was determined at 1500, 1600, 1700, and 1800°C. In these experiments, a specimen was loaded initially at the lowest available cross-head speed until slightly more than 0.2% plastic strain was obtained. At this point, the load was immediately released, and the specimen was allowed to anneal for 30 min. This procedure was repeated at successively higher strain-rates for the same specimen. In order to determine the validity of this experimental approach, a specimen was loaded continuously at the slowest cross-head speed to 1% plastic strain, and the load was immediately removed. After annealing the sample for 30 min, the specimen was reloaded at the same speed. It was observed that the 1% pre-strain and subsequent anneal had a negligible effect on the observed yield stress.

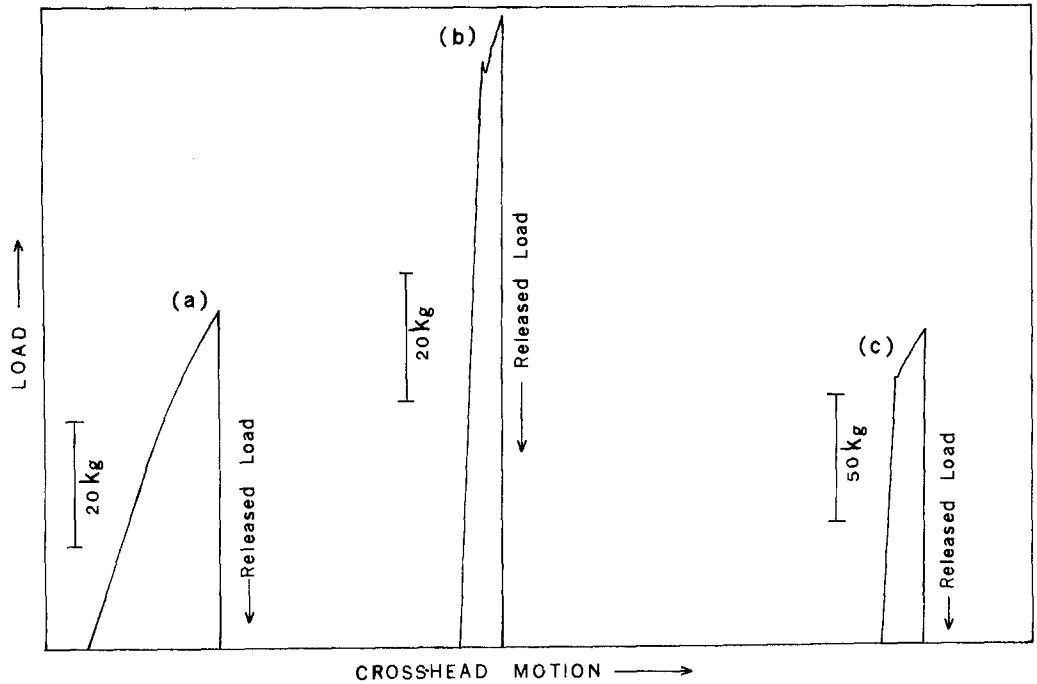

Figure 1 An Instron recorder tracing showing load versus cross-head motion for a ZrC specimen tested at 1700° C, at a strain-rate of $3 \times 10^{-4}\,\text{sec}^{-1}$, (b) $3 \times 10^{-3}\,\text{sec}^{-1}$, (c) $6 \times 10^{-3}\,\text{sec}^{-1}$.

3. Results and discussion

Yield drops were observed with plastic strain-rates greater than $3 \times 10^{-3} \sec^{-1}$, but they were not observed with the slower strain-rates. Fig. 1a is a typical Instron recorder tracing showing load versus cross-head displacement for a specimen tested at 1700° C with a strain-rate of 3×10^{-4} $\sec^{-1}$; there is no yield drop. Figs. 1b and c show that yield drops appear at strain-rates of 3×10^{-3} and $6 \times 10^{-3} \sec^{-1}$, respectively. Yield drops have not been reported previously for transition metal carbides [3, 4] or for single crystal ZrC [4]. In the latter work, the absence of a yield drop was attributed to an excess of initial mobile dislocations and to the use of a soft machine. In the present work, the use of TaC compression pads, in contrast with the graphite pads used in earlier studies [4, 5], was expected to increase the effective machine hardness and to enhance the probability of observing yield drops. With the exception of the strain-rate, the various parameters that can govern the appearance or non-appearance of a yield drop were assumed to be held constant for the series of tests at 1700°C. Such parameters include the specimen chemistry, geometry, and grain size as well as sample alignment and machine hardness. While the determination of the magnitudes of the yield drops was not a goal of the present work, their appearance at the faster strain-rates is in agreement with Williams [3] who has shown that yield drops should be expected at higher strain-rates and for those materials whose strain-rate sensitivity parameters m lie in the range 1 to 10. It is shown below that the values of m for the present specimens lie well within this range.

The compressive yield stresses at the various temperatures are summarized in Fig. 2. There was no observable plastic deformation at temperatures below approximately 1200°C, and specimens tested at these lower temperatures fractured catastrophically into small fragments. The fracture stresses varied considerably for these specimens, and no attempt was made to interpret the data.

At the higher temperatures, the yield strength varies from 755 MN m^{-2} (77 kg mm^{-2}) at 1200° C

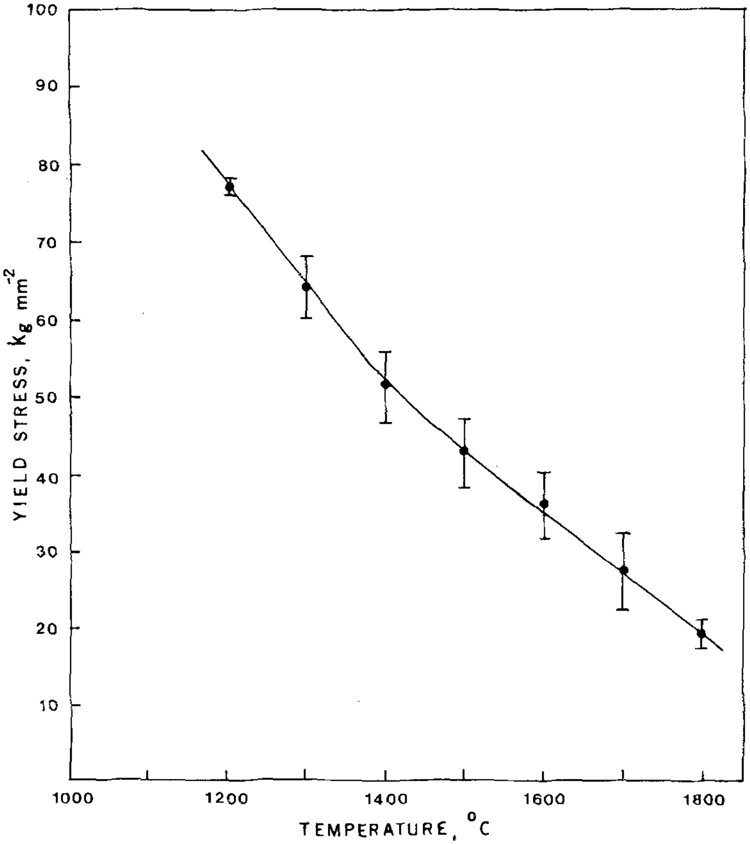

Figure 2 Compressive yield stress of $ZrC_{0.94}$ from 1200 to 1800° C. The arithmetic mean value along with the standard deviation is shown at each temperature.

to 186 MN m^{-2} (19 kg mm^{-2}) at 1800°C, with extensive ductility being observed at temperatures greater than approximately 1500°C. The present yield strength values are nearly eight times greater than those reported for single crystal ZrC [4], and they are greater than the reported values for hot-pressed and sintered carbides of groups IV and V transition metals [6, 7].

A strain-rate sensitivity parameter m was determined for each temperature using the relation:

$$m = \frac{\Delta \ln \dot{\epsilon}}{\Delta \ln \sigma} \qquad (1)$$

where $\dot{\epsilon}$ is the plastic strain-rate, and σ is the 0.2% yield stress. Fig. 3 shows the variation of yield stress with strain-rate for 1600°C and for 1800°C. The values of m calculated from the slopes of such plots were found to be 6.5, 5.4, 4.6, and 3.8 at 1500, 1600, 1700 and 1800°C, respectively.

The relationship between m and the dislocation velocity stress exponent m^* is given by

$$m\sigma^* = m^*\sigma \qquad (2)$$

where σ^* is the effective stress; the addition of an internal stress σ_i to σ^* gives the applied stress σ. This equation is based on the assumptions that the density of mobile dislocations and the internal stress remain constant during a change in strain-rate.

Johnston and Stein [8] have described a method whereby a value for m^* may be obtained by the extrapolation of a plot of m versus plastic strain to zero strain. Fig. 4 shows four such plots and also shows that m^* is essentially equal to m for the strain range used; that is, σ_i is approximately zero at these temperatures. Similar results appear for 1500° C and 1700° C. The product $m^*(T)$ has been shown to decrease with temperature [9] or to either increase or decrease

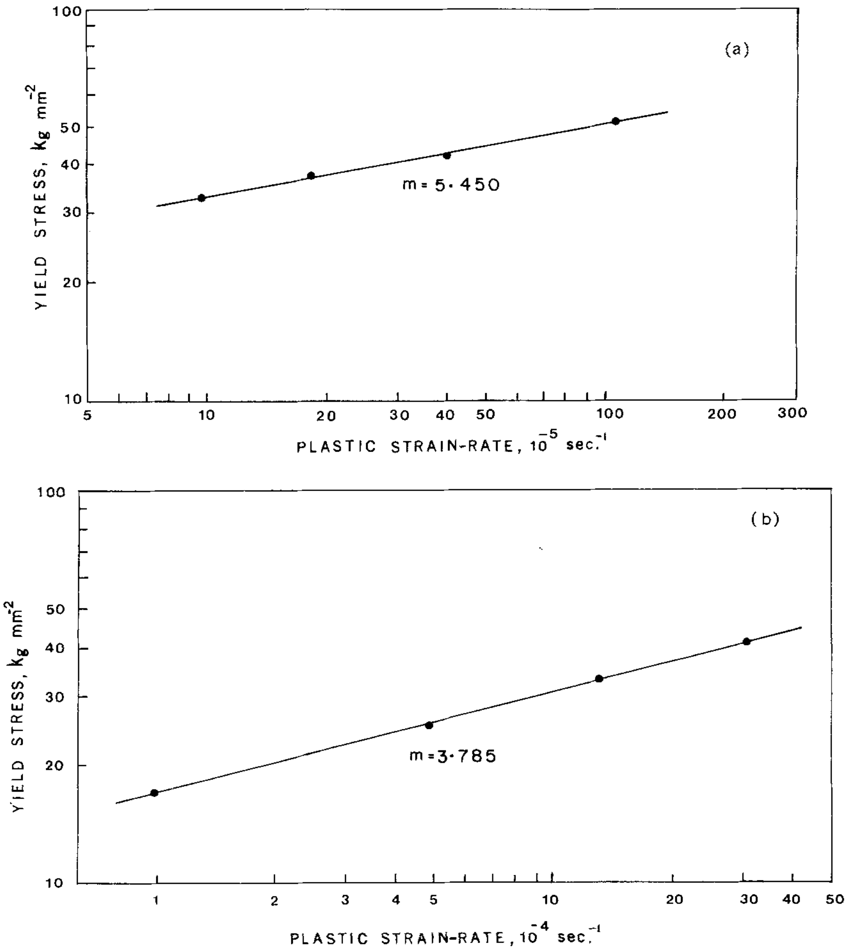

Figure 3 The variation of the yield stress of $ZrC_{0.94}$ with the plastic strain-rate at (a) 1600° C and (b) 1800° C. The lines are drawn by a least square fit.

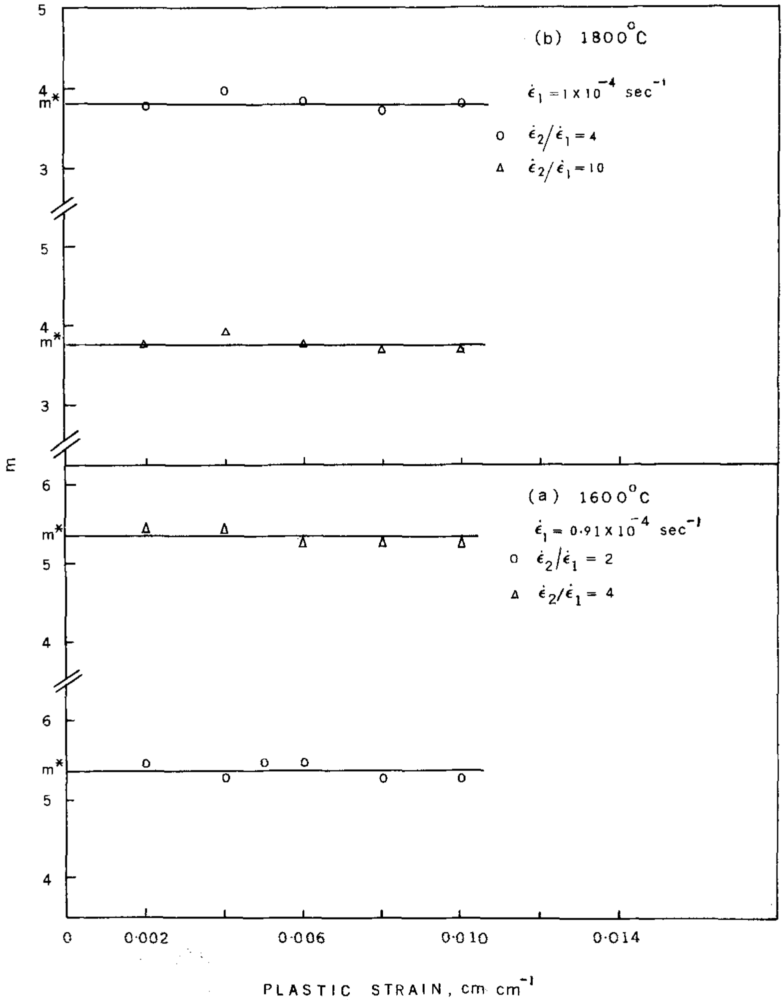

Figure 4 The extrapolation of m versus strain to zero strain to give values for m^*: (a) 1600° C, (b) 1800° C.

with temperature [10]; taking m to be equal to m^*, Fig. 5 indicates that $m^*(T)$ decreases linearly with temperature for polycrystalline $ZrC_{0.94}$. Values for the strain-rate sensitivity parameter have been reported for only two other carbides: Becher [11] determined m to be 13.3 below 1455°C and 4.5 above 1640°C for hot-pressed $TaC_{0.95}$, and Williams [3] found that m varies from 1 to 10 for single crystal TiC at 1400°C. In the latter work, m was found to be a function of the strain-rate in that a plot of $\ln \dot{\epsilon}$ versus $\ln \sigma$ was non-linear.

The analysis of the present data by the use of a variety of exponential type rate equations was carried out. With one exception, all the analyses yielded activation energy values which were either inconsistent with known deformation mechanisms or required observed variable parameters to be constant. The exception is the equation given by Martin *et al.* [6] in their study of the plastic deformation of TaC:

$$\dot{\epsilon} = A(\sigma - \sigma_i) \exp[(\sigma - \sigma_i) V/kT] \exp(-\Delta U/kT) \quad (3)$$

where A is a constant, V an activation volume, and ΔU an activation energy. Their interpretation of this equation was based on a model proposed by Kelly and Rowcliffe [1] for slip in TiC. Briefly, the model is based on the unpinning of Shockley partial dislocations by the diffusion of carbon atoms to alternate octahedral sites in the transition metal carbides having the NaCl type structure. The plastic strain-rate is thus governed by carbon diffusion near dislocations.

Since a test of the rate equation requires knowledge of the activation volume, this quantity was calculated from the relationship:

$$V = kT\frac{\Delta \ln \dot{\epsilon}}{\Delta \sigma} \quad (4)$$

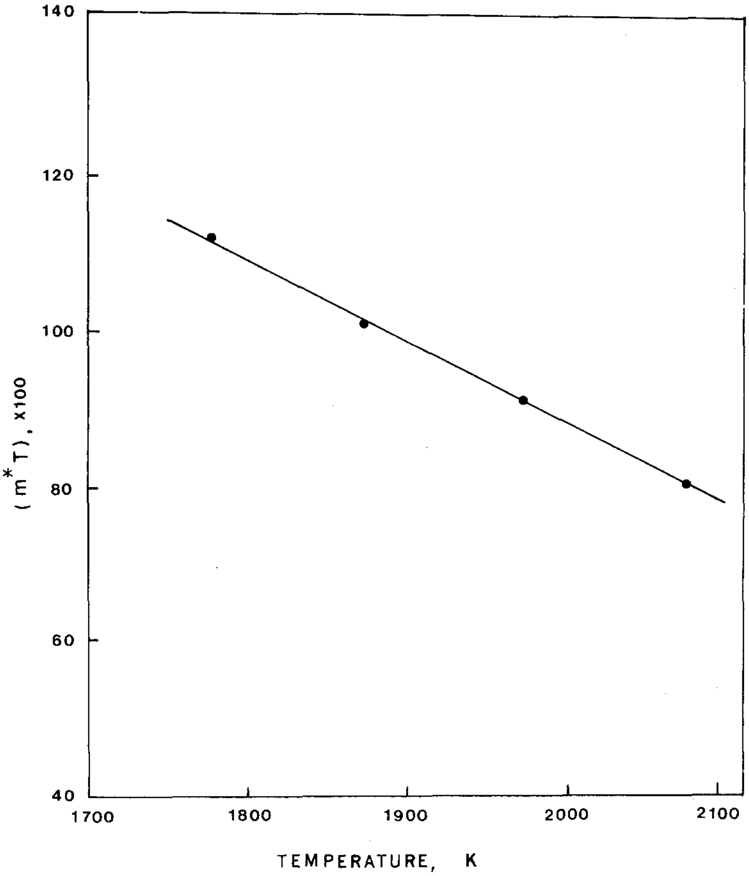

Figure 5 The variation of the product $m^*(T)$ with temperature, showing the inverse relationship discussed by Evans [9].

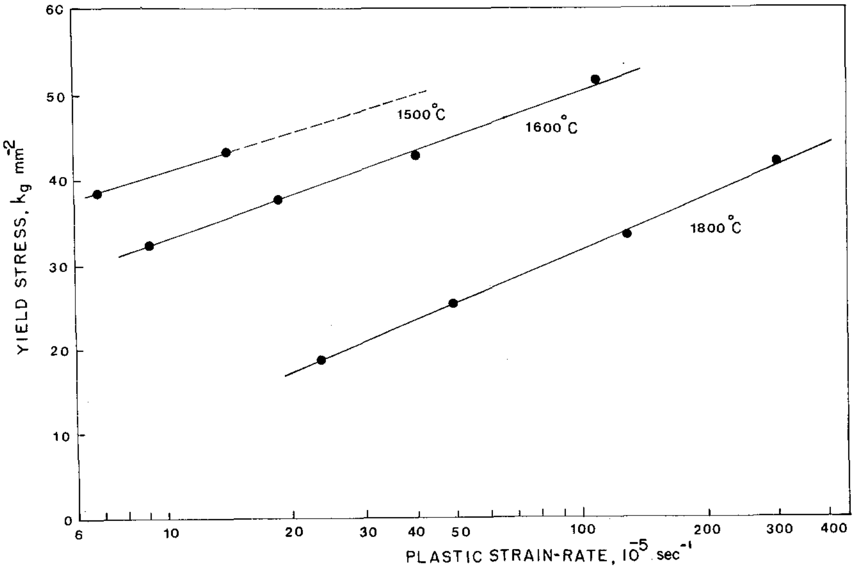

Figure 6 Plots of log $\dot{\epsilon}$ σ necessary for the calculation of the activation volume according to Equation 4.

and the required plots are shown in Fig. 6 for three temperatures. The results yield 392, 366, and 330 Å^3 for 1500, 1600 and 1800° C, respectively. Only two datum points were determined for 1500°C, and an average of the latter two values, 348 Å^3, was used for the subsequent calculations. In the case of ZrC, the appropriate Burgers vector b is $a/2[1\bar{1}0]$; a room temperature lattice parameter of 4.697 Å was determined from Debye Scherrer X-ray patterns of five different specimens.

Adjusting [12] this parameter to temperatures in the range 1200 to 1800° C, the activation volume of 348 $Å^3$ is within 2% of $9b^3$.

The values for the activation volume determined from Fig. 6 are nearly independent of temperature in the reported temperature range, an observation consistent with that observed [13] for a number of materials, e.g. polycrystalline copper, AgBr single crystals, Mg–12% Li, potassium, and several b.c.c. metals and alloys. In the case of the transition metal carbides, a nearly constant ($50b^3$ to $55b^3$) activation volume has been reported only for TaC [14] for applied stresses above 10 kg mm^{-2}.

Taking σ_i to be zero as before, the plot of ($\ln \sigma + \sigma V/kT$) versus $1/T$ shown in Fig. 7 yields an activation energy of 5.2 ± 0.2 eV/atom for $ZrC_{0.94}$; inserting an arbitrary high value of 5 kg mm^{-2} for σ_i decreases the calculated value of ΔU by only 0.1 eV/atom. The diffusion coefficient for ^{14}C in $ZrC_{0.97}$ has been reported to be 4.9 eV/atom by Sarian [15]. This energy is primarily motional energy since the relatively large concentration of carbon vacancies implies a near-zero formation energy; the magnitude of the energy reflects the strong covalent bonding in ZrC [16]. Sarian has also shown that the diffusion activation energy increases with an increasing atom fraction of carbon vacancies, and it would thus be expected that the carbon self diffusion energy in the present $ZrC_{0.94}$ would be somewhat greater than 4.9 eV/atom.

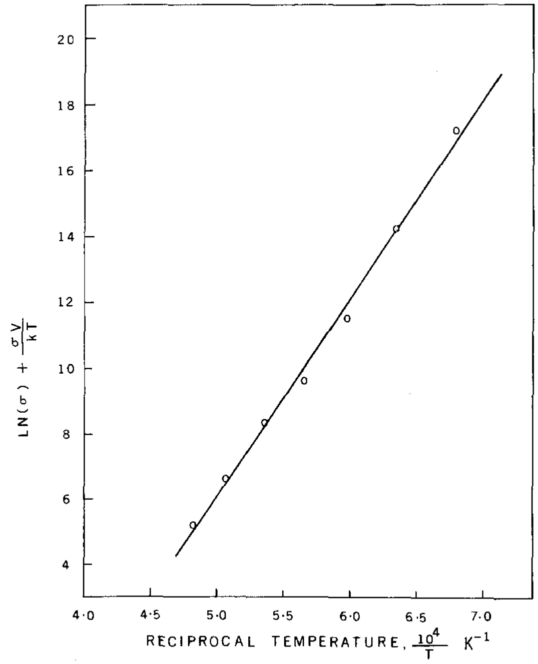

Figure 7 Plot of $\ln \sigma + \sigma V/kT$ versus $1/T$ for $ZrC_{0.94}$. The point at each temperature is the arithmetic mean of all datum points at that temperature. The straight line is drawn by a least square fit.

Babad-Zakhryapina [17] determined the diffusivities of C in polycrystalline $ZrC_{0.96}$ from 1580 to 2080°C and reported an activation energy of 4.9 eV/atom. Neglecting his value for the diffusivity at the high temperature, which does not fall on a straight line Arrhenius plot, an activation energy of 5.9 eV/atom was calculated from the remainder of the data points.

Lee and Haggerty [4] have studied the creep of single crystals of $ZrC_{0.945}$ in the temperature range 1400 to 2000°C and found the activation energy for creep to be 4.8 eV/atom. They used a conventional creep equation:

$$\dot{\epsilon} = k\sigma^5 \exp\left(\frac{-Q}{kT}\right) \qquad (5)$$

where k is a constant, and Q is the activation energy for creep. This energy value is also in good agreement with the energy of carbon self diffusion in $ZrC_{0.97}$; indicating that carbon diffusion controls the creep rate in single crystal ZrC. Recently, Sarian [18] has investigated the creep behaviour of hypostoichiometric, stoichiometric, and hyperstoichiometric uranium carbides and has concluded that the creep mechanism involves the unpinning of Shockley partials by carbon vacancy diffusion.

The data [4, Fig. 7] for the creep of single crystals of $ZrC_{0.945}$ were applied to Equation 3 with σ_i taken as zero, and a value of 4.3 eV/atom was obtained. Based on the similarity of the activation energies (4.8 eV/atom versus 4.3 eV/atom) calculated by the two equations, it would appear that equation 3 could also be used to describe the creep data.

Miloserdin *et al.* [19] studied the creep behaviour of hot-pressed ZrC in the temperature range 2175 to 2550°C and obtained a value of 5 ± 0.78 eV/atom for the activation energy for the process controlling creep; they concluded that creep is controlled by the diffusion of carbon.

There appears to be adequate support, therefore, to conclude that the high temperature deformation of zirconium carbide is controlled by the diffusion of carbon, and that carbon diffusion-assisted dislocation glide is the most probable rate-controlling deformation mechanism. The Kelly–

Rowcliffe model requires the existence of dislocation dissociation. Martin *et al.* [6] have demonstrated such splitting for $TaC_{0.75}$, but were unable to detect dissociation in nearly stoichiometric TaC_x. The distance between the partial dislocations was found to decrease as TaC_x approached the stoichiometric composition, thereby diminishing the likelihood of resolving the dissociation. Later, Martin [20] did observe dissociation in $TaC_{0.98}$ by using the weak beam technique of electron microscopy. Future work should reveal similar dislocation dissociation in nearly stoichiometric ZrC.

Acknowledgement

This work was totally supported from funds made available to the University of Washington through NASA grant NGL48-202-004, Multidisciplinary Research Concerning the Nature and Properties of Ceramic Materials.

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Received 16 June and accepted 14 July 1975.