MASTER

PROGRESS REPORT
ON
INELASTIC DEFORMATION IN CRYSTALLINE NON-METALLIC MATERIALS

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by

D.L. Kohlstedt, Associate Professor
Department of Materials Science and Engineering
Cornell University

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D.L. Kohlstedt, Principal Investigator

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ABSTRACT

This report discusses progress made in six areas during the past year.

- (1) A preprint of a paper, submitted for publication, on "Liquid-phase Sintering of TiC Containing Ti Metal" describes our results on preparing polycrystalline TiC for TiC plus Ti powders at temperatures above the melting temperature of Ti metal. An abstract of a paper to be presented at the American Ceramic Society Spring (1981) meeting cover this same topic.
- (2) Samples of much higher density than those produced by sintering have now been prepared by hot-pressing TiC + Ti below the solidus temperature. These results are described briefly, here, and more extensively in the associated renewal proposal.
- (3) A hand-written, first draft of a paper on hot-pressing in the system TiC-VC-Ti-V elaborates on processing of (Ti,V)C samples to be used in creep experiments this next year.
- (4) A short summary of our results on creep of TiC single crystals is included. These experiments have just been completed. A paper should be in hand by this summer.
- (5) A preprint of a paper, submitted for publication, on "Chemical Diffusion in NbC Crystals" details and compares results on single -rystals with those on polycrystals. This diffusion study lays the ground work for future deformation experiments on NbC.
- (6) An abstract of a paper on grain boundaries in NbC, which I will present at the Spring meeting of the American Ceramic Society, is also attached.

In addition, reprints of three papers are attached describing research in which my research time was supported by the Department of Energy:

- (i) "Faulted Dipoles in Germanium: A high-resolution TEM Study".
- (ii) "Constricted Segments on Faulted Dipoles in Germanium".
- (iii) "Electron Diffraction and Microscopy Studies of the Structure of Grain Boundaries in Al_2O_3 ".

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SECTION 3

HOT PRESSING IN THE
SYSTEM TiC-VC-Ti-V

V. M. Sura and D. L. Kohlstedt

1. INTRODUCTION

There is a rapidly increasing demand for structural materials capable of working at high temperatures when subjected to mechanical stress.

The monocarbides of the fourth and fifth group of the transition metals possess a unique set of properties for such applications, including high melting temperatures and excellent elastic hardness and wear resistance characteristics.^(1,2)

It is significant to note that of these carbides the carbides of Ti and V have considerably lower densities than those of NbC, TaC and HfC and, therefore, are potentially more useful because of their large strength-to-density ratio.⁽⁴⁾ At the same time, however, use

~~of~~ of the pure TiC or VC is restricted because of rapid decrease in the plastic yield strength with increasing temperature^(1,5). At elevated temperatures, the binary alloys between TiC and VC show significantly higher strength than the parent carbides. Even the temperature dependence of the yield strength is different in form from that of the pure carbides.⁽⁶⁾ It has been established that TiC and VC form a continuous solid solutions series.⁽⁶⁾ Both carbides exist over a broad composition range, so that there is an appreciable vacancy concentration on the nonmetallic sublattice. Ordering of the vacanci

can also occur giving rise to a domain structure.⁽⁸⁾ Consequently the mechanical properties of the alloys not only depend on Ti/V ratio but also on Me/C ratio. A limited amount of work has been performed on the alloys of TiC and VC. In these studies the metal : metal ratio was maintained but no attempt was made to control the stoichiometry. Thus, it is of interest to examine the ternary alloys controlling both the Ti/V ratio and the Me/C ratio.

In this connection, the present work was undertaken to examine the effects of stoichiometry and temperature

On the hot pressing characteristics of TiC-VC alloys. The ratio of Ti to V was kept constant in all specimens and substoichiometric monocarbide alloys were prepared by hot pressing the nearly stoichiometric monocarbides with Ti or V powders. (3, 4)

2. EXPERIMENTAL TECHNIQUE

2.1 Experimental Apparatus

All specimens described in this report were fabricated in a 'CENTORR M-60' high-temperature vacuum hot press mounted on an Instron machine. The furnace was resistance heated. The heating element was made of tungsten while radiation heat shields consisted of concentric layers of molybdenum. The furnace chamber was water cooled. The push rods inside the furnace as well as the die cases were fabricated from high strength graphite. [Type HPD-3 by Poco Graphite Inc] Automatic closed loop control utilizing Tungsten 5% Rhenium - Tungsten 26%.

Rhenium thermocouple, was used to maintain temperature stability of $\pm 2-3^{\circ}\text{C}$, while the vacuum was maintained in the range of $1 \times 10^{-4} - 5 \times 10^{-5}$ mm of Hg.

A 500 kgm load cell was used with an output of 1 mv per 50 kgm to calculate the pressure on the powder during the hot pressing. An LVDT was used to determine the change in the length of the specimen at any instant during densification. The Load cell and LVDT output was measured by a DVDM at a predetermined rate of one reading per 1 seconds. The data were recorded on

on magnetic tape and were analyzed on a computer.

2.2 Test Materials

The starting materials employed were Ti, V, TiC and VC powders of mean particle size of 1-5 microns. The chemical composition of the powders are presented in Table 1.

Charge compositions were calculated on the basis of the reactions —

or

In these reactions x' and y' were

calculated from the composition of the

carbide powders using total carbon instead of combined carbon. X and Z represent the stoichiometry required in the final solid solution. By fixing these quantities, the coefficients a and b were determined.

2.3 Experimental Procedure

Initially all charges were subjected to a thorough dry mixing for 5-6 hours. Then the respective powder charges were placed in cylindrically shaped graphite dies of 3.175 mm diameter and 25.4 mm length. Subsequently these powder batches were cold pressed at a pressure of 6.9×10^7 Nt/m².

The cold pressed specimens were then uniaxially hot pressed at either 1400 or 1800 °C.

The rate of temperature rise was approximately 40 °C /min. The pressure was applied by

moving the crosshead downward at a constant

compression rate. The maximum pressure

applied was limited by the compressive

strength (1.7×10^8 Nt/m²) of the die

material. To achieve as high density

as possible, compression, load relaxation,

compression cycles were repeated several

times. The measurements of load and

specimen length were begun when the desired

temperature was reached. At the end of the

pressing the specimens were cooled at a rate of $50^{\circ}\text{C}/\text{min}$.

Specimens for optical microscopy and grain size determination were cut from the hot pressed samples with a low speed diamond saw and then polished by normal metallographic techniques. An etchant of 3 part lactic acid, 1 part HNO_3 , 1 part HF by volume was used.⁽¹⁰⁾ The grain size measurements were made by counting the number of grains intersecting a line of known length. Each grain diameter is the average of several measurements.

A JEOL 733 Superprobe was

was used for electron microprobe analysis.

The samples for microprobe analysis were unetched and uncoated.

3. RESULTS

From the measurement of load, pressure (P_e) as a function of time was calculated assuming that deformation was uniaxial and that the cross-sectional area remained constant.

From measurements of the length as a function of time and the initial length of the specimen, the instantaneous densities ($\rho^*[t]$) under isothermal hot pressing conditions were calculated. The resulting data were used to determine the densification parameter as a function of hot pressing duration as follows:

$$\text{Densification Parameter } (t) = \frac{\rho^*(t) - \rho_0}{\rho_{th} - \rho_0} \quad (I)$$

where ρ_0 = Initial density
 ρ_{th} = Theoretical density.

The values of the lattice parameter required for the calculation of theoretical density were taken from the reference by F. Rudy.⁽⁶⁾

Using these data, a series of plots of pressure as a function of densification parameter [Fig. 1 and 2] were generated.

These figures reveal a pronounced effect of chemical composition on the densification characteristics of the samples at the constant temperature of 1800 and 1400 °C.

The results of the hot pressing runs are tabulated in Table 2.

As shown in figure 1, densification

characteristics improve as the amount of metal added decreases from 27% Ti [sample (h)] to 11% [sample (d) and sample (f)] to no metal [sample (b)]. The same pattern is observed at 1400 °C [Fig. 2] except in the final period, where sample (e) [11% V] shows better densification characteristics than sample (a) [No metal].

In figure 1 sample (d) [11% Ti] shows better kinetics of densification than sample (f) [11% V], while the reverse is true in figure 2 for sample (c) [11% Ti] and sample (e) [11% V].

It is also evident in figures

1 and 2 that for samples [(a) and (b)], [(c) and (d)] the densification rate is more rapid at the higher temperature, while temperature has the opposite effect on samples [(e) and (f)], [(g) and (h)]. It is important to note that the densification curves for samples (a) through (e) are concave up, while for samples (f) through (h) are concave down.

All the specimens had small regions rich in Vanadium. As shown in a typical micrograph [fig. 3], the carbide solid solution consisted of bright oval shaped regions rich in vanadium and darker areas rich in titanium. According to the calculated composition

all specimen should be single phase with Ti to V ratio of 70/30. Thus apparently some agglomeration occurred in VC powder. Figures 4 and 5 show the effect of the presence of the metal phase on the microstructures at 1800°C and 1400°C , respectively. Microprobe results and microstructural observations are summarised in Table 3; these results are discussed more fully below.

The presence of the metal phase along the grain boundaries can be seen in samples (c) a through (f). The porosity is distributed randomly intragranularly as well as

along the boundaries in all samples. The increase in temperature leads to increase in grain size by a factor of 3 to 4 for the samples with the same calculated composition.

The presence of 11% Ti or V results in the doubling the grain size compared to the samples without the metal phase, both at 1400 and 1800 °C. Investigation have also shown that deviation from stoichiometric composition is accompanied by a increase in the grain growth rates^(12,13).

The samples (g) and (h) could not be analyzed on the electron microprobe or scanning electron microscope because of their poor densification characteristics.

4. DISCUSSION

In the intermediate and final stages of hot pressing, the four mechanisms which directly contribute to densification are

- (1) Lattice Diffusion, (2) Grain-boundary Diffusion, (3) Power law Creep and (4) Rate Independent

Plasticity. ⁽¹⁴⁾ To find which of these mechanisms

contributes the most, the following rate equations were considered —

Lattice Diffusion ⁽¹⁵⁾

$$\dot{\epsilon} = \frac{12 D_L \Omega}{G^2 K T} \frac{(1-\rho)^{1/3}}{1 - (1-\rho)^{1/3}} \rho \quad \text{--- (II)}$$

Boundary Diffusion ^(14, 15)

$$\dot{\epsilon} = \frac{32 \delta D_B \Omega}{G^3 K T} \frac{1}{1 - (1-\rho)^{1/3}} \rho \quad \text{--- (III)}$$

(14, 15, 16)
Power Law Creep

$$\dot{\rho} = \frac{3A}{2} \frac{\rho(1-\rho)}{[1-(1-\rho)^{1/n}]^n} \left(\frac{3|P|}{2n} \right)^n \quad (IV)$$

Plastic Flow ()

$$\dot{\rho} = \begin{cases} 0 & \text{if } \rho > \rho_{\text{lim}} \\ \infty & \text{if } \rho < \rho_{\text{lim}} \end{cases} \quad (V)$$

$$\text{and } \rho_{\text{lim}} = 1 - \exp\left(-\frac{3}{2} \frac{P}{\sigma_y}\right)$$

where

ρ relative density of the compact = $\frac{\rho^*(t)}{\rho_{th}}$

$\dot{\rho}$ densification rate

T absolute temperature

G grain size

δ boundary width

Ω atomic volume

D_L lattice diffusion constant

D_B boundary diffusion constant

K Boltzmann constant

σ_y material flow strength

n stress exponent in power law

$$P = P_e - P_i + \frac{2\gamma}{a}$$

P_e externally applied pressure

P_i pressure within pores

γ surface free energy per unit area

a pore radius

A pre exponential term in power law

In equations (II) to (IV), relative density ρ and densification rate $\dot{\rho}$ as a function of time were calculated from the instantaneous length of the sample during pressing, while P_e was calculated from

load measurement, which is equal to

$(P + P_i - \frac{2\gamma'}{a})$. As hot pressing was isothermal

T is a constant. The data was plotted as

P_e versus $\frac{\dot{\gamma} [1 - (1 - \dot{\gamma})^{1/3}]}{(1 - \dot{\gamma})^{1/3}}$ for lattice diffusion

P_e versus $\dot{\gamma} [1 - (1 - \dot{\gamma})^{1/3}]$ for boundary diffusion

and P_e^n versus $\frac{\dot{\gamma} [1 - (1 - \dot{\gamma})^{1/n}]^n}{\dot{\gamma} (1 - \dot{\gamma})}$ for power

law creep assuming $n = 3$. Then linear

equations to fit these data points were

found by a least square curve fitting

minimizing χ^2 ⁽¹⁷⁾. The mechanism with lowest

χ^2 value was taken as a dominant one

for that particular sample.

It was found that lattice diffusion

is a prominent mechanism in densification of

samples (a) through (c), while grain boundary

diffusion contributes the most towards the densification of samples (f) through (h). It is important to recall that the samples (a) through (e) have densification curves which are concave upward while the densification curves for samples (f) through (h) are concave downward.

The equations describing lattice diffusion in samples (a) through (e) were of the following type

$$P_e = m \left\{ \frac{P_i [1 - (1-s)^{1/3}]}{(1-s)^{1/3}} \right\} + C \quad \text{--- (VI)}$$

Comparing this ^{equation} with equation (II) gives

$$m = \frac{G^2 K T}{12 D_h \Omega} \quad \text{--- (VII)}$$

while

$$C = P_i - \frac{2\gamma}{a} \quad \text{--- (VIII)}$$

From equations (VII) values of lattice diffusion coefficient (D_v) were estimated, which are tabulated in table 4.

The equations describing grain boundary diffusion in samples (f) through (h) were of the following type

$$P_e = m' \left\{ \dot{\gamma} [1 - (1 - \dot{\gamma})^{1/3}] \right\} + C' \quad \text{--- (IX)}$$

Comparing this ^{equation} with equation (III) gives

$$m' = \frac{G^3 K T}{32 \int D_B \Omega} \quad \text{--- (X)}$$

and

$$C' = P_i - \frac{2\gamma}{a} \quad \text{--- (XI)}$$

The values of grain boundary diffusion coefficient calculated from equation (X), are also tabulated in Table 4.

It can be seen in Table 4 that with the ~~increasing~~ increase in temperature, the lattice diffusion coefficient increases by 20-25 times; the presence of 11 % Ti or increases the diffusivity 4 to 5 times. The comparison of sample (C) [11 % Ti] and sample [11 % V] reveals that the diffusion coefficient is higher ~~with~~ in sample with 11% than the sample with 11 % Ti. Sarian found the self diffusion coefficient in VC_x to be higher than that in TiC_x for a given temperature.

The data on grain size, diffusion coefficient coupled with densification behavior leads to the conclusion that variation of the densification characteristics of samples (a)

Through (e) is dependent on diffusion coefficient as well as grain growth. With increase in temperature, the increase in diffusion coefficient is much greater than increase in grain size giving better densification characteristics at the higher temperature, as seen in samples (a), (b) and samples (c), (d). With the addition of a metal phase, even though the ~~liquid~~ diffusion coefficient increases, the effect of grain growth is more prominent, which adversely affects the densification characteristics; as seen in samples (a), (c) and samples (b), (e). In samples (c) and ~~e~~ (e), both of which

have a grain size of 10μ , sample (e) with V as the metal phase shows better densification characteristics than sample (c) with Ti as the metal phase apparently because of higher diffusion rates in the former system.

Now if we look at samples (e) through (h), temperature has an adverse effect on densification. Just comparing samples (e) and (f) reveals that in sample (e) hot pressed at 1400°C lattice diffusion is the dominant mechanism, while in sample (f) hot pressed at 1800°C , the main contribution towards densification is grain boundary diffusion, with a higher diffusivity than sample (e) as shown.

in Table (4). This observation suggests that higher diffusivity results in the faster rate of formation of solid solution between TiC and V which is significantly stronger than either TiC or VC⁽⁴⁾ making densification more and more difficult with increase in temperature and with amount of metal phase added. The experiment done on TiC + Ti system demonstrated that the densification rate increases as the Ti content is increased and samples hot-pressed from Ti + TiC densify much more rapidly⁽¹⁹⁾ than ~~the~~ do the samples discussed here which also contain VC and V.

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TABLE 1

CHEMICAL COMPOSITION OF POWDERS* (in weight)

Powder	Total	Free	Impurities								Balance
	C	C	H	N	O	Cl	Fe	Si	Cr	Ni	
Ti	—	—	0.003	.005	.023	.15	.026	.002	.01	.01	Ti
TiC	19.33	0.25	50 Ppm	1800 Ppm	1600 Ppm	.02	.095	—	—	—	Ti
V	—	—	—	—	—	—	.14	.18	—	—	V
VC	18.20	1.30	.001	.005	.13	—	—	—	—	—	X

[* Powders supplied by Atlantic Equipment

Engineers Division Micron Metals, Inc;

Bergenfield N.J.]

TABLE 2

Sample No.	Symbol	Calculated Composition	Amount of metal added [Wt %]	Temperature [$^{\circ}\text{C}$]	Total time at this temperature [min.s]	Theoretical density S_{th} [gm/cc]	Initial density S_0 [gm/cc]	Final hot pressed apparent density [gm/cc]	Final densification Parameter
(a)	Δ	$(\text{Ti}_{0.71}\text{V}_{0.29})\text{Co}_{0.95}$	—	1400	154	5.0977	2.9367	4.4643	0.7068
(b)	+	$(\text{Ti}_{0.71}\text{V}_{0.29})\text{Co}_{0.95}$	—	1800	128	5.0977	3.0175	4.517	0.7208
(c)	X	$(\text{Ti}_{0.71}\text{V}_{0.29})\text{Co}_{0.82}$	11% Ti	1400	140	4.9618	2.9060	4.2585	0.6580
(d)	$\diamond$	$(\text{Ti}_{0.71}\text{V}_{0.29})\text{Co}_{0.82}$	11% Ti	1800	150	4.9618	2.9206	4.4258	0.7374
(e)	$\uparrow$	$(\text{Ti}_{0.69}\text{V}_{0.31})\text{Co}_{0.82}$	11% V	1400	124	4.9618	2.9957	4.3956	0.7121
(f)	$\times$	$(\text{Ti}_{0.69}\text{V}_{0.31})\text{Co}_{0.82}$	11% V	1800	160	4.9618	2.9036	4.5744	0.8118
(g)	Z	$(\text{Ti}_{0.71}\text{V}_{0.29})\text{Co}_{0.65}$	27% Ti	1400	124	4.8231	2.8938	4.0962	0.6232
(h)	Y	$(\text{Ti}_{0.71}\text{V}_{0.29})\text{Co}_{0.65}$	27% Ti	1800	88	4.8231	2.8654	3.6772	0.4147

TABLE 3

Sample No.	Symbol	Calculated Composition Formula	Microprobe Analysis												
			Atomic %			Ti rich region					V rich region				
			Ti	V	C	Formula	Ti	V	C	Grain Size μ	Formula	Ti	V	C	
(a)	Δ	(Ti _{0.71} V _{0.29})C _{0.95}	36.43	14.85	48.71	(Ti _{0.85} V _{0.15})C _{1.07}	40.98	7.33	51.69	4-5	(Ti _{0.04} V _{0.96})C _{0.87}	2.26	51.54	46.20	
(b)	+	(Ti _{0.71} V _{0.29})C _{0.95}	36.43	14.85	48.71	(Ti _{0.81} V _{0.19})C _{1.07}	39.03	9.41	51.55	17-18	(Ti _{0.24} V _{0.76})C _{0.90}	12.62	40.03	47.30	
(c)	X	(Ti _{0.71} V _{0.29})C _{0.82}	39.00	15.89	45.11	(Ti _{0.77} V _{0.23})C _{0.92}	39.92	12.16	47.92	10	VC _{0.825}	—	54.80	45.20	
(d)	$\diamond$	(Ti _{0.71} V _{0.29})C _{0.82}	39.00	15.89	45.11	(Ti _{0.76} V _{0.24})C _{0.967}	38.56	12.27	49.16	35-40	(Ti _{0.03} V _{0.97})C _{0.73}	1.39	55.97	42.64	
(e)	$\uparrow$	(Ti _{0.69} V _{0.31})C _{0.82}	37.92	16.99	45.09	(Ti _{0.49} V _{0.51})C _{0.825}	26.63	28.17	45.20	10	(Ti _{0.05} V _{0.95})C _{0.489}	0.31	58.92	40.78	
(f)	X	(Ti _{0.69} V _{0.31})C _{0.82}	37.92	16.99	45.09	(Ti _{0.60} V _{0.40})C _{0.844}	32.52	21.71	45.76	30	(Ti _{0.04} V _{0.96})C _{0.473}	2.57	65.29	32.13	
(g)	Z	(Ti _{0.71} V _{0.29})C _{0.65}	43.25	17.43	39.32										
(h)	Y	(Ti _{0.71} V _{0.29})C _{0.65}	43.25	17.43	39.32										

95

TABLE 4

Sample

Lattice diffusion

m Newton-sec
met²C Newton/met² D_L = Lattice diffusion coeff cm²/sec(a) 16.9808×10^{11} -4.3648×10^7 1.4441×10^{-11} (b) 13.9925×10^{11} -5.3789×10^7 2.6599×10^{-10} (c) 14.2130×10^{11} -1.6201×10^7 6.8818×10^{-11} (d) 12.3560×10^{11} -1.6271×10^7 1.3794×10^{-9} (e) 13.8150×10^{11} -2.8531×10^7 7.080×10^{-11}

Grain boundary diffusion

m' Newton sec
met²C Newton/met² D_B = Boundary diffusion coeff. cm²/sec(f) 16.1322×10^{11} 2.1952×10^7 5.7650×10^{-9} ($\delta = 1.3 \times 10^{-6}$ met)(g) 25.4930×10^{11} -0.9356×10^7 (h) 45.548×10^{11} -5.65×10^7

FIG.1 EFFECT OF CHEMICAL COMPOSITION ON DENSIFICATION
PARAMETERS AT TEMPERATURE 1800 C

FIG.2 EFFECT OF CHEMICAL COMPOSITION ON DENSIFICATION
PARAMETERS AT TEMPERATURE 1400 C

Variation in
 γ

Variation in
 T_i

Fig. 3 Typical micrograph of carbides solid solution [Mag - 86 X]

Sample (h), with V liq. phase
 30 μ — 1800°C

Sample (f)
 (Ti-69V-31)C-8
 Grain Size
 30 μ

Fig. 4 Effect of liquid phase on microstructure
 at temperature = 1800°C [Mag. 750X]

TEMP 1800°C II NO LIQ PHASE
TiCo_{0.95}-30% VCo_{0.95}

Sample Cb
(Ti_{0.79}V_{0.21})Co_{0.9}
Grain size
17-18 μ

TEMP 1800°C II
TiCo_{0.83}-30% VCo_{0.83}

Sample Cc
(Ti_{0.79}V_{0.21})Co_{0.8}
Grain size
35-40 μ

10 μ with X by phase 1400°C
 (Ti_{0.70}V_{0.30})Co_{0.83}

Sample (e)
 (Ti_{0.69}V_{0.31})Co_{0.8}
 Grain size
 10 μ

Fig. 5 Effect of liquid phase on microstructure
 at temperature = 1400°C [Mag. 750 X]

TEMP = 1400°C NO LIQ PHASE
 $Ti_{0.95}Co_{0.05}$

Sample (a)
 $(Ti_{0.71}V_{0.29})C$
 Grain size
 5 μ

TEMP 1400°C
 $Ti_{0.83}Co_{0.17}$

Sample (c)
 $(Ti_{0.71}V_{0.29})C$
 Grain size
 10 μ

SECTION 4

65

HIGH-TEMPERATURE CREEP OF TiC SINGLE CRYSTALS

Ten single crystals of $\text{TiC}_{0.97}$ have been deformed under compressive creep conditions. The stress was applied along the $[111]$ direction. Crystals were strained at least 10%. The stress exponent, m , was in the range 4-5. As was observed in our early work on germanium, the deformation response of the $[111]$ crystals is quite different from that of the $[100]$ crystals. In Ge, we attributed the difference to the fact that, in the $[111]$ orientation, the slip planes are oriented to permit easy cross-slip of screw dislocations. We believe that the same explanation applies to TiC. The activation energy for creep along $[111]$ is 100,000 cal/mole $^{\circ}\text{K}$; the activation energy for creep along $[100]$ is 25,000 cal/mole $^{\circ}\text{K}$. The former energy is in excellent agreement with the activation energy for carbon diffusion in TiC. The activation for Ti diffusion is 180,000 kcal/mole $^{\circ}\text{K}$. Thus, high-temperature creep in TiC crystals cannot be controlled by climb of edge dislocations. Rather, it is controlled by cross-slip of screw dislocations.

A paper on this topic is currently in preparation. It will be in preprint form by this summer.