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The micro-Vickers hardness of TiC single crystals up to 1500° C

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The behaviour of mechanical properties of TiC single crystals grown by r. f. floating zone process with nearly stoichiometric composition and low dislocation density were studied by the measurement of microhardness up to the temperature of 1500° C. First, anistropy in the microhardness of (1 0 0), (1 1 0) and (1 1 1) planes at room temperature, second the variation of indentations on (1 0 0) [0 0 1] orientation, (1 1 0) [0 0 1] orientation, and the (1 1 1) [1 $\bar{1}$ 0] orientation at high temperature were described. Temperature dependency of the relaxation behaviour of indentation (900 to 1200° C) yields the activation energy for creep which is close to that obtained for self-diffusion of carbon in TiC.

1. Introduction

The refractory carbides have caused interest in engineering applications because of their great strength, hardness, very high melting points, and superior chemical stability at high temperature. The experiment utilizing single crystals is of importance not only from the standpoint of engineering application, but also from that of material science research [1]. However, the preparation of single crystals of these refractory compounds has been considered to be fairly difficult because of their high melting point – 3000° C or above. Recently, several reports on the growth of TiC [2–5], VC [2, 5], NbC [5], ZrC [5, 6], ZrB_2 [7], and Ta_2C [8] crystals by floating zone technique have been published. We have also succeeded in preparing large TiC single crystals (10 to 15 mm diameter, 30 to 80 mm long) [3, 4] and in developing an excellent point emitter [9] using them. Furthermore, with the aim of making their mechanical behaviour in high temperatures clear, we have studied the microhardness characteristics of TiC single crystals considering that the indentation hardness can be used as a suitable measure of the plastic properties.

It is well known that the hardness depends on crystallographic orientation of the axis of the indenter for other cubic crystals, e.g. rock salt [10–15], diamond [16], fluorite [13, 17], fcc [12, 13, 17, 18] and bcc [14, 19, 20] type crystals. Brookes *et al* [13] pointed out that the anisotropy in hardness is essentially determined by crystal structure and the primary slip system.

Hardness anisotropy in such transition metal carbides as TiC [21–26], VC [21, 25, 26], ZrC [21, 25, 26], NbC [21, 25, 26], TaC [21, 22] and HfC [22] has been examined only in the (1 0 0) plane up to high temperatures (600 to 1500° C). However, in the indentation experiment above 1000° C, it is not considered easy to obtain reliable data because of certain problems, such as lack of accuracy in the temperature measurement and failure of the tip [26] during contact with the high temperature specimen.

This paper explains first the anisotropy in microhardness of the (1 0 0), (1 1 0) and (1 1 1) planes at room temperature, secondly, the high temperature hardness up to 1500° C measured along the [0 0 1] direction in the (1 0 0) plane, [0 0 1] in (1 1 0) and [1 1 0] in (1 1 1), and

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finally the relaxation behaviour of indentation at 900 to 1200° C.

2. Experiments

The single crystals were prepared by floating zone process under rather lower ambient gas pressure of 3 atm [4]. They have uniform and nearly perfect composition in their stoichiometry, $TiC_{1.00 \pm 0.02}$ determined by the gravimetric analysis. The fact that the obtained crystals have low dislocation density is confirmed by etch-pit and X-ray topographic techniques [4]. The surface of the specimens was pretreated by metallographical-polishing and electrochemical etching prior to indentation. Indentations were repeated and arithmetic average of these observations was taken as their hardness.

The experiments at room temperature were carried out using a micro-Vickers hardness tester, Akashi Seisakusho Ltd under strictly controlled loading cycle conditions to ensure a constant time of 20 sec under full load of 200 g. High temperature indentation was performed in a vacuum of 1×10^{-5} to 3×10^{-4} Torr using a Nikon high-temperature microhardness tester Model QM (Fig. 1). It is so designed that both indenter and specimen can be heated and controlled automatically at the same temperature within an accuracy of ± 10° C at 1500° C in separate furnace. In Fig. 2a and b, a sample holder and the heating furnace are shown, respectively. A high temperature of 1600° C can be obtained with a 0.6 diameter tantalum wire heater wound spirally

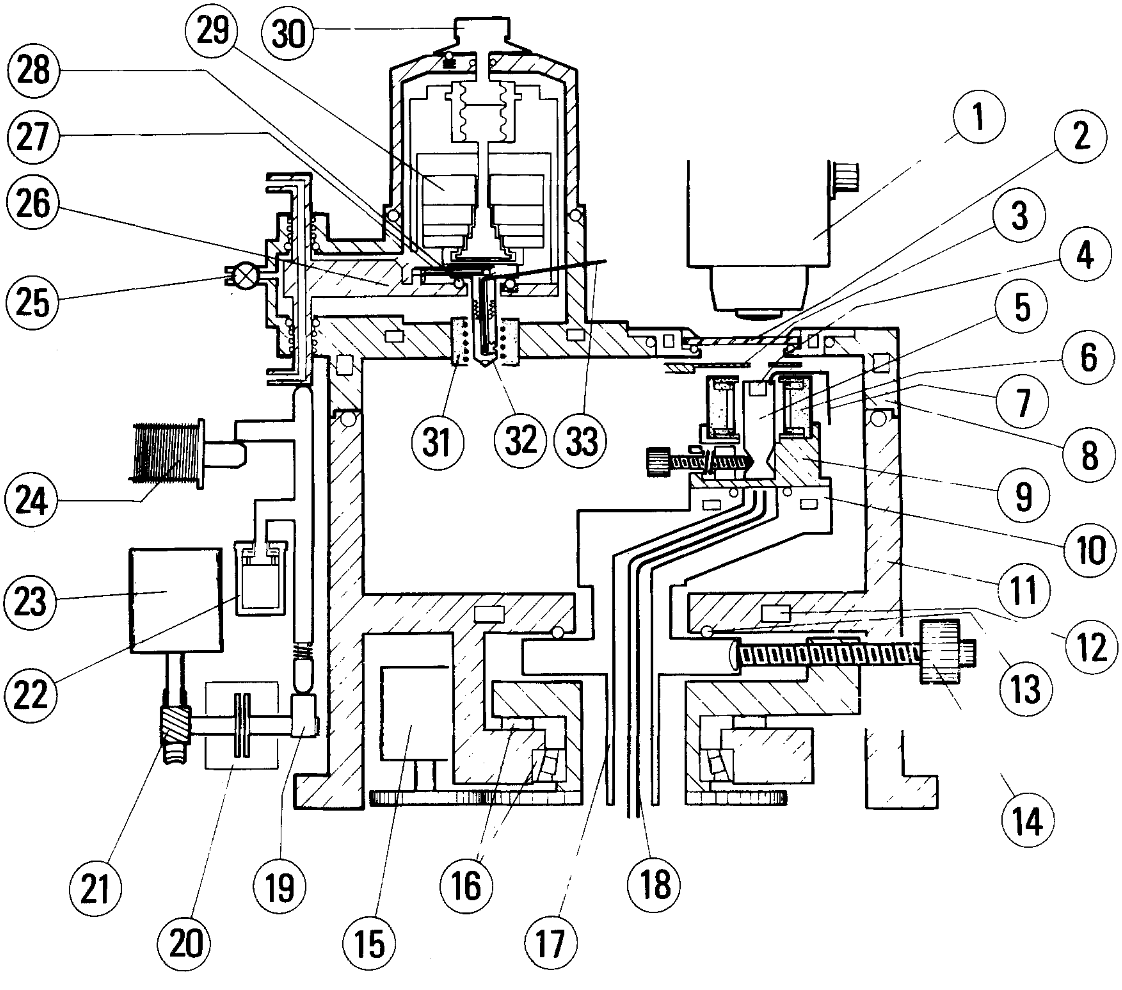

Figure 1 An illustration of high temperature hardness tester. 1, Microscope; 2, quartz window; 3, shutter; 4, specimen; 5, specimen holder; 6, 31, furnaces; 7, 33, thermocouples; 8, 11, chamber; 9, specimen holder; 10, anvil; 12, water channel; 13, O-ring, 14–16, X-Y-R moving stage; 17, 18, quenching device; 19–24, 26–28, automatic loading device; 29, loading weights; 30, load selecter; 32, indenter.

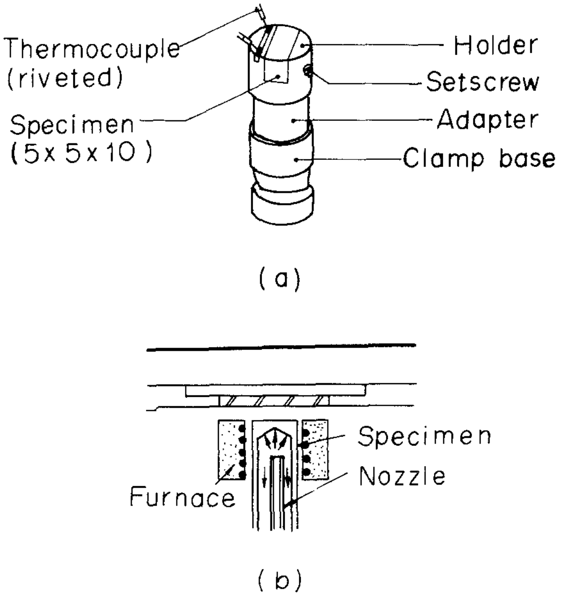

Figure 2 Sample holder and the heating furnace.

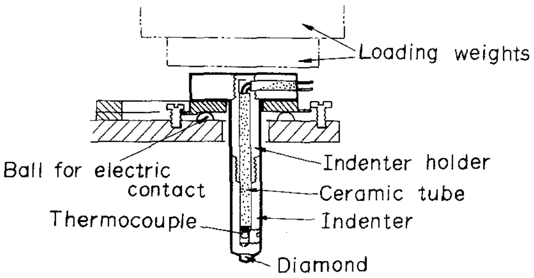

Figure 3 An illustration of an indenter.

outside the alumina furnace body. An indenter is shown in Fig. 3. A diamond tip is mounted on a tantalum body which is heated in a cylindrical furnace. The tip temperature is measured with a Pt–Pt 13% Rh thermocouple inserted into a tubular hole with a tantalum body. It is possible to protect against diamond tip failure with automatically controlled loading by means of a new loading mechanism employing a digital timer accurate to within 0.1 sec. Indentation measurements were performed by repeating the indentation in such a way that the selected edges are arranged parallel to each other. The length of each indentation and its appearance were observed using an optical microscope at a magnification of x 400 at high temperatures with an accuracy of ± 15 μm. The loading time was chosen as 10 sec under normal operation, and 1 to 100 sec for the creep test. The indenter retained its shape and size after the high temperature cycle.

3. Results and discussion

3.1. Vickers hardness at room temperature

The periodicity of the hardness curves, i.e. four-, two- and three-fold symmetry in the (1 0 0), (1 1 0), and (1 1 1) planes respectively, are shown in Fig. 4. On the (1 0 0) plane the minimum and maximum hardnesses are found in the [0 0 1] and [1 1 0] directions respectively. On the (1 1 0) plane the minimum hardness is in the [0 0 1] direction, and the maximum in the [1 1 1] direction; the hardness in the [1 1 0] direction has a value intermediate between those in the [0 0 1] and [1 1 1] directions. In the case of the (1 1 1) plane, the maxima appear in the [1 1 2] direction and the minima in the [1 1 0] direction. Fig. 4 shows the well known anisotropy in the hardness characteristics [13]. These are summarized in Table I. The magnitude of anisotropy is largest for the (1 0 0) plane, and the small anisotropy in the (1 1 1) plane is due to its high symmetry.

The anisotropy in the hardness is related to the effective resolved shear stress, i.e. the hardness maxima and minima correspond to the effective resolved shear stress minima and maxima, respectively [13]. According to the theoretical curve

TABLE I The anisotropy of micro-Vickers hardness (MVH) of TiC single crystals

Plane	Direction	Average MVH (kg mm^{-2})	$\frac{(\mathrm{MVH})_{\max} - (\mathrm{MVH})_{\min}}{(\mathrm{MVH})_{\min}}$
(1 0 0)	⟨0 0 1⟩	2600	36.9%
	⟨1 1 0⟩	3560	
(1 1 0)	⟨1 0 0⟩	2370	27.0%
	⟨1 1 0⟩	2500	
	⟨1 1 1⟩	2990	
(1 1 1)	⟨2 1 1⟩	3010	10.7%
	⟨1 1 0⟩	2720	

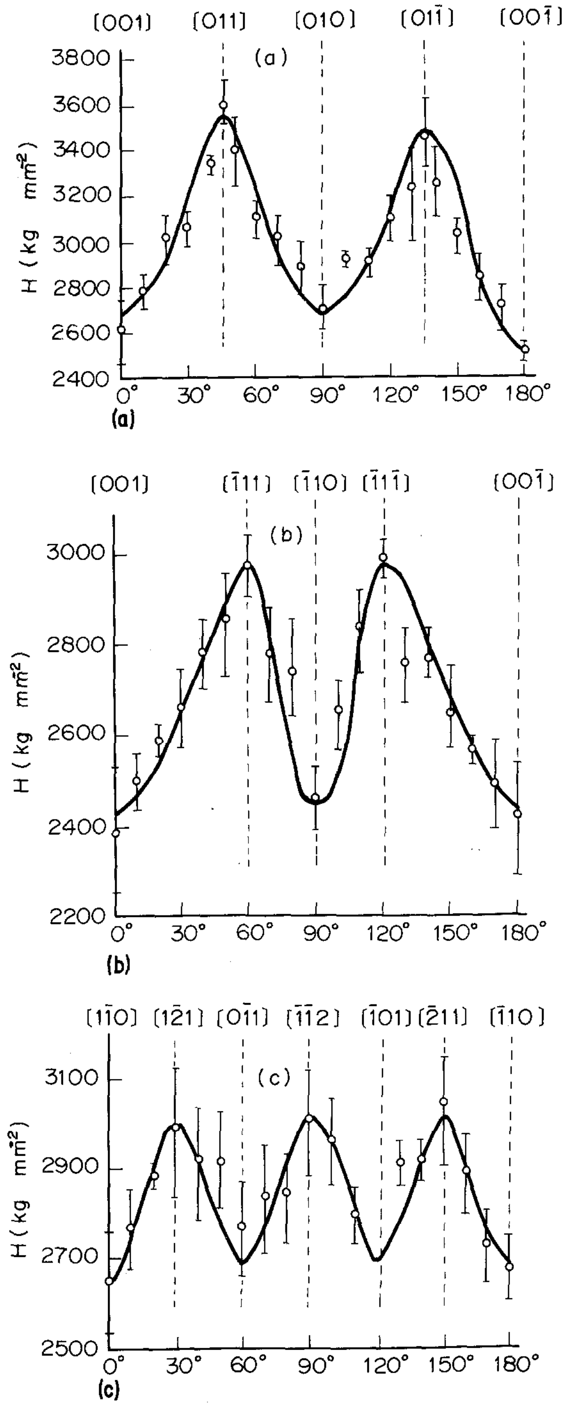

Figure 4 Periodicity of the hardness curves. (a) (1 0 0) plane, (b) (1 1 0) plane, (c) (1 1 1) plane.

given by Hannink *et al.* [25] and Kohlstedt [26], the primary slip system of TiC should be (1 1 0) [1 $\bar{1}$ 0] at room temperature; the present experimental results coincide with this. The anisotropy in the (1 0 0) plane is observed as 37%, which is larger than the values reported by other investigators [24, 25] by about 25%. It is known that large anisotropy depends mainly on the crystal perfection. TiC single crystals grown by the floating zone process have a more uniform composition and more perfect structure, i.e. low dislocation density, than those grown by the arc-Verneuil technique which causes the precipitation of carbon and/or boron [27–32] characterized as "Mondrian precipitates" [27].

The indentations are accompanied by cracking, which is direct evidence of a low dislocation mobility. This is due to the fact that plastic flow at the tip of a propagation crack is inadequate to absorb enough energy to arrest crack.

3.2. High temperature hardness

Typical behaviour of cracks generated by indentation at various temperatures are shown in Fig. 5. Cracks observed at each corner at room temperature diminish with increasing temperature and are seen as slip traces above 900° C (Fig. 5a to d). These facts indicate that the primary slip system, (1 1 0) [1 1 0] at room temperature changes to (1 1 1) [1 $\bar{1}$ 0] [28, 33] above 900° C.

In spite of temperature cycling, the specimens exhibited no change in either the intensity ratio $\mathrm{Ti}K\alpha$: $\mathrm{C}K\alpha$, or the $\mathrm{O}K\alpha$ intensity in the X-ray microanalysis, which confirms that no change in the status of the specimen occurred.

A logarithmic plot of hardness versus homologous temperature T/T_m, where T_m represents the melting point, is shown in Fig. 6. It consists of three regions as is observed in MgO single crystals [23] measured by mutual-indentation technique. A drop in hardness of more than × 10 occurs between room temperature and 1000° C. The hardness reaches $\sim 100\,\mathrm{kg\,mm^{-2}}$ at about 1400° C($\sim 1/2\ T_m$), being comparable with that of copper at room temperature. High hardness at room temperature would be due to tight atomic bonding and a drop in hardness to an increase in carbon atom mobility.

Region I shows the elastic behaviour generating a crack around the indentation, while region III shows plastic behaviour away from the crack. Region II is the transition area between regions I and III. A linear relationship between log H and $1/T$ is shown in Fig. 7, suggesting that there are two thermally activated processes corresponding to both regions I and III in Fig. 6. This is consistent with the report by Kohlstedt [26], which

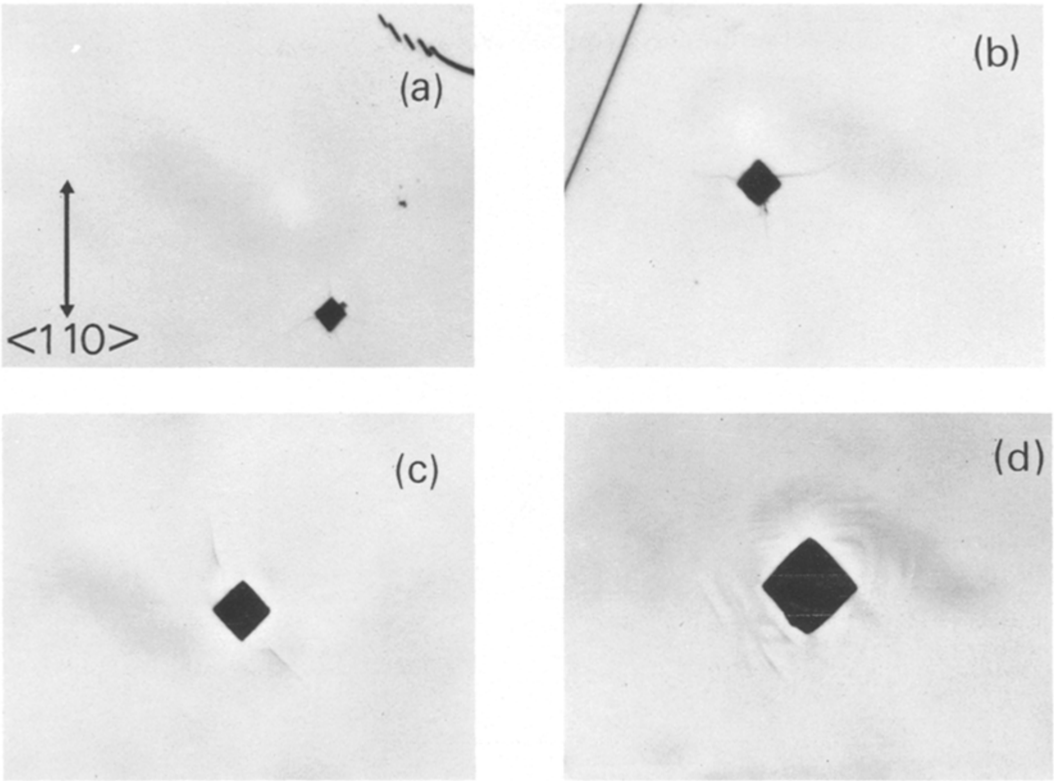

Figure 5 Cracks generated by indentation in the (1 1 1) plane at various temperatures: (a) 25° C; (b) 300° C; (c) 600° C; (d) 900° C.

correlates all yield–stress data [34], with the transition temperature. The lower transition temperature observed in the present experiment indicates the good crystal quality and low dislocation density, as explained in Section 3.1.

It is generally known that information on the mechanical characteristics is closely related to the bonding state. At low temperatures behaviour is characteristic of covalent bonding. The change from covalent- to metallic-like hardness suggests a change in predominant bonding over a wide temperature range from covalent to metallic cohesion as the temperature is raised. This is due to the fact that electrons must be thermally activated from the localized state into less localized metallic states (s-states) as proposed by Hannink *et al.* [25]. This causes the change in slip system from (1 1 0) [1 1 0] to (1 1 1) [1 1 0].

The creep test was performed by varying the loading time under a given load at constant temperature at 900 and 1200° C. Indentation hardness decreases with decrease in loading time. A series of the straight lines were obtained as shown in Fig. 8. The following relationship [35] exists between the indentation stress (H) and the loading time (t),

$$B/t = H^m \exp(-Q/RT) \qquad (1)$$

where m and B are constants, R is the gas constant, and Q the activation energy for creep.

The relationship between hardness (H) and temperature (T) is given by

$$H = A \exp(-BT) \qquad (2)$$

where A is a constant.

Figs. 6 and 8 and Equations 1 and 2 yield the values m and Q shown in Table II. It is found that our values of Q are close to that obtained for the self-diffusion of carbon in TiC [36], which would suggest that the mechanism of slip phenomenon is

TABLE II Values of constant m and activation energy Q

Orientation	m	Q (kcal mol^{-1})
(1 0 0) [0 0 1]	3.85	80.4
(1 1 0) [0 0 1]	4.05	81.2
(1 1 1) [1 1 0]	3.73	77.0

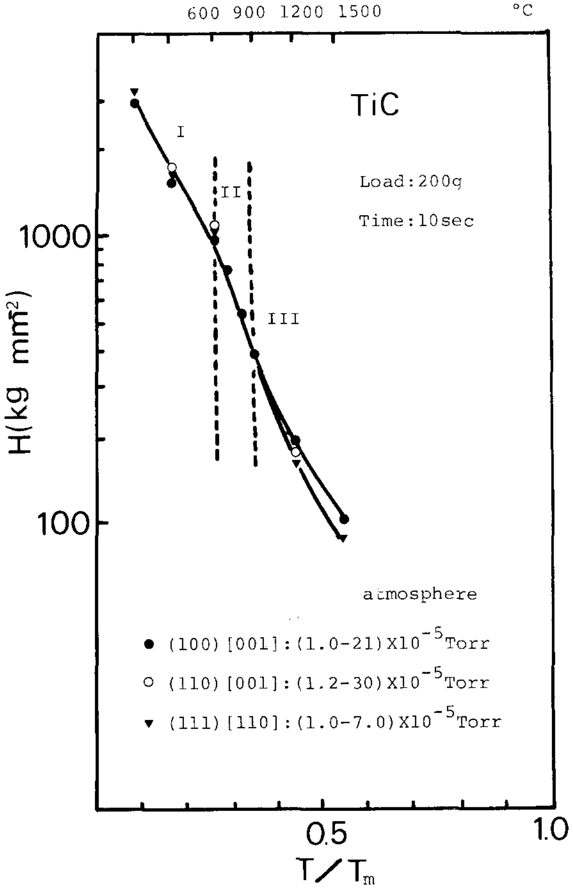

Figure 6 A logarithmic plot of hardness versus homologous temperature.

governed by carbon diffusion and dislocation climb [1, 37, 38].

4. Conclusions

From the experiments on the microhardness of TiC single crystals, the following results were obtained.

(1) There exists a remarkable anisotropy in the hardness characteristics at room temperature, which originates from the crystal perfection, e.g. good stoichiometry, low dislocation density, no precipitation of carbon, etc.

(2) The generation of cracks by indentation occurred up to 600° C, but diminishes above 900° C. This is explained in terms of the dislocation mobility in each temperature region.

(3) From the temperature dependency of the relaxation behaviour of indentation (900 to 1200° C), the activation energy for creep was calculated to be 77.0 to 81.2 kcal mol^{-1}, which

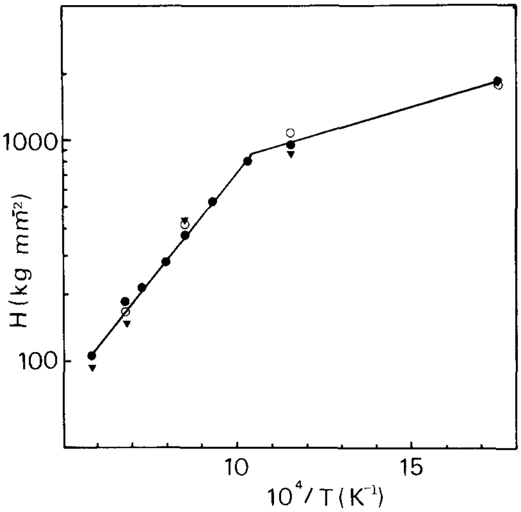

Figure 7 Log *H* versus 1/*T*.

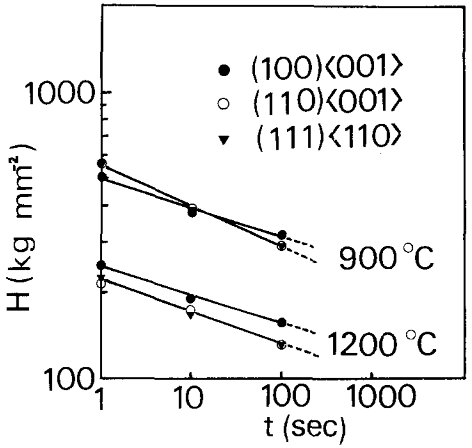

Figure 8 Relation between indentation stress and loading

was closely equivalent to that obtained for the self-diffusion of carbon in TiC.

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References

1. G. E. HOLLOX, "Mechanical and Thermal Properties of Ceramics" Nat. Bur. Stand. Spec. Pub. 303 (1969) p.201.
2. W. PRECHT and G. E. HOLLOX, *J. Crystal Growth.* **3/4** (1968) 818.
3. Y. KUMASHIRO, A. ITOH and S. MISAWA, *J. Less-Common Metals.* **32** (1973) 21.
4. *Idem, Jap. J. Appl. Phys.* **15** (1976) 921.

5. M. E. PACKER and M. J. MURRAY, *J. Crystal Growth.* **16** (1972) 240.
6. D. W. LEE and J. S. HAGGERTY, *J. Amer. Ceram. Soc.* **52** (1969) 641.
7. J. S. HAGGERTY, J. F. WENCKUS and D. W. LEE, Proceedings of the 3rd International Symposium on High Temperature Technology (Butterworths, London, 1967) p.547.
8. R. N. STOREY and R. A. LAUDISE, *J. Crystal Growth.* **6** (1970) 261.
9. K. SENZAKI and Y. KUMASHIRO, Proceedings of the 6th International Vacuum Congress: *Jap. J. Appl. Phys. Suppl.* 2 part 1 (1974) p. 289.
10. F. P. BOWDEN and C. A. BROOKES, *Proc. Roy. Soc. Lond.* **A295** (1966) 244.
11. J. W. MOORE and L. H. VAN VLACK, Proceedings of the Symposium on Anisotropy in Refractory Compound Single Crystals, Vol. 1 (Plenum Press, New York, 1968 p. 220.
12. E. RIEWALD and L. H. VAN VLACK, *J. Amer. Ceram. Soc.* **52** (1969) 370.
13. C. A. BROOKES, J. B. O'NEILL and B. A. W. REDFERN, *Proc. Roy. Soc. Lond.* **A322** (1971) 73.
14. M. GARFINKLE and R. G. GARLICK, *Trans. Met. Soc. AIME.* **242** (1968) 809.
15. C. A. BROOKES, R. P. BURNAND and J. E. MORGAN, *J. Mater. Sci.* **10** (1975) 2171.
16. C. A. BROOKES, *Nature, Lond.* **228** (1970) 660.
17. E. R. PETTY, *J. Inst. Met.* **91** (1962) 54.
18. A. L. VECCHIA and W. NICODEMI, *Met. Italiana* **9** (1965) 321.
19. G. O. REICK, G. H. G. VAESSEN and D. L. VOGEL, *Trans. Met. Soc. AIME* **242** (1968) 575.
20. D. G. ALEXANDER and O. N. CARLSON, *ibid,* **245** (1969) 2592.
21. D. J. ROWCLIFFE and G. E. HOLLOX, *J. Mater. Sci.* **6** (1971) 1270.
22. *Idem, ibid* **6** (1971) 1261.
23. A. G. ATKINS and D. TABOR, *Proc. Roy. Soc.* **A292** (1966) 441.
24. W. S. WILLIAMS, "Propriétés Thermodynamiques, Physiques et Structurales des Dérivés Semi-métalliques", Centre National de la Recherché Scientifique, Paris (1967) p. 181.
25. R. H. J. HANNINK, D. L. KOHLSTEDT and M. J. MURRAY, *Proc. Roy. Soc. Lond.* **A326** (1972) 409.
26. D. L. KOHLSTEDT, *J. Mater. Sci.* **8** (1973) 777.
27. W. S. WILLIAMS, *J. Appl. Phys.* **32** (1961) 552.
28. W. S. WILLIAMS and R. D. SCHAAL, *ibid* **33** (1962) 955.
29. W. S. WILLIAMS, *ibid* **35** (1964) 1329.
30. S. SARIAN, *ibid* **39** (1968) 3305.
31. *Idem, ibid* **40** (1969) 3515.
32. J. VENABLES, *Phys. Stat. Sol.* **15** (1966) 413.
33. G. E. HOLLOX and R. E. SMALLMAN, *J. Appl. Phys.* **37** (1966) 818.
34. W. S. WILLIAMS, *ibid* **35** (1964) 1329.
35. A. G. ATKINS, A. SILVERIO and D. TABOR, *J. Inst. Metals* **94** (1966) 369.
36. D. L. KOHLSTEDT, W. S. WILLIAMS and J. B. WOODHOUSE, *J. Appl. Phys,* **41** (1970) 4476.
37. J. WEERTMAN, *ibid* **26** (1955) 1213.
38. L. E. TOTH, "Transition Metal Carbides and Nitrides" (Academic Press, New York, 1971) p. 165.

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