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Plastic Flow and Fracture of Tantalum Carbide and Hafnium Carbide at Low Temperatures

D. J. ROWCLIFFE, G. E. HOLLOX†
Brown Boveri Research Centre, 5401 Baden, Switzerland

Knoop and Vickers hardness measurements have been made on tantalum carbide and hafnium carbide single crystals. The hardness varies with orientation of the indenter in the crystal, but indentations in the two carbides are of very different character. TaC behaves in a relatively ductile manner and deforms plastically before cracking, while HfC exhibits extremely limited plastic flow and cracks on indentation. Moreover, the preferred slip plane is {111} in TaC but is {110} in HfC. These results are related to the reported physical properties of these carbides. In particular, the observed mechanical behaviour of TaC appears to be consistent with the more metallic nature of this carbide.

1. Introduction

The transition metal carbides are among the hardest and most refractory materials known and are therefore of potential use for high strength or high temperature application in bulk form, or as reinforcing dispersions or fibres in alloy systems. At low temperatures, however, the carbides are generally brittle and their extreme notch-sensitivity severely limits their usefulness. Bulk plastic flow has been studied in some detail [1] whereas little information on the low temperature mechanical behaviour is available. Indeed, the effects of limited dislocation motion in these materials remain to be established, and certainly the origin of the brittleness is not understood. The microindentation test is a most useful method for studying the influence of small amounts of plastic flow on the deformation behaviour of seemingly brittle solids, even though the stress distribution cannot be exactly described. Under such testing conditions, some dislocation motion at room temperature seems possible in all materials, including diamond [2]. The present work is particularly concerned with an examination of microindentations at low temperatures in TaC and HfC and represents part of a larger effort on the deformation characteristics of carbides. TaC having a carbon-to-metal ratio close to the stoichiometric value differs from other cubic transition-metal carbides, since it is relatively soft and considerable slip is exhibited in regions adjacent to micro-indentations. Rowcliffe and Warren [3] have reported that the primary slip plane of TaC is {111}; however, similar data are not available for HfC.

2. Experimental

Small single crystals of TaC and HfC, about 1 to 2 mm in size, were grown from molten iron solutions as described previously [3]. Lattice parameter measurements gave 4.455 and 4.640Å, respectively, suggesting that the carbon-to-metal ratios corresponded to those of the maximum stoichiometry [4], namely $TaC_{0.96}$ and $HfC_{0.98}$.*

Microprobe analysis indicated the presence of a small amount of iron in both crystals and in addition that the HfC contained ~ 0.8% zirconium. These crystals, which had {100} growth faces, were mounted in bakelite and polished automatically with 1 μm diamond paste. A final polish was given with "Miro-Met" with additions of potassium ferricyanide and sodium hydroxide solutions. All crystals of TaC were etch-pitted [3] prior to indentation so that only dislocation-free areas were tested. Such control was not possible for HfC since no suitable etch-pitting solution was found.

Vickers and Knoop indentations were made using a Leitz microhardness tester. The Knoop

*Throughout this paper, TaC and HfC will be used to describe these two compositions.
†Now at International Nickel Limited, Birmingham Research Laboratory, Wiggin St, Birmingham, U K.

hardness values quoted in the results were determined with 100 gm load and the Vickers with 200 gm. In addition, loads up to 500 gm were used to investigate certain aspects of the deformation of the carbides. In all cases the total loading time, from the release of the indenter to its removal was 30 sec.

All indentations were made on (001) surfaces of crystals. In particular, the effect of varying the orientation of the indenter in the crystal surface was studied, and the following notation regarding the relative orientation of the crystal and the indenter is used throughout: when the long axis of the Knoop or one of the diagonals of the Vickers indenter lay in a [100] direction on a (001) surface this was defined as a 0° indentation. Indentations in other directions were referred to this direction as origin, i.e. when the long axis of the Knoop lay in the [1 $\bar{1}$ 0] direction, this was defined as a 45° indentation. Similarly, indentations with the indenter diagonal direction along [010] were 90° indentations. Depending upon the size of the crystal, between six and ten indentations were made at intervals of 10° from 0° to 90° including 45°. The arithmetic mean of each set was taken and the root mean square error, σ, calculated. The individual hardness readings in each set deviated from the mean by less than $\pm$ 3 σ.

3. Results and Discussion

3.1. Deformation at Knoop Indentations

A distinct difference in the variation of Knoop hardness with indenter orientation on the (001) surfaces of TaC and HfC was observed, fig. 1. In TaC the maximum hardness is at 0° indentations while the minimum is at 45°. Conversely, for HfC, peak hardness occurs at 45° indentations. Optical micrographs of microindentations at 0° and 45°, in both carbides, are illustrated in figs. 2 and 3. While the slip patterns around the two TaC indentations are different, fig. 2, the slip traces which are revealed after etch-pitting lie in [110] and [1 $\bar{1}$ 0] directions, consistent with deformation on the {111} slip plane, as reported previously [3]. More slip appears at the surface at 0° than at 45°, due to the fact that four {111} planes operate in the former case while only two are activated in the latter. Considerably less slip was observed in HfC crystals, fig. 3. However, at 0° indentations, slip lines in the [100] direction parallel to the indenter long axis, were clearly revealed using Nomarski interference microscopy. The small deviations in the directions of the slip

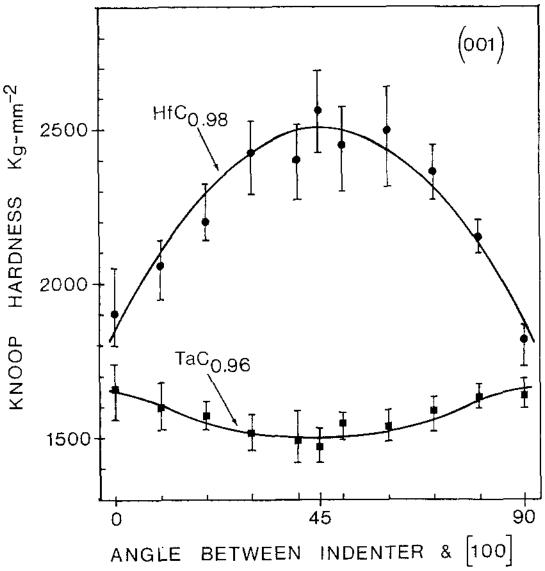

Figure 1 Variation of Knoop hardness with indenter orientation in TaC and HfC (100 gms load). The maximum hardness in HfC is at 45° while that of TaC is at 0° indentations.

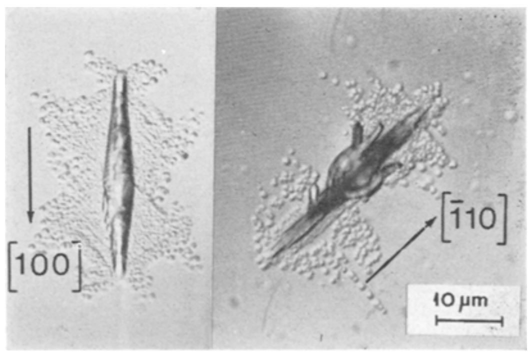

Figure 2 Distribution of slip around (a) 0° and (b) 45° Knoop indentations in TaC (100 gms load).

lines about [100], seen in fig. 3a, are probably due to surface distortion. No slip could be detected around 45° indentations. At 90° indentations, slip traces were again observed, lying in the [010] direction, parallel to the long axis of the indenter. A two-surface analysis of the slip traces was not possible because the deformed region was so small. However, ⟨010⟩ traces on a (001) surface could arise from {101} type slip planes which intersect the surface at 45° or from {100} planes normal to the (001) face. Such slip traces cannot arise from {111} slip.

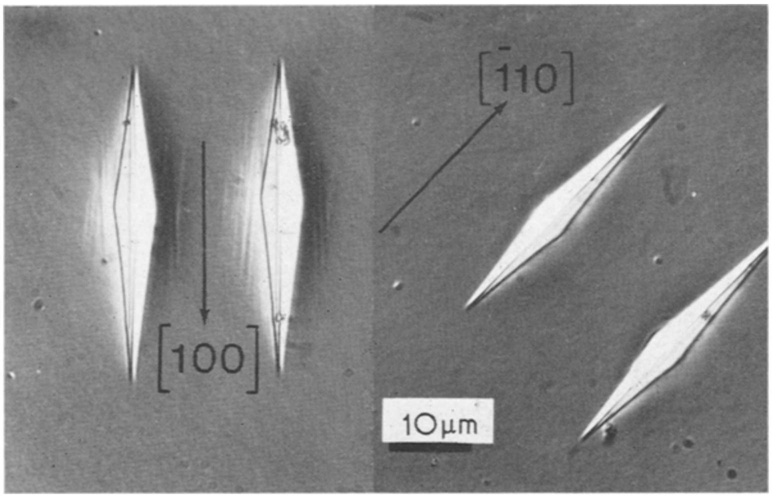

Figure 3 Nomarski interference-contrast micrographs of (a) 0° and (b) 45° Knoop indentations in HfC (200 gms load).

An explanation of the forms of the curves of fig. 1 requires a knowledge of the operative slip planes and the stresses on them. An analysis of the effective stress on different planes for Knoop indentations in various crystal directions has been made by Daniels and Dunn [5] and extended by Brookes *et al* [6], who have calculated the change of effective resolved shear stress with indenter direction on an (001) surface for the cases of $\{111\}\langle 1\bar{1}0\rangle$, $\{110\}\langle 1\bar{1}0\rangle$ and $\{100\}\langle 0\bar{1}1\rangle$ slip. For $\{111\}\langle 1\bar{1}0\rangle$ and $\{100\}\langle 0\bar{1}0\rangle$ slip, the effective stress on the slip planes is a minimum in [010] and a maximum in [$1\bar{1}0$] directions while the opposite is true for $\{110\}\langle 1\bar{1}0\rangle$ slip. Brookes *et al* [6] have shown that the hardness is a maximum when the effective resolved shear stress on the slip plane is minimised. This occurs when the long axis of the indenter lies at 0 or 90° for $\{111\}\langle 1\bar{1}0\rangle$ or $\{100\}\langle 0\bar{1}1\rangle$ slip, and at 45° for $\{110\}\langle 1\bar{1}0\rangle$ slip. This is in exact agreement with the observed orientation dependence of hardness of TaC where the slip plane is known to be {111}. Moreover, the form of the hardness anisotropy curve for HfC shows that deformation must take place on $\{110\}\langle 1\bar{1}0\rangle$ slip systems, consistent with the observed slip traces.

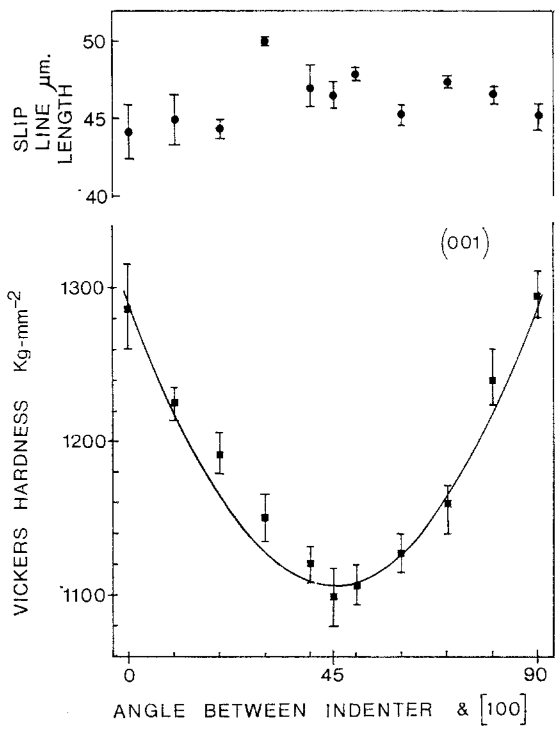

Figure 4 Variation of Vickers hardness and slip line length with indenter orientation in TaC (200 gms load).

3.2. Deformation at Vickers Microindentations

The variations in hardness of TaC and HfC with indenter orientation on the (001) plane are shown in figs. 4 and 5 respectively. In both carbides the hardness is a maximum at 0 and 90° and a minimum at 45°, the variation between these extremes being symmetrical. Slight differences in absolute hardness were observed from specimen to specimen, due probably to minor composition variations. The data for HfC also exhibited considerably greater scatter.

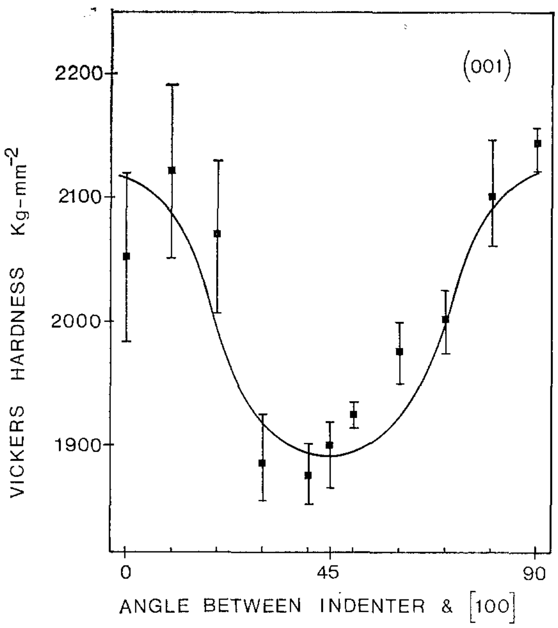

Figure 5 Variation of Vickers hardness with indenter orientation in HfC (200 gms load).

Accompanying the change in hardness was a change in appearance of indentations. As shown in fig. 6, 0° indentations in TaC had a characteristic "barrelled" shape, whereas those at 45° were "pin-cushioned". Indentations in HfC were somewhat different in shape, a more regular appearance being exhibited, fig. 7. The stress field under a Vickers indenter has been described as one of approximately radial compression, similar to that of a ball being impressed into a material [7, 8]. Thus, little difference in resolved shear stress on the active planes can be expected for 0° and 45° indentations in contrast to the analysis suggested for Knoop indentations. However, a hardness variation with orientation is observed and can be explained in TaC by considering the interaction between the pyramidal indenter and a surface which has become distorted by anisotropic plastic deformation [7]. Interference microscopy has shown that the surface of the crystal immediately around the hardness indentation is lowered slightly with respect to its original position, particularly around [100] and [010] directions, but the major effect is one of surface raising in [110] and [1$\bar{1}$0]. This is most clearly demonstrated by the scanning electron micrograph shown in fig. 8. Since the surface is raised in [110] and [1$\bar{1}$0] directions in TaC, the indentation is elongated in these directions. For 0° indentations this means that the sides of the impression are elongated to give a "barrel" shape, while at 45° the diagonals are extended giving a "pin-cushion" appearance. Consequently, when the length of the indentation diagonal is used to calculate hardness, the material then appears softest at 45°, however, this is an apparent change in hardness and not a real one. A more sensitive measure of the hardness or the yield strength is given by the amount

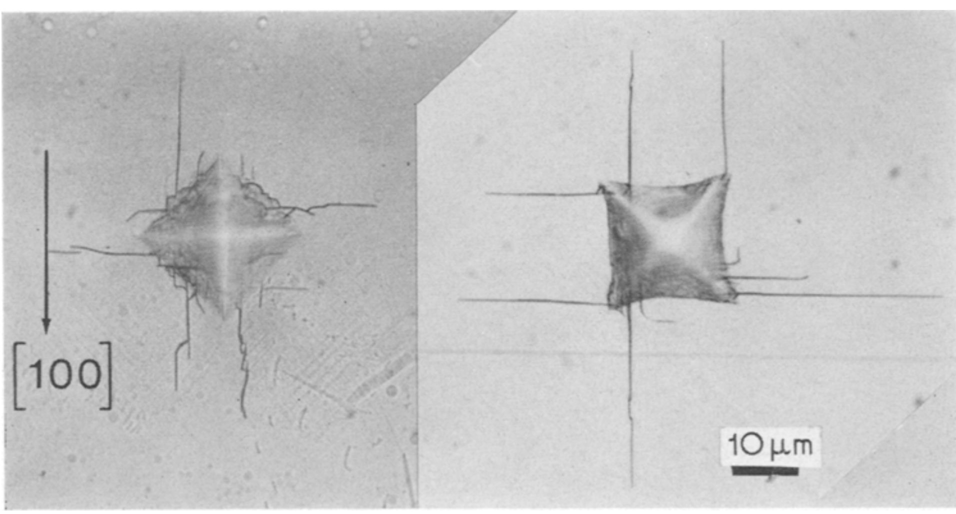

Figure 6 (a) "Barrelled" 0° and (b) "Pin-Cushioned" 45° Vickers indentations in TaC. A distinct difference in crack pattern is also exhibited at the two indentations (500 gms load).

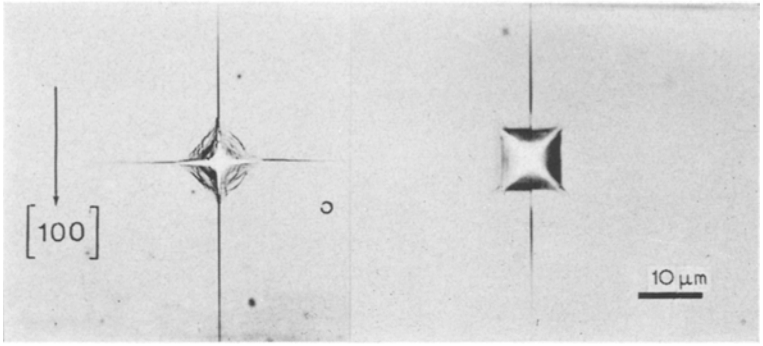

Figure 7 Vickers indentations at (a) 0° and (b) 45° in HfC (200 gms load). Cracks pass through the centre of the indentation.

of dislocation motion away from the indentation, i.e. the slip band length as defined in fig. 9 and plotted as a function of orientation in fig. 4 for TaC. The extent of the deformation does not appear to change with crystal direction, which suggests that the variation in hardness is due, primarily, to the orientation differences between the surface pile-up and the indenter diagonals, rather than any changes in the properties of the crystal. It has not been possible to detect significant plastic deformation outside Vickers indentations in HfC. Although HfC prefers to deform on {1 1 0} planes at room temperature, the extent of the deformation is so limited that surface raising effects play little part in the observed hardness anisotropy.

3.3. Cracking at Vickers Microindentations

In addition to differences in indentation shape, clear differences between cracking at 0° and 45° indentations were observed in both of the carbides. 0° indentations in TaC, fig. 6, exhibited many small cracks along the sides of the indentation, while fewer, but longer cracks were produced from near the corners of 45° indentations. At all orientations in HfC, cracks were observed to pass through the centre of the indentation, fig. 7. Moreover, Hertzian or ring cracking was observed, particularly at 0° and 90° indentations and within 25° of these orientations. There is one further difference between the two carbides – when indentations were sectioned parallel to the plane of indentation, (0 0 1), a crack was always observed immediately under the indentation in HfC, however, none was observed in TaC.

The observation of cracks passing immediately through the centre of indentations in HfC suggests that the crack is produced at or immediately after the initial contact between indenter and crystal. The response of the crystal to the high point-stresses is to fail by cleavage. It is possible that the change of Vickers hardness of HfC with orientation may be controlled by cracking which is more extensive at 0° indentations where both Hertzian and cleavage cracks occur. Hertzian cracking is absent at 45° indentations. Consequently, more of the applied stress is relieved by plastic flow than in the 0° case, and hence the material appears softer at this orientation. The variation in hardness may be qualitatively explained in this manner, but a more rigorous analysis is clearly required.

While cracking is one of the earliest events in Vickers indentation of HfC, it is one of the final processes to occur in TaC. The absence of cracks under the indenter tip in TaC crystals suggests

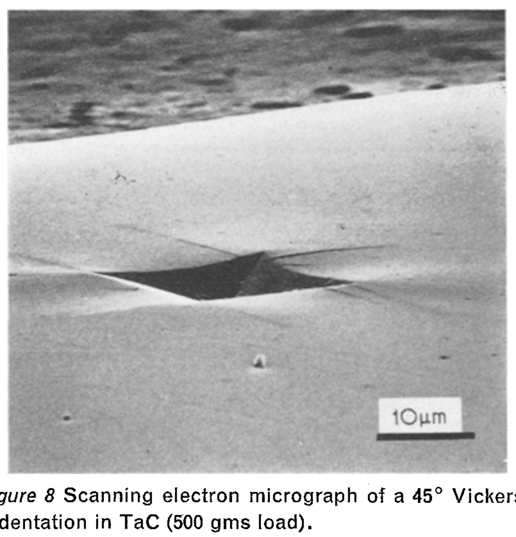

Figure 8 Scanning electron micrograph of a 45° Vickers indentation in TaC (500 gms load).

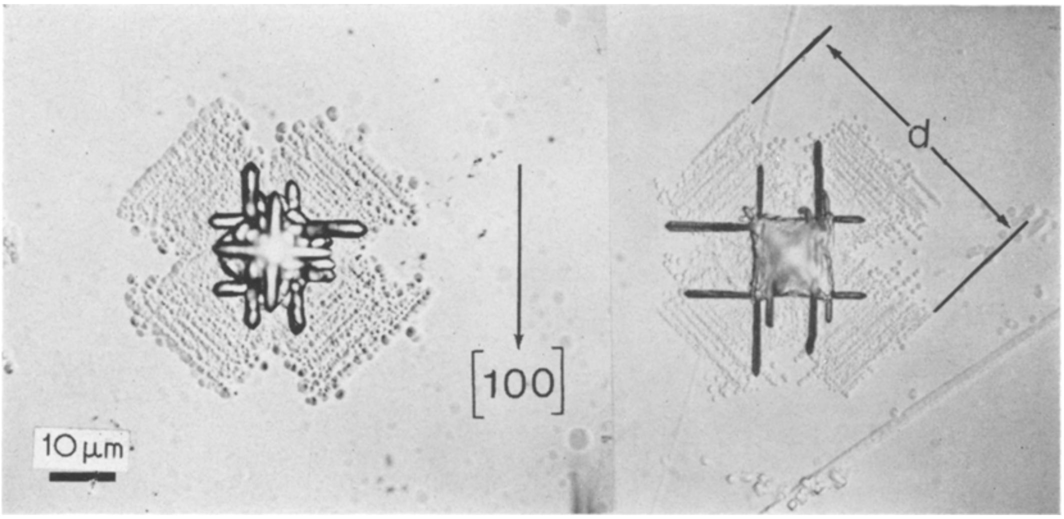

Figure 9 Etch-pitted Vickers indentations (a) at 0° and (b) at 45° in TaC (200 gms load). The distance "d" defines the slip line length.

that brittle cleavage makes no contribution to the initial accommodation of the indenter, but rather that the crystal deforms by slip. Cracking in TaC appears to result from dislocation interactions, and is influenced by the geometry of the hardness indenter. At the start of indentation, dislocations flow into the bulk of the crystal, for example, on a $(\bar{1}11)$ plane, but then pile-up since the stress level drops rapidly with distance from the point of indentation. The stress concentrations can be relieved by slip on other $\{111\}$ planes, in this case $(1\bar{1}1)$, to transfer material to the surface. Interactions between $(\bar{1}11)$ and $(1\bar{1}1)$ slip bands can nucleate cracks directly through dislocation pile-ups which produce tensile stresses across the cleavage plane, or by dislocation interactions of the type:

$$a/2\ [101] + a/2\ [10\bar{1}] \rightarrow a\ [100]$$

Such a dislocation can act as a crack nucleus that propagates along the (100) cleavage plane.

If cracks form through pile-ups or interactions of dislocations then the most likely nucleation points will be in the centres of intersecting slip bands, where slip is densest. In addition, cracks will form preferentially where stress concentrations exist. At 0° indentations the slip bands meet the side of the indenter where there are no preferred sites for crack nucleation and many cracks are formed. At 45° the line of intersection of adjacent faces of the indenter runs through the middle of the slip band. Consequently, it is likely that an additional stress concentration exists along this line and this provides favourable sites for crack nucleation within the slip bands. In general, one or two cracks are formed and can propagate with equal probability in both cleavage planes, i.e. in [010] and [100] directions. At positions close to 45° indentations, e.g. at 30° and 60°, fig. 10, cracking takes place only in one direction from each corner, but the crack patterns around the two indentations are mirror images. This is due to the asymmetric distribution of stress from the indenter faces, the cleavage plane closer to the line of intersection of adjacent faces experiencing the greater stress.

The analysis of crack patterns discussed above suggests that the "degree of brittleness" of a material may be revealed by the crack pattern around indentations. Cracks at indentations in predominantly brittle materials will pass through the centre of the indentation, while those in materials having some plasticity will not be formed until a considerably later stage of deformation and will emanate from the sides of indentations. Since the hardness of TaC increases with decreasing carbon content within the single-phase carbide to values in excess of 2000 kg/mm^2 [3], it might be expected that indentations in low carbon content TaC would resemble those in HfC. This is indeed the case, as shown in fig. 11, cracks passing through the centre of indentations in $TaC_{0.83}$. No deformation was observed

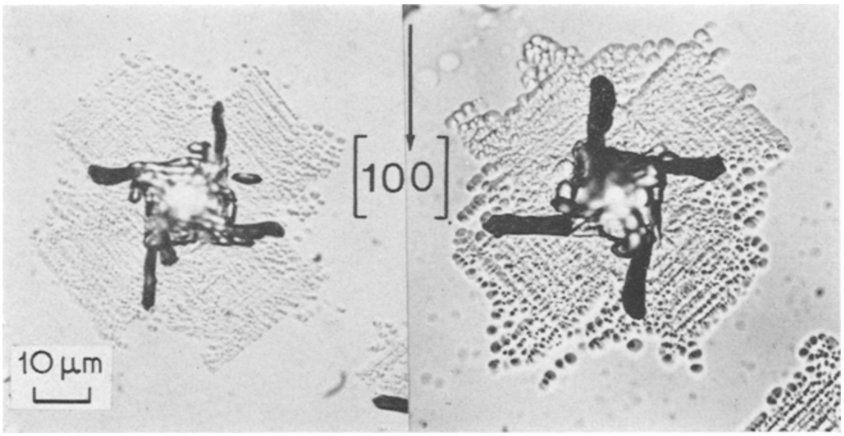

Figure 10 (a) 30° and (b) 60° Vickers indentations in TaC showing mirror relationship in crack pattern (200 gms load).

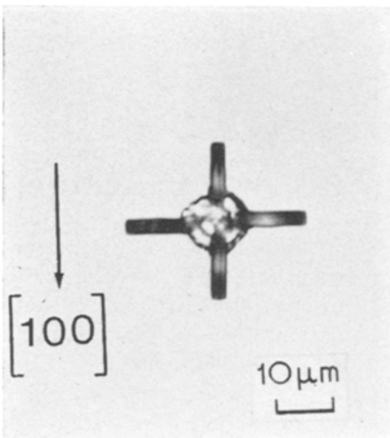

Figure 11 Cracking at a 0° Vickers indentation (100 gms load) in $TaC_{0.83}$ resembles that in HfC.

outside the indentations and the active slip plane was not determined.

A similar effect might also be expected by producing indentations in TaC at lower temperatures. At liquid nitrogen temperature the hardness of TaC increased. Unexpectedly, the same hardness variation with orientation was observed, together with significant plastic flow around indentations. For loads of 100 and 200 gm the slip pattern was similar to that seen at room temperature. At 500 gm load, slip traces in $\langle 100 \rangle$ directions were seen in addition to the usual $\langle 110 \rangle$ traces. An example is given in fig. 12. Two surface analyses showed that the $\langle 110 \rangle$ traces were due to slip on $\{111\}$ planes, but the $\langle 100 \rangle$ traces were the result of $\{110\}$ slip. The operation of a secondary slip system at low temperatures is a surprising result. One possible explanation might be that at 77°K, work hardening rates on the $\{111\}$ planes are sufficiently high that the critical resolved shear stress for slip on $\{110\}$ planes is exceeded before all the stress is accommodated. In accord with the increased hardness, cracks tend to pass through the centre of indentations, particularly at 45° indentations. The crack plane does not appear to be confined to $\{100\}$, although positive identification of the cleavage plane was not made.

4. General Discussion

In view of the extreme variations in hardness with indenter orientation in TaC and HfC and also previously reported for TiC [9], it is somewhat surprising that regular variations of microhardness with carbon-to-metal have been reported in polycrystalline carbides [10-13] where indenter orientation was not controlled. Further work is clearly necessary to substantiate such trends and also any differences in hardness between the various carbides. Alternative variations of hardness with orientation at different carbon-to-metal ratios in the same carbide must also be considered.

From the observations reported in section 3, it is clear that the responses of TaC and HfC crystals to hardness indentation are very different. TaC behaves as a relatively ductile material, i.e. it deforms plastically before it cracks and the cracks arise from dislocation motion. In contrast,

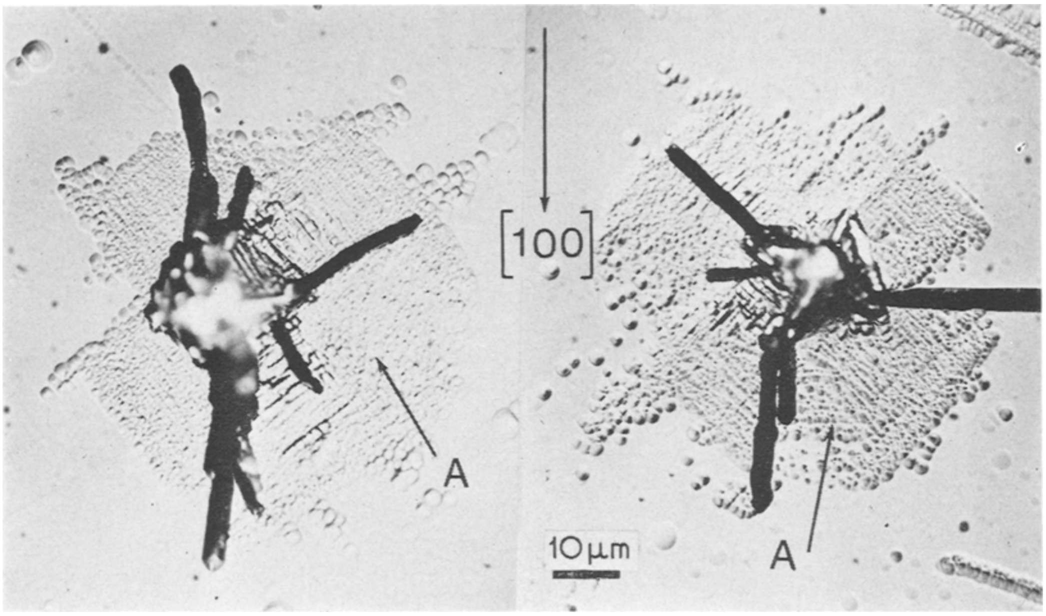

Figure 12 (a) 0° and (b) 45° Vickers indentations (500 gms load) produced at 77°K in TaC. Note the appearance of slip lines parallel to [100] and [010] e.g. at A.

HfC is extremely brittle and exhibits limited plastic flow. Cracking takes place on indentation and in some orientations, Hertzian cracking is also observed. From these differences in properties, it would seem likely that the bulk brittle-to-ductile transition temperature of TaC would be lower than that of HfC. Comparative data for material where carbon-to-metal ratios are accurately controlled are not available, however, Martin and Costa [14] have shown that measurable plastic strain is observed in polycrystalline TaC deformed at temperatures above 720°C, while the lowest temperature at which plasticity in single crystal HfC has been reported is 1000°C [10]. Moreover, dislocations are produced in the TaC component when the directionally solidified eutectic Co-Cr-TaC is deformed at room temperature [15].

At room temperature, plastic flow in TaC takes place on {111} planes, consistent with the deformation of other cubic carbides at high temperatures [1]. One of the most unexpected observations is that of the {110} slip plane of HfC at room temperature. Such a slip plane is usually associated with the deformation of ionic crystals with the rocksalt structure [16]. This implies that the bonding in HfC may be more ionic than that in TaC, however the concept of ionic bonding being a predominant factor for either of these carbides seems unlikely in view of their high electrical conductivity and the inherent electron screening effects. On the other hand, Zeller [17] has pointed out that several of the physical properties of TaC suggest that it is more metallic in nature than HfC. In particular, TaC has a relatively high superconducting transition temperature $\sim$ 9°K while that of HfC is less than 1.4°K [18].

According to van der Walt and Sole [19] a {110} slip plane is also consistent with the deformation behaviour expected from a cubic compound where the bonding forces are predominantly covalent in nature and where the ratio of the radii of the atomic species is close to 0.414. No information on the nature of bonding in HfC is available, however, its physical properties suggest that it is similar to that of TiC, in which the predominant contribution appears to be from covalent metal-metal interactions. Lye [20] has suggested that carbon atoms donate electrons from their p-shell into the titanium atom d-bands. Such charge transfer could cause carbon atoms to contract and the required radius ratio could be achieved. In the present work, it is not possible to apply such considerations unambiguously, since there is considerable controversy over the direction of charge transfer in the carbides. In particular, Ramqvist [13], who has recently summarised the literature in this field, has concluded that charge transfer takes place from metal atoms to carbon atoms, with a result that the carbon atoms would be quite large if this model is correct. Further discussion on the effect of radius ratios will be presented in more general terms to account for the behaviour of carbides other than TaC and HfC, in a later paper [21].

Finally, the most important practical outcome of this work is the observation of relatively extensive plastic flow in TaC at low temperatures. Since notch-sensitivity and brittleness currently limit technological exploitation of carbides, it is significant to note that TaC at high carbon-to-metal ratio exhibits more plastic flow than any other carbide having the rocksalt structure and it may be somewhat tougher than competitive ceramics, although no data to evaluate this are yet available. The potential relative toughness of TaC may also be important in dispersion strengthened alloys. In such systems, cracks can initiate at brittle particles and lead to failure of the alloy. The additional crack resistance and tendency towards plastic deformation in TaC may therefore be a factor in governing the selection of hard particles as dispersions.

Acknowledgements

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References

1. G. E. HOLLOX, *Mater. Sci. Eng.* **3** (1968/69) 121.
2. C. A. BROOKES, *Nature* **228** (1970) 660.
3. D. J. ROWCLIFFE and W. J. WARREN, *J. Mater. Sci.* **5** (1970) 345.
4. E. K. STORMS, "The Refractory Carbides", Academic Press, 1967.
5. F. W. DANIELS and C. G. DUNN, *Trans. ASM* **41** (1949) 419.
6. C. A. BROOKES, J. B. O'NEILL, and B. A. W. REDFERN, *Proc. Roy. Soc.* **A 322** (1971) 73.
7. F. P. BOWDEN and D. TABOR, "The Friction and Lubrication of Solids", Oxford University Press, 1964.
8. D. M. MARSH, *Proc. Roy. Soc.* **A 279** (1964) 420.
9. W. S. WILLIAMS, International Conf. on Semi-Metallic Compounds, Orsay, 1965.
10. W. F. BRIZES, University of Pittsburg, SRCC Report No. 117 (1970).
11. R. STEINITZ in "Nuclear Applications of Non-Fissionable Ceramics", American Nuclear Society, Illinois (1966).
12. I. CADOFF, J. P. NIELSEN, and E. MILLER, *Plansee Proceedings* **2** (1955) 50.
13. L. RAMQVIST, *Jernkont. Ann.* **153** (1969).
14. J. L. MARTIN and P. COSTA, O.N.E.R.A., Paris, private communication.
15. H. BIBRING, G. SEIBEL, and M. RABINOVITCH, Transactions Second International Conference on The Strength of Metals and Alloys (1970), 1178.
16. J. J. GILMAN, *Acta Met.* **7** (1959) 608.
17. H. R. ZELLER, Brown Boveri Research Centre, private communication.
18. G. V. SAMSONOV, "High Temperature Materials", Plenum Press, New York (1964).
19. C. M. VAN DER WALT and M. J. SOLE, *Acta Met.* **15** (1967) 459.
20. R. G. LYE in "Atomic and Electronic Structure of Metals", ASM, Cleveland (1967).
21. D. J. ROWCLIFFE and G. E. HOLLOX, *J. Mater. Sci.*, to be published.

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