Structure and Properties of Tantalum Carbide Crystals

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Single crystals of tantalum carbide, up to 2 mm in size have been grown from solution in a bath of molten iron. The slip plane was found to be {111} using a two-surface analysis on etch-pitted crystals deformed by microindentation at room temperature. Observations of etch-pit patterns around inclusions suggest that slip occurs on other planes at elevated temperatures. Maximum microhardness values between 3800 and 5200 Knoop (100 gm load) were found at a composition $TaC_{0.83\pm0.01}$. In regions of crystals with a carbon content less than $TaC_{0.83}$ a phase transformation was seen close to microhardness indentations in samples decarburised below 2200° C. The mechanical behaviour of tantalum carbide is discussed with reference to a general model for the electronic structure of carbides.

1. Introduction

Like the other monocarbides of the Group IVA and VA transition metals, tantalum carbide possesses the rock salt structure and exists over a wide range of substoichiometry. The most recent phase diagram [1] indicates the composition limits for single-phase tantalum carbide as $TaC_{0.75}$ to $TaC_{0.98}$ below about 1500° C. A maximum melting point of 3983° C occurs at $TaC_{0.98}$. Storms [2] has suggested that the maximum melting point might lie at $TaC_{0.8}$ but he also points out that the actual values of composition and temperature are subject to some uncertainty due to the experimental difficulties in making the measurements [3]. A number of authors have reported a zeta-phase tantalum carbide [4–6] which might be a metastable compound [2, 4, 5]. Its composition has been determined as $TaC_{0.75}$ [5] or $TaC_{0.74}$ [6], but it also appears to exist over a range of substoichiometry [7]. Yvon and Parthé [7] have recently shown that the structure of the zeta-phase consists of an arrangement of twelve close-packed metal atoms in a unit cell, with the carbon atoms in octahedral interstices. The arrangement of the metal atoms can be regarded as alternate layers of hcp and fcc stacking, i.e. a close-packed structure containing 50% stacking faults. Such a structure with a high density of faults is in accord with recent electron microscope studies of $TaC_{0.75}$ which show the existence of a second phase associated with intrinsic stacking faults [8, 9].

A recent review [10] has pointed out that little information on the deformation characteristics and strengths of single crystals of tantalum carbide is yet available, although single crystals have been grown by several workers [11–14]. Mechanical property measurements have been made on a range of substoichiometric polycrystalline tantalum carbides made by carburising tantalum [15–18] or by hot-pressing powders [19, 20]. The hardness of tantalum carbide increases as the carbon content decreases from that of stoichiometric material [16, 18, 19]. Santoro [16] detected a maximum hardness at a composition $TaC_{0.83}$. In agreement with the hardness results, creep rate data suggest an increase in strength at elevated temperatures as the carbon content is reduced from $TaC_{1.0}$ to $TaC_{0.8}$ [19]. Conversely, the bend and tensile strengths at room temperature and the tensile strength at elevated temperatures all pass through minimum values which lie between $TaC_{0.8}$ and $TaC_{0.9}$ [16, 17].

The mechanical behaviour of tantalum carbide is clearly not well understood. The apparently conflicting results so far reported for polycrystalline tantalum carbide may be partly due to differences in the physical characteristics of

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material prepared by various methods. The present work was therefore directed towards growing single crystals of tantalum carbide and examining the hardness and deformation behaviour at room temperature.

2. Experimental

Single crystals of tantalum carbide were prepared by solution and growth from a bath of molten iron, following Robins [11]. Spectrographically pure tantalum powder was mixed with reactor grade graphite and electrolytic iron powder to give a final concentration of 15 wt. % tantalum carbide in iron. The powders were cold-pressed into slugs and melted in a graphite crucible in a graphite tube furnace under one atmosphere of helium. The crucible temperature was maintained at 2200 ± 50° C for one hour then the melt was cooled at approximately 10° C/hour to 1450° C when the furnace was shut down. The crystals were extracted by leaching the iron regulus with warm concentrated hydrochloric acid.

Under these preparation conditions, several hundred golden, cube-shaped crystals of tantalum carbide were produced from a starting weight of 30 gm tantalum. The largest crystals were 2 mm along a cube edge but the majority were between $\frac{1}{2}$ and 1 mm. As reported by Robins, lower bath temperatures resulted in smaller crystals. It was also found that the yield of large crystals was diminished by higher cooling rates and larger concentrations of tantalum. The lattice parameter of crushed crystals was determined to be 4.456 Å using a 57.3 mm diameter Debye-Scherrer camera. Using similar crystal growth conditions, Robins determined values of the lattice parameter between 4.4550 and 4.4555 Å, the composition of the crystals being determined as $TaC_{0.96}$. According to the data of Bowman [21], a lattice parameter of 4.456 Å corresponds to a composition $TaC_{0.99}$. Electron microprobe analysis showed that the bulk of each crystal contained only tantalum and carbon but in some crystals one or two small inclusions of iron and carbon were present.

For decarburisation experiments, crystals were placed on a tantalum sheet and electron beam heated between 1700 and 2250° C at approximately 10^{-6} torr, for up to 6 h. For optical metallography, crystal orientation and microhardness testing, crystals were mounted in bakelite and mechanically polished with 1 μm diamond paste with a final polish using "Cer-Cre" with an addition of sodium hydroxide and potassium ferricyanide solution. Dislocation etch-pits were produced in tantalum carbide using a solution of 40 ml HCl, 10 ml HNO_3, 1 ml HF at 60 to 70° C for 4 min. Crystal faces were oriented using a Laue back-reflection technique and Knoop and Vickers hardness indentations were made using a Leitz microhardness tester with 100 g load.

3. Results

3.1. As-grown Crystals

Laue back-reflection patterns established that the tantalum carbide crystals were bounded by {100} faces. Using 100 g load, the averages of at least seven Knoop hardness indentations per crystal, on five different crystals, on {100} faces were 1650, 1500, 1500, 1500 and 1450 kg mm^{-2}. In each case, the indenter was aligned with its long diagonal parallel to a ⟨010⟩ crystal edge. On etch-pitting, considerable slip was revealed in the regions immediately adjacent to the indentations as shown in fig. 1. The rows of etch-pits extend in ⟨011⟩ directions on a {100}-type face. To determine the slip plane, indents were sectioned on a {001} plane and etch-pitted. Again the slip traces were found to lie in ⟨110⟩ directions as can be seen in fig. 2. Thus, the slip plane must be {111}.

Some tantalum carbide crystals were found to contain inclusions which were approximately

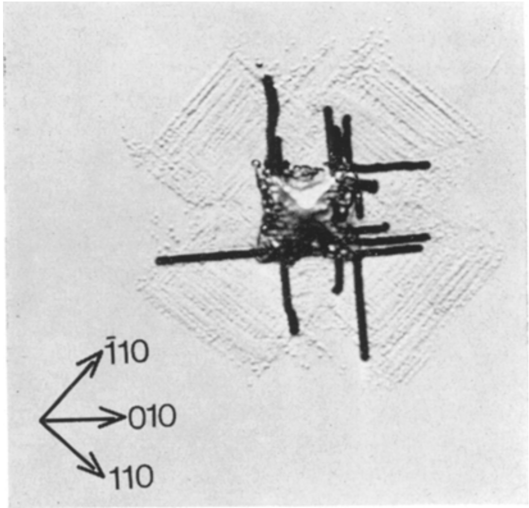

Figure 1 A Vickers hardness impression on a {100} plane in tantalum carbide after etch-pitting, showing ⟨110⟩ slip traces and ⟨010⟩ crack traces (× 756).

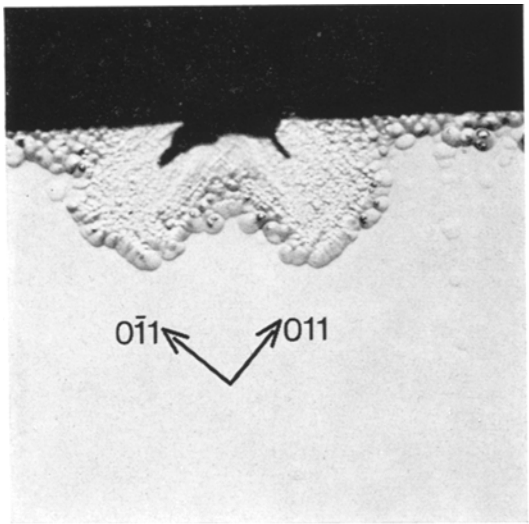

Figure 2 Etch-pitted $\{001\}$ plane section of a Vickers hardness impression ($\times$ 343).

orthogonal and whose edges lay in $\langle 100\rangle$ directions. Electron microprobe analysis of these inclusions indicated that they were composed of iron and carbon. Etch-pitting revealed rows of pits in the area of the crystal adjacent to an inclusion, as shown in fig. 3. Four crystals containing inclusions were examined and in each case lines of pits were seen in $\langle 010\rangle$ and $\langle 110\rangle$ directions on $\{100\}$ planes. It is thought that these pits corresponded to dislocations generated during cooling, following growth. The carbon-rich iron inclusions which arise from the bath are expected to solidify at approximately 1200° C. The stresses set up by the differential thermal contractions of the carbide and the inclusions apparently cause the surrounding crystal to deform. The slip pattern suggests that tantalum carbide can deform on other slip planes in addition or in preference to $\{111\}$ at elevated temperatures. The $\langle 110\rangle$ traces could be due to slip on $\{111\}$ or $\{011\}$ planes and the $\langle 010\rangle$ traces could be caused by slip on $\{001\}$ or $\{011\}$ planes. Since $\{111\}$ slip has been observed during indentation at room temperature, this is a likely mode of deformation at higher temperatures; however the identifications of the second slip plane cannot be made positively from the present data.

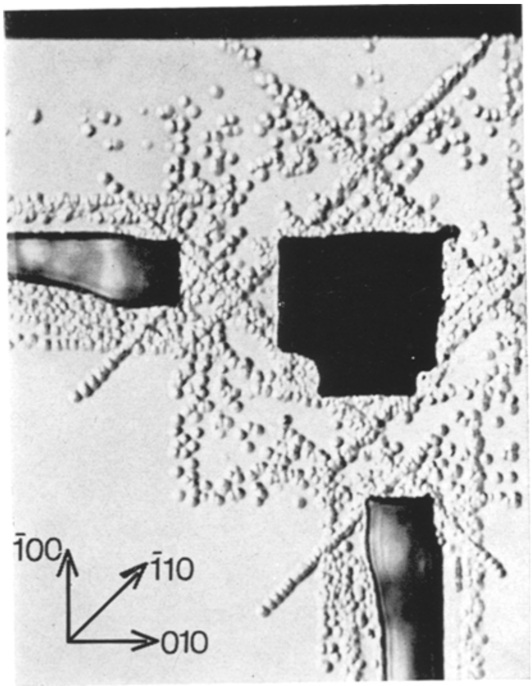

Figure 3 Slip patterns around inclusions in tantalum carbide ($\times$ 687).

3.2. Decarburised Crystals

On decarburisation, the colour of tantalum carbide changed from golden to grey. In cross-section the crystals consisted of three distinct regions, viz. (a) a single-phase area adjacent to the tantalum, thought to be polycrystalline Ta$_2$C; (b) a multi-phase region, and (c) the bulk of the tantalum carbide crystal. The extent of the Ta$_2$C and the multi-phase regions were greater for higher annealing temperatures and times. The multi-phase region is reported to consist of TaC, the zeta-phase and Ta$_2$C [1, 4]. Knoop and Vickers microhardness traces were made across $\{100\}$ crystal faces. Indentations made in the bulk crystal just beyond the visible limit of the multi-phase region produced a structure which is similar to that of the multi-phase region, as shown in fig. 4. The traces associated with the indentations are parallel to those seen in the multi-phase region and lie in $\langle 110\rangle$ directions on the $\{100\}$ tantalum carbide surface. The markings could be due to slip or a phase transformation. It seems unlikely that these are slip lines because (a) slip lines were very difficult to detect in indented as-grown crystals before etch-pitting and (b) rows of etch-pits could not be produced in the regions containing the markings. The similar appearances of the multiphase region and the structures at the indents suggest that a phase transformation, which might be stress induced, has occurred.

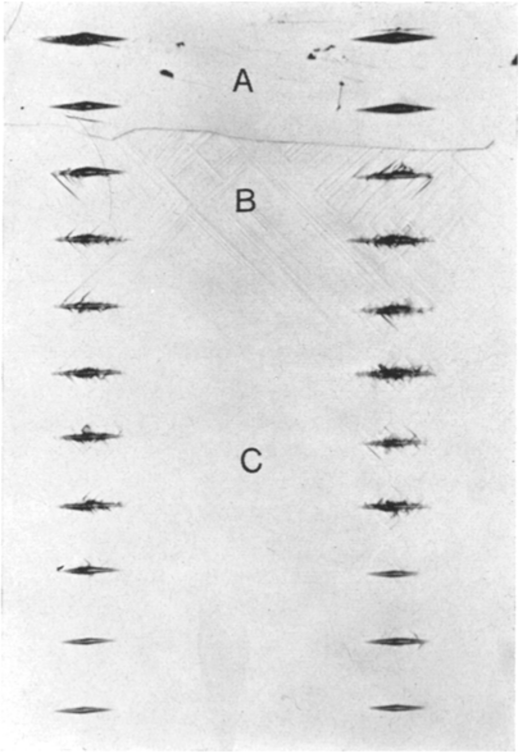

Figure 4 Indentation traces across a crystal of tantalum carbide decarburised at 2200° C for 5 h (×343). A Ta_2C. B Multi-phase region. C Region of phase transformation at indents.

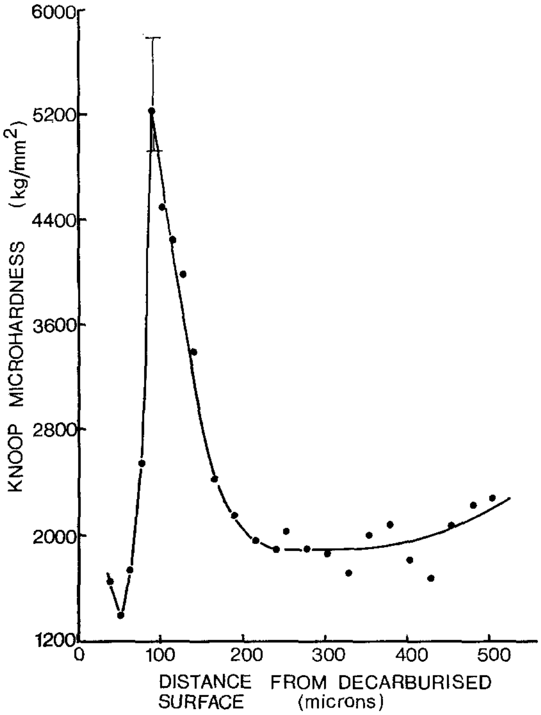

Figure 5 The variation of Knoop hardness (100 g) with distance from the decarburised surface in tantalum carbide.

The variation of Knoop hardness (100 g load) with distance across a crystal decarburised for 6 h at 2250° C is shown in fig. 5. The region of very high hardness extends for approximately 100 μm. In fig. 5, the error band inserted for the maximum value at 5200 kg mm^{-2} assumes that the length of the indent diagonal can be read to $\pm$ 0.5 μm. Two parallel hardness traces on the same crystal confirmed the position and value of this maximum. In the hardest region of the crystal no dislocation etch-pits were visible outside the indents and there was a noticeable absence of random etch-pits in this region. In the bulk of the crystal, a small amount of slip occurred outside each indent and many random etch-pits were also visible. The phase transformation seen at indents in crystals decarburised at 2200° C for 5 h (fig. 4) and in crystals decarburised at 1900 and 1750° C was not seen in this sample. In addition, the maximum hardnesses in these other crystals were in the range 3600 to 3900 kg mm^{-2}. A crystal from the batch decarburised at 2250° C was mounted on the face which had been in contact with the tantalum sheet. The sample was polished until the multi-phase region had disappeared. The average of five indentations gave the hardness of the new surface as 3800 Knoop (100 g), so it was assumed that the region of highest hardness had been reached. The lattice parameter of this surface was measured using a back-reflection diffractometer technique. Peaks were recorded for the (002) (004) (006) and (008) reflections using MoKα radiation. The calculated lattice parameters were plotted against the Taylor-Sinclair function, $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$, and extrapolated to $\theta = 0°$. The corrected lattice parameter was 4.430 $\pm$ 0.002 Å. This corresponds to a composition $TaC_{0.83\pm0.01}$ using the data of Bowman[21].

4. Discussion

The observation of $\{111\}$ slip in tantalum carbide is an expected result since this is the plane on which titanium and vanadium carbides deform, in the plastic range. The hardness values for stoichiometric tantalum carbide agree with those generally reported for polycrystalline material and with recent data on single crystals also grown from a metal bath [14]. It is notable that stoichiometric tantalum carbide is considerably softer than most of the other monocarbides of the Groups IVB and VB transition metals. In titanium carbide, which has a hardness of approximately 3000 kg mm^{-2}, slip patterns are not seen on etch-pitting crystals indented at room temperature [22]. It was noticed in the present work that when the hardness of decarburised tantalum carbide exceeded approximately 2000 kg mm^{-2} then little slip was seen outside the indentations. Little can be said about the slip behaviour of tantalum carbide at elevated temperatures from the present observations at inclusions. However, it has been shown that single crystals of zirconium carbide can be made to slip on $\{111\}$ $\{110\}$ and $\{100\}$ planes above the ductile-brittle transition temperature, depending upon the deformation conditions [10]. The phase transformations observed near indentations in decarburised crystals occur for compositions between the multi-phase boundary, $TaC_{0.75}$ and the position of the hardness maximum, $TaC_{0.83}$. Considering the recent data on the structure of the zeta-phase [7–9] it is suspected that the transformation could be due to the generation of stacking faults associated with the zeta-phase. This idea also receives some support from the work of Zaplatynsky [5] who found that the zeta-phase can be generated from tantalum carbide of the same composition, under compressive stresses. The phase transformation was not seen on indenting crystals decarburised above 2200° C, which confirms a previous observation that the formation of the zeta-phase is temperature-sensitive [6]. Brizes has observed similar markings at indents in substoichiometric tantalum carbide and suggests that they are due to the precipitation of zeta-phase or Ta_2C [18].

The position of a hardness maximum at the composition $TaC_{0.83}$ is in agreement with the results of Santoro [16] who examined carburised tantalum filaments. The hardness values determined in the present study are considerably higher, however, and the hardness maxima between 3800 and 5200 Knoop, determined in different crystals, appear to be the highest hardness reported for any pure carbide. The composition $TaC_{0.83}$ lies close to that of the maximum melting point of 3983° C in the tantalum-carbon system. Tantalum carbide is one of the most refractory materials known, and it might be expected that its hardness should be very high. Obviously the correlation between melting point and hardness is only a general one since these two properties reflect the strength of the interatomic bonds in different ways. The explanation of the high hardness in $TaC_{0.83}$ probably requires a detailed knowledge of the band structure. Dempsey [23] has made a general approach to the electronic structure of transition metals and some of their compounds, based upon reported melting points. He considers that the bonding in the transition metal carbides is mainly metallic and he suggests that the p electrons of the carbon atoms become located in the metal d band when the carbides are formed. On an empirical basis an optimum d band number of about 6 electrons is arrived at for compounds of greatest stability. According to Dempsey's model stoichiometric tantalum carbide has approximately 6.5 electrons in its d band whereas hafnium carbide has 5.5 electrons. The reported maximum melting point alloy between these two carbides [24, 25] is thus expected on the basis of a change in the number of electrons in the d band to the ideal of 6. A similar argument can be advanced to account for the peaks in hardness and melting point observed in substoichiometric tantalum carbide. However, this view is somewhat speculative in the absence of band structure calculations.

5. Conclusions

1. The hardness of single crystals of tantalum carbide grown from solution in iron ranges between 1450 and 1650 Knoop (100 g) on the $\{100\}$ planes in the $\langle 010 \rangle$ directions.
2. The slip plane for stoichiometric tantalum carbide, indented at room temperature, is $\{111\}$.
3. Above approximately 1200° C slip can occur on other planes which might be $\{001\}$ or $\{011\}$.
4. A phase change occurs at microhardness impressions made in tantalum carbide compositions lying between $TaC_{0.75}$ and $TaC_{0.83}$.
5. A maximum hardness in the tantalum-carbon system occurs at a composition $TaC_{0.83\pm 0.01}$.
6. The hardness of $TaC_{0.83}$ lies between 3800 and 5200 Knoop (100 g).
7. The hardness maximum at the composition $TaC_{0.83}$ is broadly explicable in terms of the attainment of an optimum number of bonding electrons in the d band.

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