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Deformation behaviour of single crystals of titanium carbide

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Single crystals of titanium carbide were deformed in compression over a wide range of temperature, and the operative slip systems were determined by etch-pitting and electron microscopy. Around the brittle–ductile transition temperature, the slip system undergoes a gradual change from $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$ to $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$; this is interpreted to be the mechanism governing the brittle–ductile transition in titanium carbide.

1. Introduction

Titanium carbide, like other monocarbides of the Group IV-A and V-A transition metals, possesses the rock-salt (B1-type) structure and exists over a wide range of substoichiometry [1]. Although TiC has many attractive properties, the low-temperature brittleness of this material restricts its wide-range applications. This brittleness is probably due to covalent-type metal–metal and metal–nonmetal hybrid bonds [2]. However, the indication of a brittle–ductile transition in TiC around 800° C [3] suggests the potential for development of this material, especially for elevated temperature applications. Efforts have been made in the past to determine the slip system in most transition metal monocarbides, including TiC, utilizing techniques such as hardness anisotropy [4–7], etch-pitting [3], and electron microscopy [8]. Establishment of the operative slip planes below the brittle–ductile transition temperature is difficult because of premature failures. The hardness anisotropy technique makes this possible, albeit indirectly, because the hardness indentation produces a large hydrostatic pressure which prevents brittle failure [9, 10].

The present paper describes experiments performed to establish, in an unequivocal manner, the operative slip systems in TiC over a wide temperature range, to obtain direct evidence of slip behaviour, particularly at temperatures below the brittle–ductile transition, and to determine the mechanism(s) of the brittle–ductile transition behaviour of TiC.

2. Experimental

The samples used in this study were obtained from a single crystal boule‡ having a C-to-Ti ratio of 0.93. This single crystal boule was oriented by the standard Laue back-reflection method to obtain the $\{1\,0\,0\}$ faces, and 3 mm thick slices were cut parallel to the $\{1\,0\,0\}$ faces from the boule. From these slices, 3 mm × 3 mm × 4 mm blocks were cut. As a check, Laue back-reflection patterns were obtained from some of the faces of these blocks chosen at random and all the faces were found to correspond to $\{1\,0\,0\}$. The faces of these blocks were given a light diamond polish to remove saw markings and to make the ends exactly parallel. These blocks were then deformed in compression along their long axis at various temperatures ranging from room temperature up to 1100° C. The tests were performed in an Instron machine at a cross-head speed of 0.002 in. min^{-1}. For high temperature tests a tungsten resistance furnace was used with the Instron assembly, and this furnace was maintained at a vacuum of 2×10^{-5} Torr. The

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‡ The $TiC_{0.93}$ single crystal was grown by Mr W. Precht of Martin Marietta Laboratories, Baltimore, and the boule was donated by Dr J. D. Venables.

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single crystal blocks were placed between two smooth hot-pressed Si_3N_4 platens for compression testing. In order to minimize friction effects, boron nitride powder was sprinkled at the interfaces of the Si_3N_4 platens and the test specimens. In each test the compressive deformation was continued up to a point just prior to specimen fracture. This was achieved by performing a few trial tests before each deformation experiment. In these trial tests identical specimens were deformed up to fracture at each temperature. From the idea of the load required to fracture these specimens at each temperature, the load was controlled to the point just prior to fracture in each deformation experiment. In these tests no visible indication of plasticity was observed on the recording chart. After each deformation, the specimens were cleaved and the cleaved surfaces checked by Laue back reflection to be {1 0 0}. These cleaved specimens were etched in boiling H_2SO_4 for 5 min, and two orthogonal surfaces of each etched specimen were observed under an optical microscope for etch-pit decorated slip traces.

Transmission electron microscopy of both as-grown and deformed single crystals of $TiC_{0.93}$ was performed by spark machining 3 mm diameter discs from 0.25 mm thick slices cut from the boule, and by electrolytic thinning of these discs employing a double-jet technique. An electrolyte mixture of perchloric acid, butanol, and methanol in the ratio 1:4:10 by volume was used, and the disc specimens were thinned in this electrolyte at 20 V and at -20° C. These thinned specimens were examined in a Philips EM 300 microscope operated at 100 kV. *In situ* annealing experiments of the deformed specimens were carried out using a heating holder for this microscope.

3. Results

The deformation geometry of the samples having {1 0 0} faces and the probable planes on which slip can take place are sketched in Fig. 1. From this figure, it is obvious that only two types of slip traces are possible – traces parallel to ⟨1 0 0⟩ and those at 45° to ⟨1 0 0⟩. The parallel traces indicate occurrence of slip only on {1 1 0}, whereas diagonal (45°) traces indicate that slip is operative on either {1 1 0} or {1 1 1}, or on both. However, due to the specific deformation geometry adopted in this study, the diagonal traces will be absent on the {1 0 0} faces of the crystal for slip on {1 1 0} (Fig. 1b). Thus, in this study traces parallel to

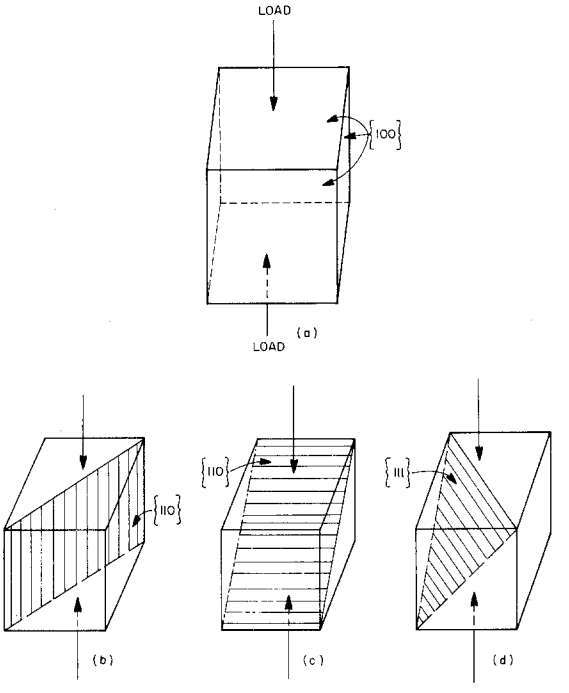

Figure 1 Probable deformation geometry of single crystal TiC.

⟨1 0 0⟩ will indicate slip on {1 1 0}, and diagonal traces will indicate slip on {1 1 1}.

Optical micrographs obtained from cleaved and etched {1 0 0} faces of crystals deformed at various temperatures are shown in Fig. 2. The edges of these photomicrographs are parallel to the ⟨1 0 0⟩ crystal edges. It can be seen from these optical micrographs that the individual pits produced have a square shape with edges in the ⟨1 0 0⟩ direction and pyramidal bottoms. Apart from etch pits produced by glide dislocations, several isolated etch pits, subgrain boundaries, and cleavage steps are visible on the etched faces of the specimens. One noticeable feature is that the glide-band density is not uniform throughout the crystal faces, except for the experiment carried out at 1100° C. For deformation at room temperature, it can be seen that the slip lines are parallel to the ⟨1 0 0⟩ edges, and similar observations are recorded for the deformation experiments carried out at 200, 400, and 500° C. Optical micrographs taken from the cleaved and etched surfaces of specimens deformed at 600 and 700° C revealed the presence of both parallel and diagonal traces, the propensity for diagonal traces being greater at both temperatures. However, for deformation experiments carried out at 800° C and above, only diagonal

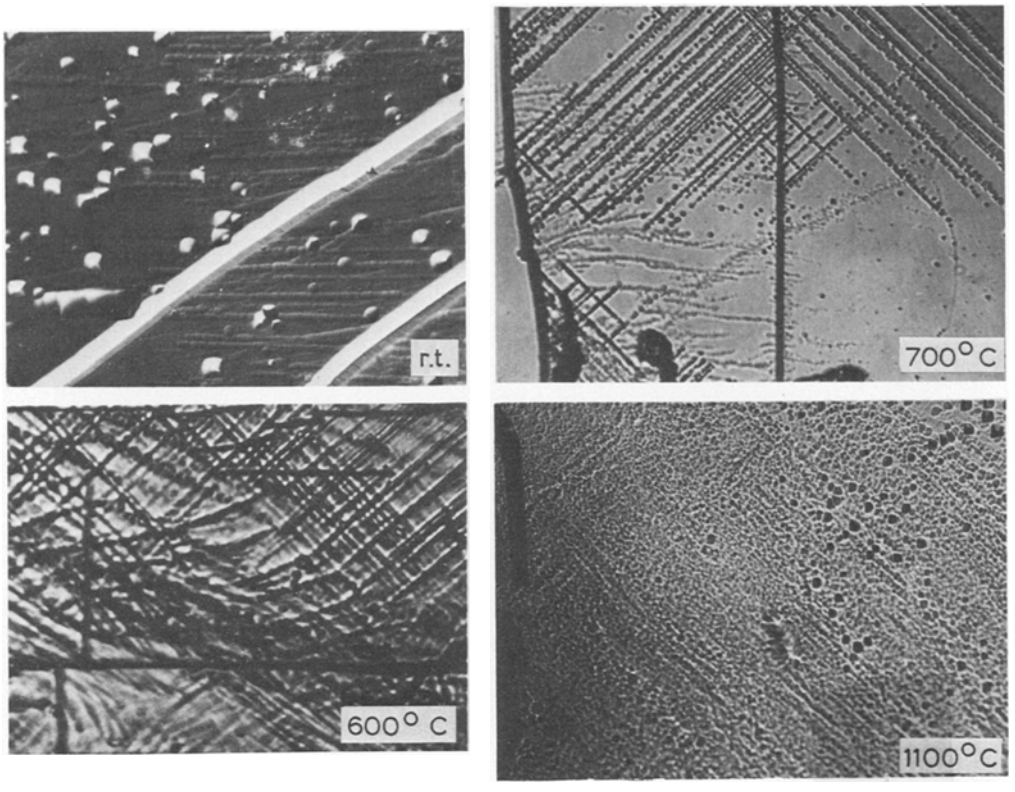

Figure 2 Photomicrographs showing slip steps formed by etch pits. Deformation temperatures are given.

slip traces were visible. The results described above hold for both transverse and longitudinal cleaved faces.

Transmission electron microscopy of as-grown crystals revealed the presence of predominantly low-angle grain boundaries. Most of the thin foils observed under the electron microscope were free from dislocations. Only a few isolated dislocations were evident in some of the foils. In the deformed specimens, however, numerous dislocations, dislocation tangles, vacancy loops, and cell structures (Fig. 3) were present. The contrast analysis of these dislocations using the two-beam condition indicated the Burgers vector to be of the form $\langle 1\,1\,0 \rangle$ (see Fig. 4).

In an attempt to confirm the slip planes by electron microscopy, a few deformed samples were subjected to an *in situ* heating experiment employing the heating stage of the EM 300. The aim of this experiment was to observe either a pile-up of planar dislocations during glide or slip traces created on the foil surface by gliding dislocations and to deduce the slip planes from these observations. Unfortunately, neither the pile-up of planar dislocations nor the slip traces were observed in these experiments – even after the foils were heated up to 950° C. Hence, determination of the slip plane by electron microscopy could not be achieved. However, an interesting observation of the *in situ* annealing experiment was the considerable reduction in the dislocation population and the clearing of the cell structure

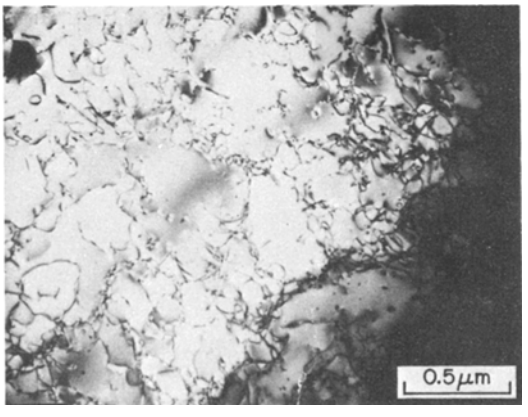

Figure 3 Dislocation structure in deformed $TiC_{0.93}$ single crystal.

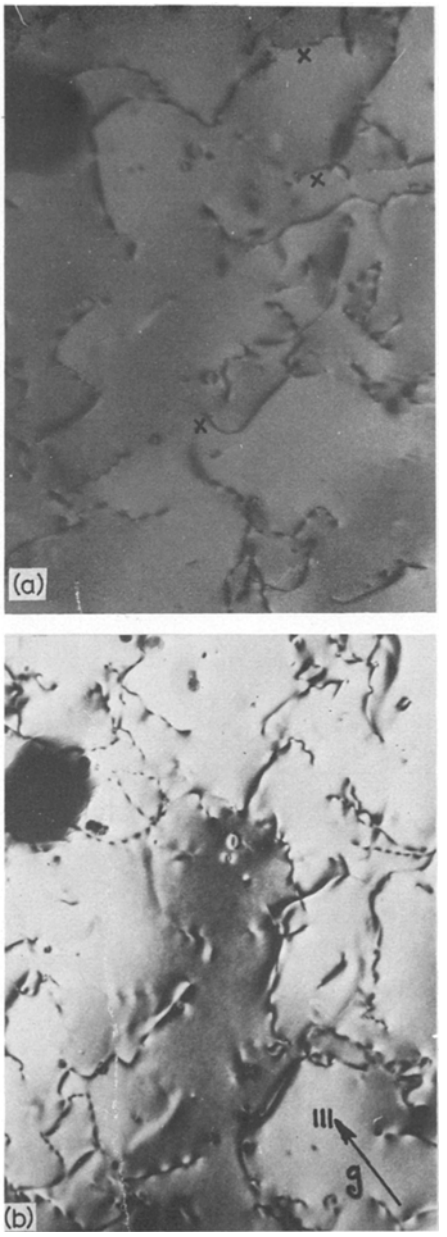

Figure 4 Dislocations in a {1 1 0} foil of deformed $TiC_{0.93}$ single crystal under two beam conditions. In (b) some dislocations marked × in (a) are out of contrast. Operating reflection is (1 1 1).

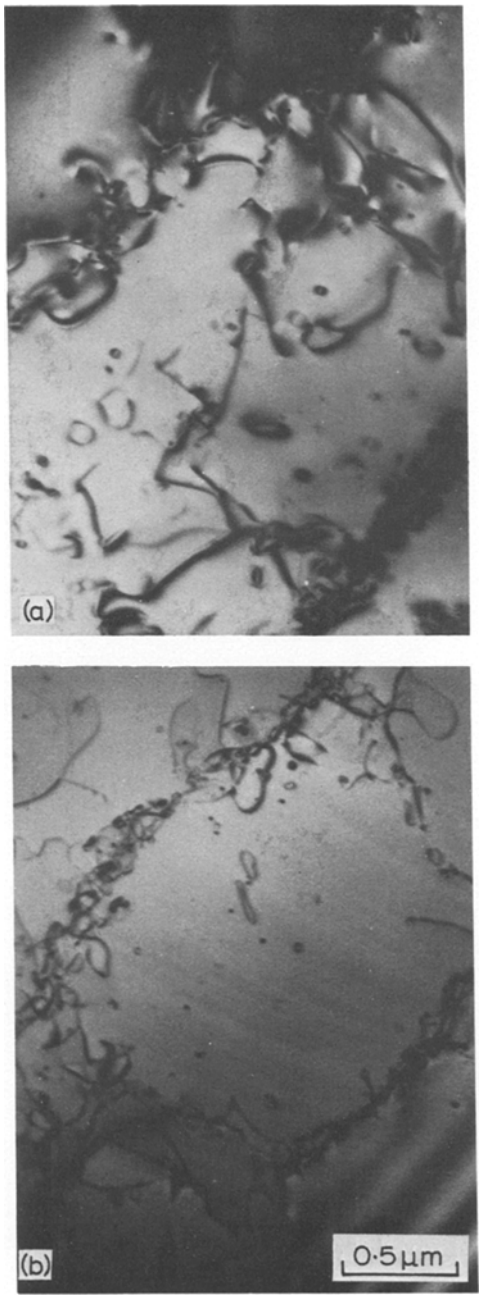

Figure 5 In situ annealing of a thin foil of $TiC_{0.93}$. (a) Before annealing. (b) Same area after 1 h annealing at 700° C.

which occurred during the course of annealing. Typical electron micrographs for an experiment conducted at 700° C are shown in Fig. 5.

4. Discussion

The observation of slip traces parallel to the ⟨1 0 0⟩ of {1 0 0} faces of single crystal $TiC_{0.93}$ produced by compressive deformation of the crystals at room temperature clearly establishes that slip is occurring on the {1 1 0} planes at that temperature. Earlier efforts on determining slip planes employing the hardness anisotropy technique [4, 6, 7] also indicated the occurrence of slip on {1 1 0} in TiC single crystals at room temperature. In those investigations, however, the presence of slip traces around hardness indentations could

not be observed. Hardness anisotropy is a well-established indirect technique for defining slip planes, particularly in brittle materials since the anisotropy is essentially determined by the crystal structure and the primary slip system of the material [5]. However, it is also known that crystal imperfections (e.g., composition inhomogeneity, carbon precipitation, and grain boundaries) contribute to anisotropy in hardness and that in hardness measurements neither the stress nor the strain rate is homogeneous. Hence, the present observation of slip lines parallel to the $\langle 1\,0\,0 \rangle$ direction of the deformed single crystals constitutes more direct evidence of slip on $\{1\,1\,0\}$ in TiC at room temperature. The observation of slip traces both parallel and at 45° to the $\langle 1\,0\,0 \rangle$ of the crystal for deformation temperatures of 600 and 700° C indicates that the active slip system undergoes a transition around these temperatures and that slip on $\{1\,1\,1\}$ along with slip on $\{1\,1\,0\}$ is also operative. The appearance of only diagonal slip lines for a deformation temperature of 800° C and above confirms that slip takes place only on $\{1\,1\,1\}$, which is in agreement with the observation made by Williams and Schaal [3].

The absence of dislocations in the thin foils of the as-grown $TiC_{0.93}$ crystal suggests that the creation of dislocations and their multiplication in this material is extremely difficult. One would expect that, during crystal growth, sufficient numbers of dislocations are created [11] and that they move in the grown crystal as a result of non-uniform thermal stresses and multiply. However, if the intrinsic lattice friction (Peierl's stress) in a material is sufficiently high, it would be extremely difficult to create dislocations and effect their multiplication. Due to the predominance of covalent bonding in TiC [2], it is thought that this material possesses a high Peierl's stress [3] which may be the reason for the absence of grown-in dislocations in crystals of $TiC_{0.93}$. Evidence of high Peierl's stress in this material can also be derived from the *in situ* heating experiments in which thin foils prepared from deformed crystals were annealed at 700° C (see Fig. 5). In this experiment the characteristic glide of planar dislocations such as that in fcc materials was not observed. Instead, a considerable reduction of dislocation population was observed as well as the clearing of the cell structure during annealing at 700° C. From this observation it seems reasonable to suggest that a dislocation climb process is operative at this temperature and that by this process the dislocations are annihilated at the foil surface.

The presence of dislocation loops and cell structures in TiC crystals deformed at high temperatures indicated that extensive cross-slip occurred during the deformation process and that the stacking fault energy of titanium carbide is sufficiently high for cross-slip to be operative. Hollox and Smallman [8] also indicated that TiC possesses high stacking fault energy, the reason for this having been explained in terms of the band structure of this material.

Contrast analysis of the planar dislocations in deformed $TiC_{0.93}$ suggested that the Burgers vector is of the form $\langle 1\,\bar{1}\,0 \rangle$; this reaffirms the findings of Hollox and Smallman [8] and postulations made by several investigators [3,4]. From the present study it can be concluded that the active slip system in $TiC_{0.93}$ undergoes a change near 600° C. Below this temperature the $\{1\,1\,0\}\langle 1\,\bar{1}\,0 \rangle$ system is active; in the range 600 to 700° C, both $\{1\,1\,0\}\langle 1\,\bar{1}\,0 \rangle$ and $\{1\,1\,1\}\langle 1\,\bar{1}\,0 \rangle$ systems are operative; at 800° C and above, only the $\{1\,1\,1\}\langle 1\,\bar{1}\,0 \rangle$ slip system is active. Incidentally, the temperature of transition of the active slip system which was observed in the present study is near the reported brittle–ductile transition temperature of TiC, which is around 800° C [3]. Ceramic materials which slip on $\{1\,1\,0\}$ planes have two independent slip systems and are essentially brittle, whereas fcc metals and alloys which slip on the $\{1\,1\,1\}$ planes have five independent slip systems. One of the necessary conditions for fully ductile deformation in a polycrystalline material is the operation of five independent slip systems (von Misés criterion) which ensures that the deformation of each grain will conform to the deformation of neighbouring grains. Hence the onset of $\{1\,1\,1\}$ slip in $TiC_{0.93}$ around 800° C satisfies a necessary condition for gross ductility in this material. The transition in the slip system shown in this investigation is consistent with the reported very rapid drop of CRSS on the $\{1\,1\,1\}\langle 1\,\bar{1}\,0 \rangle$ system in the neighbourhood of 800° C [12]. Thus, the mechanism of the brittle–ductile transition is the change of slip system from $\{1\,1\,0\}\langle 1\,\bar{1}\,0 \rangle$ to $\{1\,1\,1\}\langle 1\,\bar{1}\,0 \rangle$ which is accompanied by an appreciable reduction of CRSS at high temperatures.

5. Conclusions

(1) The brittle–ductile transition temperature of TiC is around 800° C.

(2) The slip system of TiC below the brittle–ductile transition temperature is $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$.

(3) Above the brittle–ductile transition temperature, the operative slip system is $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$.

(4) Around 600° C a gradual transition from $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$ slip to $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ occurs, and around this temperature both slip systems are operative.

(5) During high temperature deformation, extensive cross-slip occurs in this material which suggests that TiC possesses a high stacking fault energy.

(6) Transition of the slip system and operation of $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$ slip is the mechanism responsible for the brittle–ductile transition in TiC.

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