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The mechanical properties of tungsten grown by chemical vapour deposition

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ABSTRACT

The mechanical properties of polycrystalline tungsten grown by chemical vapour deposition (CVD) have been investigated. Fracture tests were performed on the material over the 24–967 °C temperature range at a low strain rate. The material was found to be brittle or semi-brittle across the entire temperature range investigated. This behaviour differs significantly from that previously found in conventionally-grown polycrystalline tungsten, which, under similar experimental conditions, is found to be ductile above approximately 120 °C. Energy dispersive X-ray analysis indicates that in the CVD tungsten, there is a significant concentration of fluorine at grain boundaries. It is therefore suggested that fluorine segregation to grain boundaries is responsible for the increased brittleness observed in the CVD tungsten.

1. Introduction

Tungsten has been proposed as a plasma-facing material for critical components in next-generation fusion reactors, such as ITER [1], where working conditions will be particularly extreme in terms of radiation damage, high temperatures and stresses. High-purity tungsten can be produced by various methods, including zone refining, electron beam crystallization, sintering, plasma spraying and chemical vapour deposition (CVD). As the method of growth affects the grain size, the shape of grains and the impurity distribution, different growth methods are expected to give rise to differences in the material's mechanical properties.

At low temperatures, many materials fail by cleavage and exhibit completely brittle behaviour. At high temperatures, as dislocation activity becomes important, such materials can show ductile behaviour, characterized by significant plastic deformation. A brittle-to-ductile transition (BDT) temperature (T_{BDT}) can be measured for each specific material and test condition. For many materials, T_{BDT} is found to vary with strain rate according to an Arrhenius relation, with a characteristic activation energy, E_{BDT}:

$$\frac{d\varepsilon}{dt} = A\exp\left(-\frac{E_{BDT}}{kT_{BDT}}\right). \tag{1}$$

In studies of BDT behaviour in single-phase materials, such as silicon [2], germanium [3] and alumina [4], it has been established that this activation energy is the same as that for dislocation glide, implying that the glide of dislocations in the region near the crack tip controls the fracture process. It has also been found empirically that E_{BDT}/kT_{BDT} is approximately 25 for a wide range of materials [5].

In a study of the BDT in single-crystal tungsten, Gumbsch et al. found E_{BDT} to be approximately 0.2 eV [6]. Dislocation velocity data for tungsten (as for BCC metals generally) are rare and data are only available at 77 K and room temperature [7]. However, numerical simulations suggest the motion of the screw dislocations that control the rate of plastic deformation [8] is controlled by an activation energy in excess of 1 eV [9]. The low value of E_{BDT} found by Gumbsch et al. can be attributed to the crystallography of the particular specimens used for their experiments in which, uniquely, the controlling process is likely to be the glide of edge dislocations. More recent work in Oxford has found E_{BDT} to be approximately 1.0 eV in both pure polycrystalline and pure single-crystal tungsten [10] and 1.45 eV in less pure sintered material [11]. This implies that, for the general case, the BDT in tungsten is controlled by screw dislocation motion. For these specimens, the BDT was in the temperature range 100–300 °C.

Research into the mechanical properties of CVD-grown tungsten indicates that its T_{BDT} is higher than that in tungsten grown by other methods [12,13]. In this study, the mechanical properties of CVD-grown tungsten were investigated using the same methodology as the recent studies on pure polycrystalline and single-crystal material [10,11]. A preliminary transmission electron microscopy (TEM) investigation was also conducted on the material.

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Table 1
Microhardness measured in different types of CVD tungsten at room temperature, using a Vickers indenter with a 200 g load and a 15 s dwell time.

Type of tungsten	Grain type	Vickers hardness [kg/mm^2]	T_{BDT} for $\frac{d\varepsilon}{dt} \sim 10^{-6}$ s^{-1} [°C]	Reference in which tested
Single-crystal	n/a	527 ± 23	119	[10]
Poly-crystalline	Small (~3 µm)	538 ± 33	118	[10]
CVD (perpendicular)	Columnar (~10–200 µm by ~10 µm)	557 ± 61	>967	This paper
CVD (parallel)	Columnar (~10–200 µm by ~10 µm)	540 ± 67	>906	This paper
Sintered and deformed	Large (~50 µm)	529 ± 65	203	[11]

2. Experimental method

A 1 mm thick layer of CVD-grown tungsten measuring 10 cm × 10 cm was supplied by Archer Technicoat Ltd. The layer was deposited at approximately 0.25 mm per hour at temperatures of approximately 500–550 °C on a copper-coated Eurofer steel substrate. As a consequence of the growth process, CVD-grown tungsten has a columnar grain structure, with the columns being orientated in the direction of growth. SEM observations of fracture surfaces showed that the grains generally have a length of 10–200 µm and a width of order 10 µm. The microhardness of the CVD-grown tungsten was not found to differ significantly from that of other types of tungsten used in earlier work [10,11], as shown in Table 1.

The CVD-grown tungsten discs were cut and ground into beams measuring approximately 1 mm^2 by 12 mm. Each beam was electropolished in 2% NaOH (with an applied voltage of 10 V) to produce smooth surfaces. Pre-cracks were introduced into the tensile faces of the beams using a sharp edge in an electrical discharge machine for a few seconds at room temperature. The resulting pre-cracks were in the form of a wedge notch with a depth of 16–32 µm. Fracture tests were performed on the specimens by four-point bending in argon atmosphere at a constant strain rate at a range of temperatures (24–967 °C). The load displacement data were used with an assumed Young's modulus of 400 GPa to deduce the strain rate to be approximately 10^{-6} s^{-1}. The rate at which specimens were strained in this current work is believed to be approximately the same as the specimens for which Giannattasio and Roberts [10] reported a strain rate of 4×10^{-5} s^{-1}. The discrepancy arises because a less accurate calculation based on cross-head displacement was used in the previous work. In order to ascertain whether the grain orientation affects the mechanical properties, one set of beams was prepared with the long axis of the grains (i.e. the growth direction) normal to the tensile surface (and thus normal to the notch) and another set of beams was prepared with the long axis of the grains parallel to the tensile surface and notch.

A 3 mm diameter TEM specimen was prepared from the CVD tungsten. Dip polishing was used to thin the as-received material into a 200 µm uniformly-thick foil. A protective Lacomit varnish coating was applied to all but the central area of this foil. This was then placed in 2% NaOH at room temperature until perforation was achieved at the centre. After removal of the Lacomit varnish, the specimen was cleaned thoroughly in methanol. Energy dispersive X-ray analysis (EDX) was performed on the specimen using a JEOL JEM-3000F FEGTEM with an accelerating voltage of 300 kV. EDX was performed while scanning the beam over an area localised to the grain boundary and an area of the bulk material well away from the boundary.

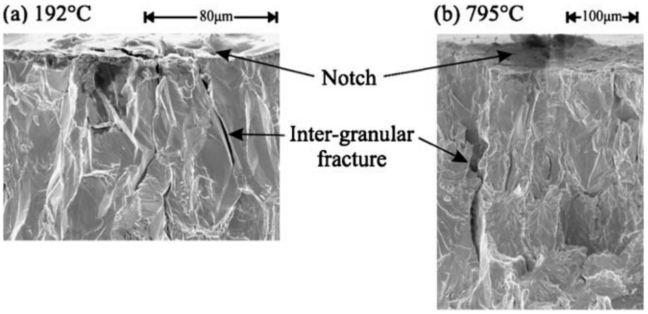

Fig. 1. Scanning electron micrographs of fracture surfaces, showing inter-granular failure in CVD-grown tungsten beams. The beams were fractured at (a) 192 °C and (b) 795 °C from notches inserted perpendicular to the growth direction.

3. Results

None of the 19 specimens tested was found to be fully ductile, even at the highest temperature used (967 °C), but most were found to exhibit some plastic deformation prior to fracture, with just five specimens failing in a purely brittle manner. Typical fracture surfaces of CVD-grown tungsten are shown in Fig. 1. The beams shown were tested at 192 and 795 °C and it can clearly be seen that they failed by inter-granular fracture. The micrographs shown in Fig. 1 are of material with the growth direction perpendicular to the tensile surface, but similar behaviour was also observed in material with the growth direction parallel to the tensile surface.

Fracture toughness (K_{IC}) is commonly used to quantify the strength of a material fractured from a crack and this is determined as $K_{IC} = \sigma_F\sqrt{\pi c}$, where σ_F is the fracture stress and c is the depth of the crack. In Fig. 2, K_{IC} for CVD-grown tungsten is plotted as a function of testing temperature. Because of limited supply of material, it was only possible to test one sample under each testing condition. For specimens notched parallel to the growth direction, K_{IC} was found to be between 4.9 and 7.2 MPam$^{1/2}$ for all but two specimens. There was no noticeable trend in K_{IC} with testing temperature for these specimens. There was more scatter in the K_{IC} values for specimens notched perpendicular to the growth direction, for

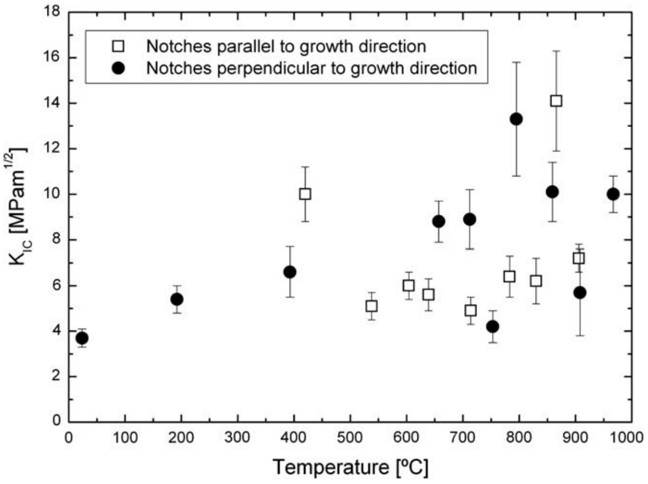

Fig. 2. Fracture toughness (K_{IC}) in CVD-grown tungsten measured as a function of temperature and notch orientation at a strain rate of approximately 10^{-6} s^{-1}.

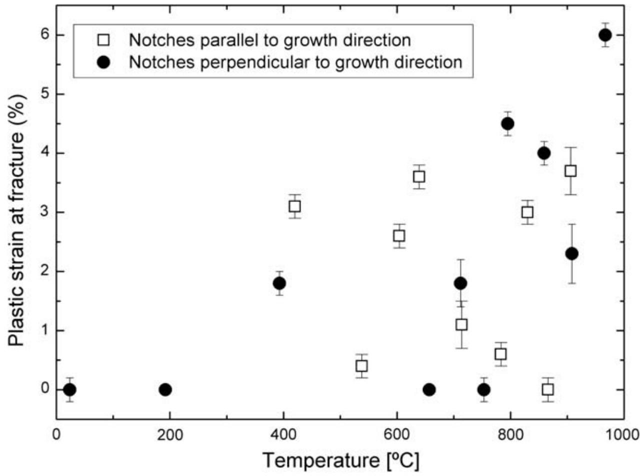

Fig. 3. Plastic strain at fracture in CVD-grown tungsten measured as a function of temperature and notch orientation at a strain rate of approximately 10^{-6} s^{-1}.

which all but one of these specimens had K_{IC} between 3.7 and 10.1 MPam$^{1/2}$. There was perhaps a slight increase in the value of K_{IC} with testing temperature in these specimens, but any trend is by no means clear-cut. However, it is clear that no specimen was fully ductile up to the maximum temperature used.

The plastic strain at fracture, defined as the difference between the strain at the tensile surface at fracture and the strain at yield, is plotted in Fig. 3. It can be seen that most specimens underwent some plastic deformation before fracture, but no specimen was able to withstand more than approximately 6% strain. There was no noticeable trend in plastic strain at fracture with temperature for specimens notched parallel to the growth direction. There was perhaps a slight increase in the value of plastic strain of fracture with temperature for specimens notched perpendicular to growth direction, but again the trend is not clear-cut.

TEM was performed on a CVD-grown tungsten sample and a representative micrograph of a region containing a grain boundary is shown in Fig. 4. A preliminary investigation using EDX in a TEM revealed the presence of carbon, oxygen and fluorine impurities in the CVD-grown tungsten. These three impurities were detected in the vicinity of a grain boundary and in the bulk of the material, as shown in Fig. 5, which indicates that the concentration of fluorine and carbon are higher at the grain boundary than in the bulk. However, it is noted that carbon and oxygen are commonly seen in EDX spectra arising from surface contamination and consequently it may be difficult to attach significance to these peaks.

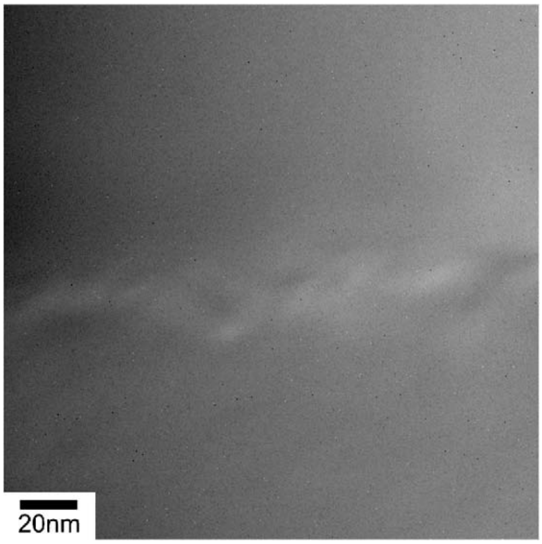

Fig. 4. Representative transmission electron micrograph of a grain boundary in CVD-grown tungsten from which the EDX spectrum for the region containing the grain boundary in Fig. 5 was obtained.

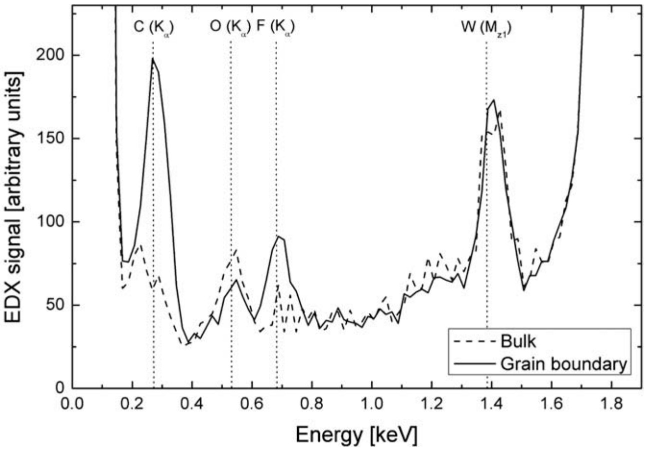

Fig. 5. Low energy section of the EDX spectra obtained from a TEM specimen of CVD-grown tungsten. The fluorine K_α peak at approximately 0.677 keV was found to be significantly higher at the grain boundary than in the bulk.

4. Discussion

CVD-grown polycrystalline tungsten beams were found not to be fully ductile at temperatures up to 967 °C, the highest testing temperature available, even with a strain rate of approximately 10^{-6} s^{-1}, which was the lowest used in previous work performed on tungsten in Oxford [10,11]. The behaviour found differs considerably from that in conventionally-grown polycrystalline tungsten, which, for similar testing conditions, was found to become ductile at above approximately 120 °C [10]. The results presented here are consistent with previous studies (using different testing configurations to those used here), which also concluded that CVD-grown tungsten has a higher T_{BDT} than tungsten grown by other means [12,13].

The scanning electron micrographs in Fig. 1 indicate that the specimens fail by inter-granular fracture, even at high temperatures. The two different testing orientations used appeared not to make a significant difference to the material's mechanical properties.

One possible explanation for the increased brittleness of CVD-grown material compared to conventionally-grown material could be via decreased mobility of dislocations; given the very large shift in the BDT, if this were the case, a large reduction in dislocation mobility would be required. If this were the case then the microhardness of the material might be expected to increase, however, the data in Table 1 show that there is no noticeable difference in hardness at room temperature between tungsten grown by CVD and by conventional means.

It is likely that segregation of a particular impurity to grain boundaries is responsible for the increased brittleness observed in the CVD-grown tungsten. To identify the responsible impurity, EDX was performed at and away from a grain boundary using TEM. The preliminary results presented in Fig. 5 suggest increased levels of fluorine and carbon at the grain boundary. Carbon is generally present as an impurity in BCC metals and it is expected that fluorine should be incorporated into the material from the tungsten hexafluoride precursor used to grow the material [14].

Previous studies have indicated that the fluorine concentration in CVD-grown tungsten is between 10 and 110 ppm [15]. The material investigated here was grown very quickly (0.25 mm/h) and consequently it is expected that the fluorine concentration in the material would be high.

Previous work has indicated that carbon is not likely to give rise to substantial grain boundary embrittlement in tungsten [16]. Furthermore, carbon is an impurity present in tungsten grown by other means, including the material investigated in previous similar experiments [10,11] in which it was possible to measure a substantially lower brittle-to-ductile transition temperature. It is therefore suggested that fluorine segregation to grain boundaries is the origin of the increase in brittleness observed.

5. Conclusions

The mechanical properties of CVD-grown polycrystalline tungsten were investigated by the use of fracture tests with a low strain rate in the temperature range 24–967 °C. The CVD-grown material was found to be brittle at all temperatures up to 967 °C, which is different from the behaviour of conventionally-grown tungsten which becomes ductile at around 120 °C for very similar testing conditions. The segregation of fluorine impurities to grain boundaries may be responsible for the increased brittleness.

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References

[1] H. Bolt, V. Barabash, W. Krauss, J. Linke, R. Neu, S. Suzuki, N. Yoshida, J. Nucl. Mater. 329–333 (2004) 66.
[2] S.G. Roberts, J. Samuels, Proc. R. Soc. London A 421 (1989) 1.
[3] F.C. Serbena, S.G. Roberts, Acta Metall. Mater. 42 (1994) 2505.
[4] S.G. Roberts, H.S. Kim, P.B. Hirsch, In: D.G. Brandon, R. Chaim, A. Rosen (Ed.), Proceedings of the 9th International Conference on the Strength of Metals and Alloys, Haifa, July 1991, Freund, London, 1991, p. 783.
[5] A. Giannattasio, M. Tanaka, T.D. Joseph, S.G. Roberts, Physica Scripta T128 (2007) 87.
[6] P. Gumbsch, J. Riedle, A. Hartmaier, H.F. Fischmeister, Science 282 (1998) 1293.
[7] H.W. Schadler, Acta Metall. 12 (1964) 861.
[8] A.S. Argon, S.R. Maloof, Acta Metall. 14 (1966) 1449.
[9] D. Brunner, Mater. Trans. 41 (2000) 152. JIM.
[10] A. Giannattasio, S.G. Roberts, Philos. Mag. 87 (2007) 2589.
[11] A. Giannattasio, Z. Yao, S.G. Roberts, submitted for publication.
[12] D.H. Lassila, A. Connor in tungsten and tungsten alloys – Recent advances, A. Crowson, E.S. Chen (Ed.), published by The Minerals, Metals and Materials Society, 1991 pp. 79–85.
[13] P.J. Sherwood, Proceedings of the 3rd International Conference on Chemical Vapour Deposition (held in Salt Lake City, Utah in 1972), 1972, pp. 728–737.
[14] C. Prentice (Technical Director, Archer Technicoat Limited), private communication (2007).
[15] J.V. Festa, J.C. Danko, in: A.C. Schaffhauser (Ed.), Proceedings of the Conference on Chemical Vapour Deposition of Refractory Metals, Alloys and Compounds (held in Gatlinburg, Tennessee from 12th to 14th September 1967), 1967, pp. 349–361.
[16] G.L. Krasko, Scripta Metallurgica et Materialia 28 (1993) 1543.