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Brittle fracture of polycrystalline tungsten

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A comparative study of the brittle fracture of three varieties of polycrystalline tungsten has been carried out using mainly impact tests, scanning electron microscopy and Auger spectroscopy. It indicates the occurrence of two modes of brittle fracture, namely cleavage and intergranular fractures, whose proportions depend on temperature and on phosphorus segregation at the grain boundaries. Scanning Auger images indicate unambiguously that phosphorus is only located on the intergranular surfaces. No phosphorus is observed on cleavage planes. Fracture surfaces are the result of the propagation of a crack through the whole sample. As the propagation follows the path which requires the lowest expenditure of energy, it depends both on a geometrical factor and on the respective values of the cleavage (γ_{Cl}) and intergranular (γ_I) works of fracture. Our results indicate an increase in γ_{Cl} and γ_I with temperature (the effect being more marked in the case of γ_{Cl}) and a large decrease in γ_I with phosphorus segregation at the grain boundaries. This impurity produces an intergranular embrittlement of the tungsten.

1. Introduction

The use of tungsten is strongly limited at room temperature by its brittleness. Consequently, many studies have been carried out to determine the causes of this brittleness and to try to find remedies. Examination by scanning electron microscopy of brittle fractures of various specimens [1–4] highlighted the presence of two modes of fracture: cleavage fracture, and intergranular fracture; and in some cases, mixed fractures (cleavage + intergranular).

Intergranular fracture has been attributed to the presence of impurity segregations at grain boundaries. Carbon and oxygen were, at first, implicated [5], then potassium associated with "bulbs" [6, 7], and finally phosphorus [8]. The range of results and interpretations stems from the fact that samples of various kinds were examined by different authors. The samples are obtained by powder processing or by arc or electron beam melting and are later submitted to thermomechanical treatments which produce different structural states. Impurity levels can also be different especially when doping additions are used to slow down the recrystallization.

In this study, we used three varieties of sintered tungsten of different purity levels submitted to a thermal treatment at 1600° C for 4 h. These conditions are such that they lead:

1. to a polycrystalline structure without a preferred orientation and with the same average grain size for the three varieties;

2. in notched specimens, to brittle fractures which are always mixed (cleavage + intergranular) for all temperatures lower than the ductile to brittle transition temperature.

Thus, they are very suitable for the study of the influence of temperature and impurity levels on each of the two modes of brittle fracture and on the corresponding works of fracture.

2. Experimental procedure

2.1. Specimens

Polycrystalline samples are obtained from three

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TABLE I Impurity levels of the three varieties of sintered tungsten

Variety	Impurity level in (ppm)												
	Al	As	C	Ca	Cr	Fe	K	Mg	Mo	N	O	P	S
A			20			35	60		400	1	3		30
B	20	20	30	10	20	40	2	10	100	20		20	20
C	10	10	30	30	10	50	10	5	300	10	30	50	30

varieties of sintered tungsten by recrystallization under vacuum (10^{-4} Pa) at 1600° C for 4 h. Table I gives their impurity levels as indicated by the manufacturers.

2.2. Mechanical tests

Fractures are produced by Charpy tests on cylindrical V-notch specimens having a 4 mm diameter and a 50 mm length. Tests are performed in the temperature range −196° C to 1000° C after a 30 min isothermal treatment.

2.3. Analysis methods

Impurities present on fracture surfaces were analysed by Auger spectrometry on samples fractured at room temperature in a Riber Spectrometer equipped with a cylindrical mirror analyser. The following experimental conditions were used: acceleration voltage of primary electrons, 3 keV; peak to peak modulation, 4 V; estimated diameter of the probe, 50 μm; erosion by 2.5 keV argon ions; and spectra recorded in the differential mode with a resolution better than 0.5%.

Auger images and depth profiles were obtained using a 590 Physical Electronics Auger microprobe. The samples were fractured at room temperature and atmospheric pressure. To remove carbon and oxygen contamination, they were submitted, before examination, to a short (15 sec) argon ion bombardment.

The experimental conditions were: primary electron acceleration voltage, 5 keV; peak to peak modulation, 6 V; estimated probe diameter, 2 μm; erosion by 4.5 keV argon ions.

3. Experimental results

The recrystallization treatment leads to polycrystalline samples having, for the three varieties, an average grain size of about 50 μm. No preferred orientations are observed (Fig. 1). The corresponding ductile to brittle transition temperatures measured at 50% of the *S*-curves of the impact energy (Fig. 2) are given in Table II.

Microscopic observation of the fracture surfaces was systematically carried out using scanning electron microscopy on all samples (Fig. 3) and indicates the presence in various proportions of two modes of brittle fracture: cleavage fracture, and intergranular fracture. We characterize their proportions by means of the ratio, R (= area with intergranular fracture/total area of fracture). The curves of these ratios in relation to temperature given in Fig. 4 show an increase in the intergranular fracture with a rise in temperature. One

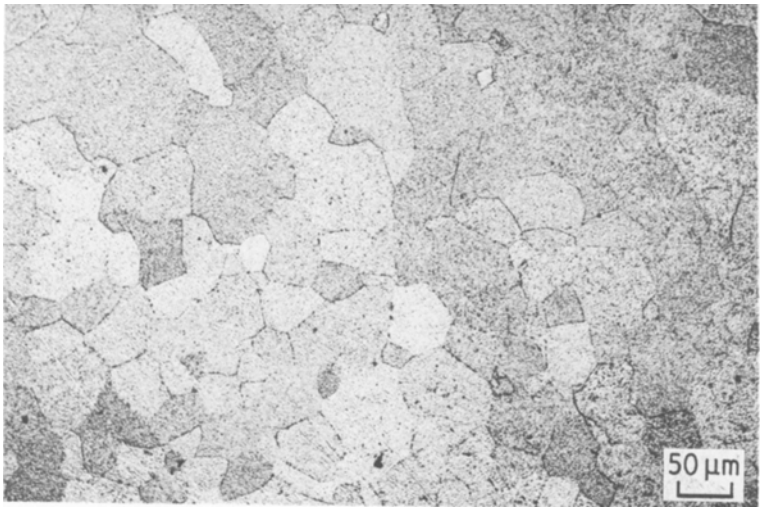

Figure 1 Optical micrograph of the polycrystalline structure obtained by recrystallization at 1600° C for 4 h.

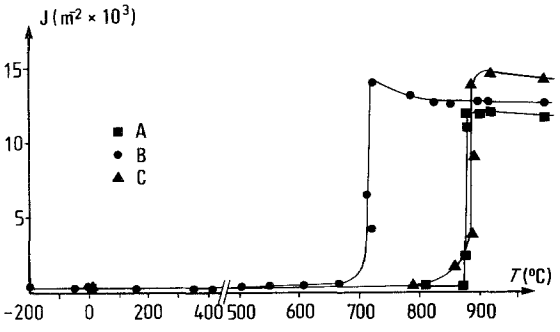

Figure 2 Impact tests S curves of the impact energy as a function of the temperature.

also notices that the values of R corresponding to the three varieties are, for all temperatures, classified in the following order:

$$R_C > R_A > R_B$$

This last observation leads us to expect an effect of the impurities on brittleness. To highlight this, we analysed, using Auger electron spectrometry, the fracture surfaces of these samples. All spectra

TABLE II Ductile to brittle transition temperatures for the three varieties (A, B, C) of tungsten

	A	B	C
Ductile to brittle transition temperature (° C)	875	715	880

contain a strong phosphorus peak (Fig. 5a) which can be easily eliminated by a few minutes' Argon ion bombardment (Fig. 5b). This means that phosphorus is only located on the fracture surfaces and is not distributed evenly within the grains.

It may even be expected that phosphorus would be present only on intergranular surfaces because Auger spectra obtained on similar samples for which cleavage is the only mode of brittle fracture (sintered tungsten with a fibre structure or single crystals), do not contain any phosphorus peak.

To verify this hypothesis, we took scanning Auger images on mixed fracture surfaces. All of them indicate unambiguously the complete absence of phosphorus on cleavage surfaces. One

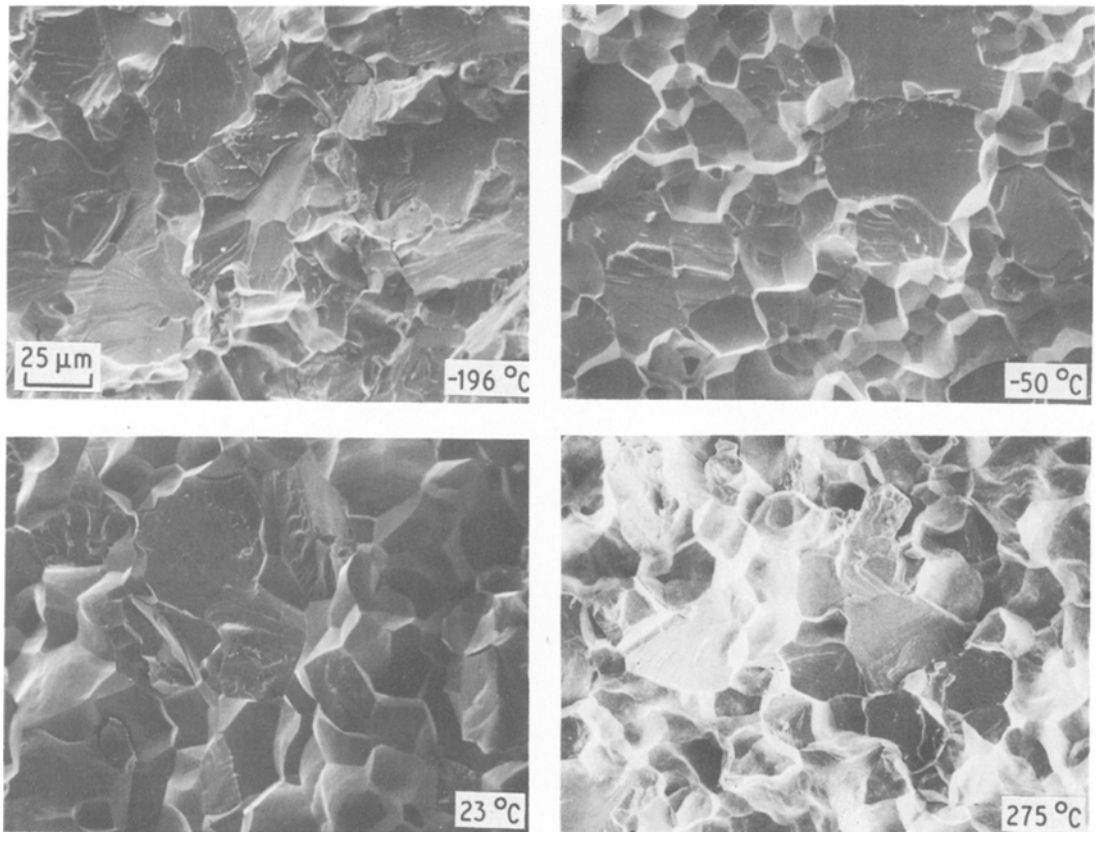

Figure 3 Scanning electron micrographs of fracture surfaces of recrystallized tungsten samples (variety B).

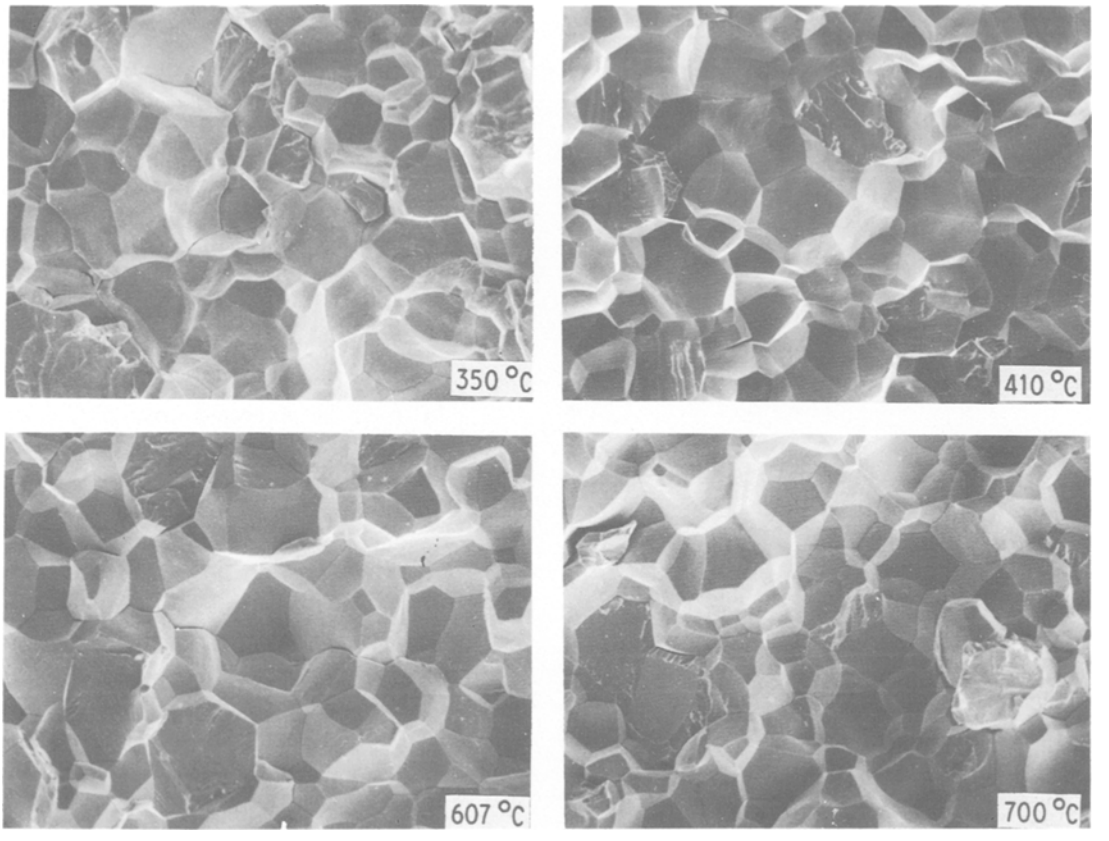

Figure 3 Continued.

example is given on Fig. 6. On the other hand, all intergranular areas exhibit a phosphorus peak whose height depends mainly on the area under examination (Figs. 7a and c). These height differences can be attributed to a non-uniform phosphorus content at the grain boundaries. This observation is in agreement with that of Suzuki *et al.* [9] who reported that segregation depends on the nature of the grain boundary.

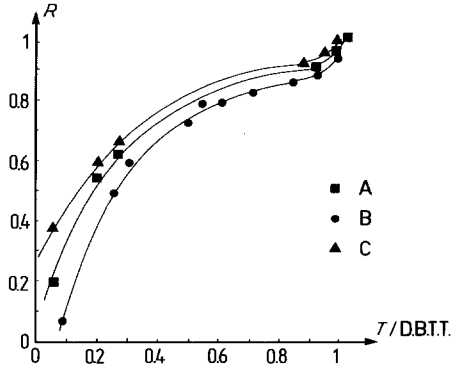

Figure 4 Values of the R ratios (area with intergranular fracture/total area of fracture) as a function of the ratio T/D.B.T.T. This ratio is used instead of the temperature because it allows comparisons between the three varieties which have different transition temperatures.

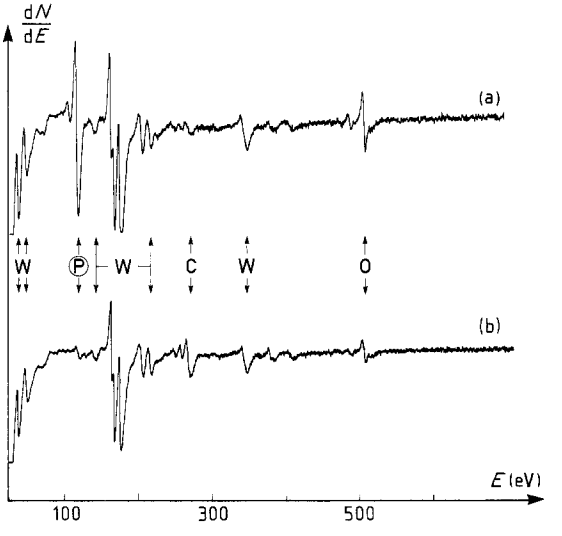

Figure 5 Auger spectra of a brittle fracture surface of polycrystalline tungsten: (a) before erosion by Argon ions; (b) after erosion.

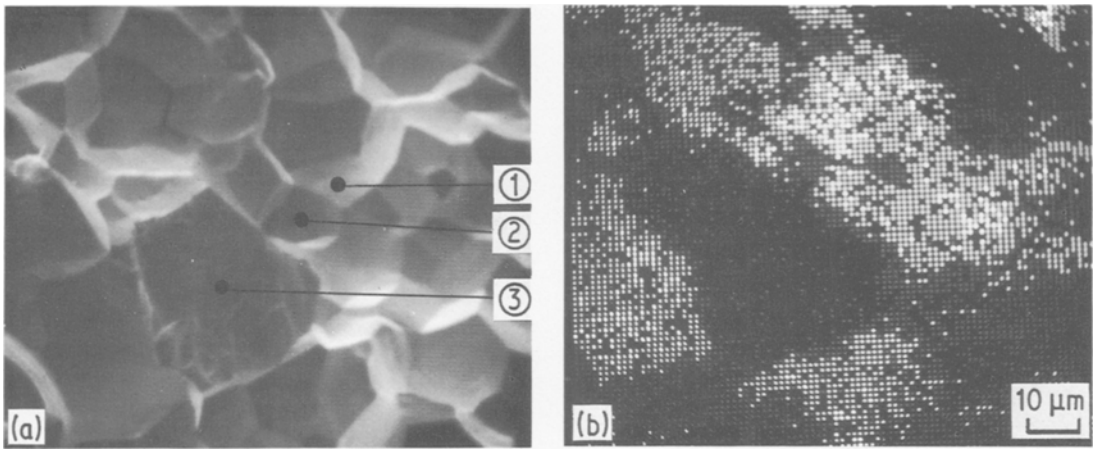

Figure 6 Scanning electron micrograph and corresponding phosphorus Auger image of a mixed fracture surface of a sample fractured at room temperature (variety A).

The difference may also be due to the fact that the intergranular surface is not flat but is composed of many intergranular facets. As each of them is differently oriented with respect to the analyser, the Auger signals that they produce should be affected [10].

Depth profiles were also performed using argon ion bombardment (Figs. 7b and d). Usually, the phosphorus peak is entirely removed after a 3 min bombardment. On account of the experimental conditions used this means that the phosphorus segregation occurs up to approximately 3 nm.

A semi-quantitative analysis of this impurity was performed by measuring the ratio of the peak height of the 120 eV phosphorus peak and the main 169 eV tungsten peak. In this analysis, we took measures to take into account two factors:

1. in the Riber spectrometer the electron probe is nearly the same size as the average grain size. Spectra are hence strongly dependent on the area analysed. To avoid this effect and to obtain significant values for the peak height ratios, we recorded a great number of spectra from which average values were deduced;

2. fracture surfaces contain a $(1-R)$ proportion of cleavage fractures which, as mentioned above, do not contain any phosphorus. To take this effect into account, we corrected by $(1-R)$ the corresponding phosphorus peak heights.

TABLE III Auger peak height ratio using the 120 eV phosphorous peak and the 169 eV tungsten peak

	A	B	C
Phosphorus peak height / Tungsten peak height	1.05	0.51	1.09

Experimental results are given in Table III. When they are considered together with those given on Fig. 4, they indicate an increase in the R ratios with a corresponding increase of phosphorus segregations at grain boundaries. Moreover, Fig. 8 indicates an increase in the ductile to brittle transition temperature with a corrresponding increase in the phosphorus segregation.

4. Interpretation

The experimental results indicate that the brittle fractures encountered in our samples are mixed fractures and that the proportion of cleavage and intergranular fractures depends mainly on the two parameters: temperature, and phosphorus segregation content at grain boundaries. Microscopic fracture surfaces are the result of the propagation through the whole specimen of a crack nucleated near the notch where high stresses are concentrated (Fig. 9). This propagation occurs in our samples running either along a cleavage plane or a grain boundary, crossing barriers at the limits of each grain with or without change in the mode of fracture. With each of the two modes of brittle fracture is associated a work of fracture per unit surface area defined by the following relationships:

$$\gamma_{Cl} = 2\gamma_S + \gamma_P$$

[11], in the case of the propagation along a cleavage plane, or

$$\gamma_I = 2\gamma_S - \gamma_B + \gamma_P$$

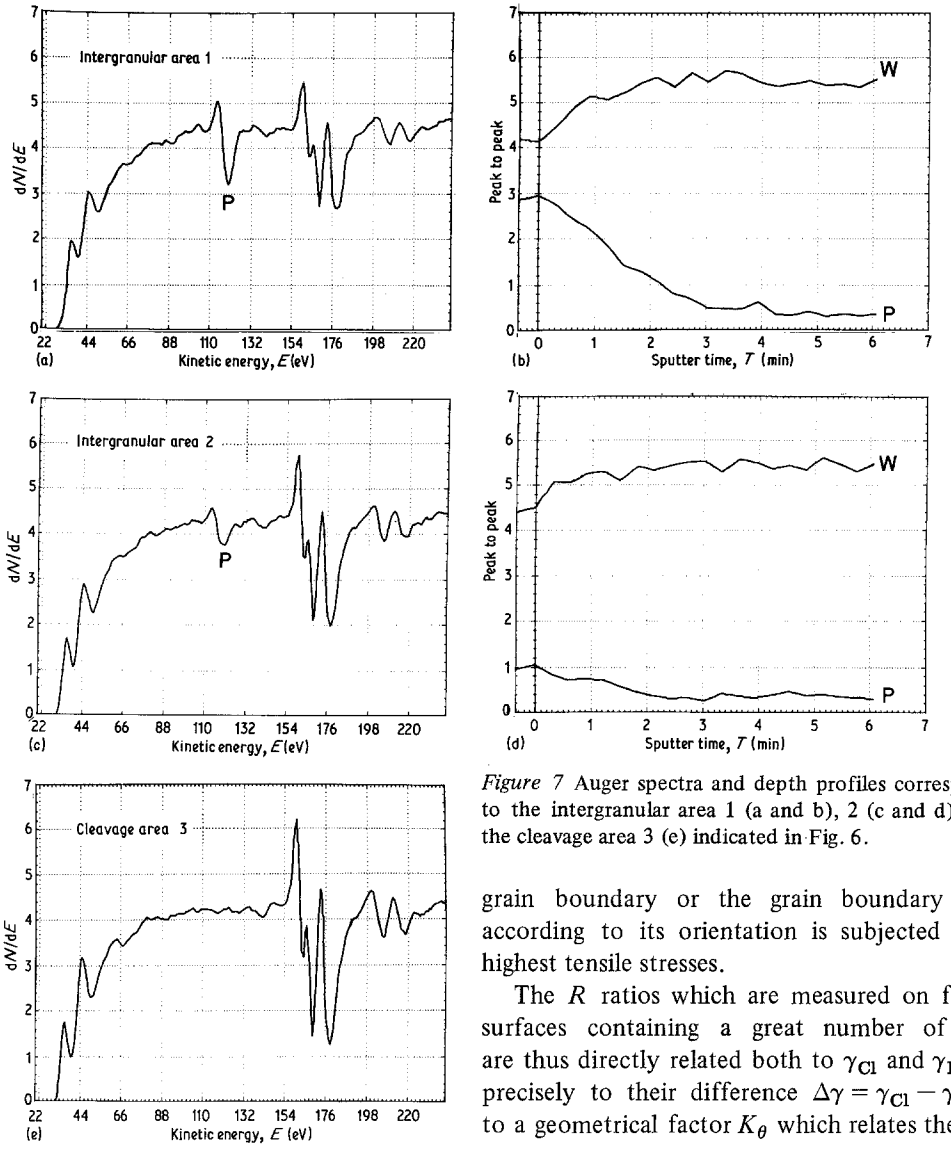

Figure 7 Auger spectra and depth profiles corresponding to the intergranular area 1 (a and b), 2 (c and d) and to the cleavage area 3 (e) indicated in Fig. 6.

[12], in the case of propagation along a grain boundary. In these expressions $2\gamma_S$ is the true surface energy. It represents the ideal work of fracture required to create the two cleavage fracture surfaces in the absence of any plastic work; γ_P is the plastic work expended during crack propagation; and γ_B is the interfacial grain-boundary energy.

The crack propagation follows the path which requires the lowest expenditure of energy. Therefore, it occurs with the fracture mode which has the lowest work of fracture. However, the relative orientation of the cleavage planes and of the grain boundaries with respect to the average direction of propagation intervenes too. The crack propagation follows either the cleavage plane at each grain boundary or the grain boundary which according to its orientation is subjected to the highest tensile stresses.

The R ratios which are measured on fracture surfaces containing a great number of grains are thus directly related both to γ_{Cl} and γ_I (more precisely to their difference $\Delta\gamma = \gamma_{Cl} - \gamma_I$) and to a geometrical factor K_θ which relates the effect

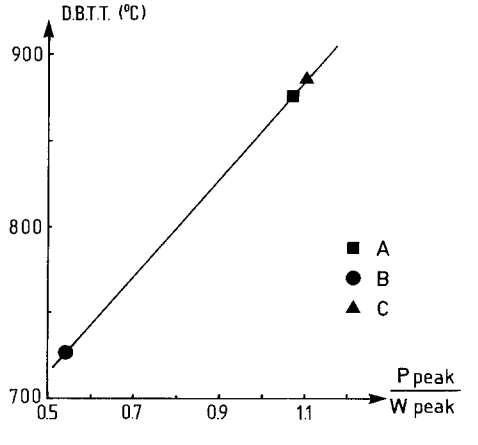

Figure 8 Ductile to brittle transition temperature as a function of the peak height ratio.

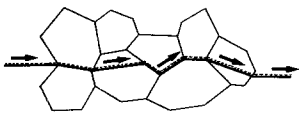

Figure 9 Propagation of a crack in polycrystalline tungsten.

of the orientation. As this K_θ factor depends mainly on the grain shape and not on the temperature and phosphorus content, the analysis of the variation of R with the temperature and the phosphorus content at grain boundary, allows us to obtain a direct determination of the effect of these two parameters on $\Delta\gamma$.

4.1. Effect of temperature on $\Delta\gamma$

R ratios increase with temperature and tend towards 1 at a temperature close to the ductile to brittle transition temperature. In the range of elevated temperatures, they indicate that the intergranular fracture is strongly favoured and that $\Delta\gamma > 0$. Nevertheless, propagation does not proceed completely in an intergranular way as a strict application of the inequality $\gamma_I < \gamma_{Cl}$ would suggest. Some cleavage planes are observed nonetheless. These are the planes which are favourably oriented during propagation and this beneficial effect compensates for the additional work thus required. This compensation is more and more difficult to realize, as the temperature approaches the ductile to brittle temperature, because $\Delta\gamma$ becomes too important. Thus, we have an explanation for the observed decrease of cleavage areas on fracture surfaces as the temperature increases.

On the other hand, at low temperatures, cleavage fracture is now favoured since R tends towards 0. In this temperature range, the cleavage fracture work γ_{Cl} is lower than the intergranular work (γ_I) and $\Delta\gamma$ becomes more and more negative. This time, it is favourably oriented intergranular boundaries which can remain on the fracture surfaces.

A change in the mode of fracture with a change in the temperature from a predominantly intergranular fracture to a predominantly cleavage fracture indicates a dependence of both γ_{Cl} and γ_I on the temperature but with a more pronounced effect for γ_{Cl}. Consequently, the slope of the $\gamma_{Cl} = f(T)$ curve is greater than those of $\gamma_I = f(T)$ as shown in Fig. 10. In this figure, we choose to give to the slopes of the two curves positive values although our experiments only

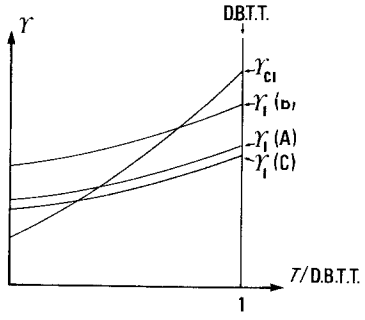

Figure 10 Schematic representations of the increases in γ_{Cl} and γ_I with T/D.B.T.T. for the three varieties of polycrystalline tungsten.

allows us to obtain the difference $\Delta\gamma = \gamma_{Cl} - \gamma_I$ as a function of temperature. We justify this choice in the following way: temperature produces a decrease of both the interfacial energies γ_B and the surface energies γ_S, on the other hand, it increases the plastic work, γ_P [13].

In body-centred metals which are not completely brittle solids, γ_P can be much larger than γ_B or γ_S (especially at high temperatures) and it is essentially the increase of γ_P with temperature which influences those of γ_{Cl} and γ_I. Hence, γ_{Cl} and γ_I increase with temperature.

In the case of intergranular fracture, γ_P also depends on the disorientation of the grains on either side of the boundary. Liu and Shen [14] report, in the case of tungsten samples, a large decrease of γ_P with the angle of misorientation which explains the lesser effect of the temperature on γ_I than on γ_{Cl}.

4.2. Effect of phosphorus segregation at the grain boundary

Using Auger spectroscopy, we showed an increase in the proportion of intergranular fractures with increase in phosphorus segregation content at a grain boundary. As a result $\Delta\gamma = \gamma_{Cl} - \gamma_I$ also increases, but as our experiments also indicate a non-dependence of γ_{Cl} on the phosphorus content, this increase is only due to the reduction of γ_I. The phosphorus effect can then be schematically shown as in Fig. 10 which gives the likely increase in γ_{Cl} and γ_I as a function of temperature for the three varieties of tungsten examined.

These results are in accord with the theoretical and experimental studies previously carried out on the intergranular decohesion phenomenon and reviewed by Seah and Hondros [15]. All attribute

the intergranular brittleness to impurity segregations at the grain boundary.

McLean [12] reported that the brittle effect of the impurities is due to the simultaneous reductions of the surface and interfacial energies. Nevertheless, the grain-boundary brittleness is not produced by the decrease in γ_B which will, on the contrary, prevent the fracture as indicated by the expression $\gamma_I = 2\gamma_S - \gamma_B + \gamma_P$ but by the much more important reduction of γ_S.

Impurities also modify γ_P. Jokl *et al.* [16] indicated that γ_P depends essentially on γ_S and that a reduction of γ_S will produce a much larger decrease in γ_P.

5. Conclusions

A comparative study of brittle fractures on three varieties of tungsten samples, each having an equiaxed structure, was carried out by impact tests and fracture surface analysis using scanning electron microscopy and Auger spectroscopy.

1. In all samples fractured at temperatures lower than the ductile to brittle transition temperature, the study revealed the simultaneous presence in various proportions of two modes of brittle fracture: cleavage mode and intergranular mode.

2. The experimental results indicate an increase in the proportion of intergranular fracture both with temperature and with phosphorus segregation content at grain boundary.

3. Auger images indicate that phosphorus is only located on intergranular fracture surfaces. It is not present at all on the cleavage surfaces.

4. The fracture surfaces result from the propagation of a crack through the whole specimen. This propagation occurs along the path for which the required expenditure of energy is lowest. Thus, it depends on a geometrical factor and on the relative values of the cleavage fracture work and the intergranular work of fracture.

Our experimental results indicate:

1. an increase of γ_{Cl} and γ_I with temperature but with a greater effect for γ_{Cl}. This difference allows us to interpret the increase in the proportion of intergranular fracture with temperature;

2. an important decrease of γ_I with phosphorus segregation content at a grain boundary and no effect of this impurity on γ_{Cl}.

These results indicate an intergranular embrittlement of the tungsten by phosphorus segregation. This harmful effect of phosphorus on tungsten which had previously been reported by Joshi and Stein [8], also occurs in other materials, for instance in steels [17]. The results are also in agreement with Seah's theoretical expectations [18]. Seah established an embrittlement criterion based on the size of the segregated atoms and their sublimation heat which predicted a brittle effect of phosphorus on tungsten.

The elimination of phosphorus by purification will decrease the ductile to brittle transition temperatures but, nevertheless, will not be able to completely eliminate the brittleness of tungsten as the cleavage fracture remains at temperatures higher than room temperature.

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