

ON THE FRACTURE OF DOPED TUNGSTEN

By

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The fracture surface of industrial tungsten wires containing potassium second phases were investigated by AES. The average size and number of potassium second phases were determined by TEM. Potassium was the main component of the fracture surface and its amount varied on the differently heat treated wires. Utilizing the TEM results the average surface concentration was estimated supposing that the fracture is independent of the potassium second phases. The measured value was higher showing that the fracture path is partly determined by the potassium second phases.

The high surface concentration of the potassium was explained by surface diffusion.

Introduction

It is widely accepted that both grain boundary segregations and second phases play a dominant role in the mechanical behaviour of metals. The detection of second phases with electron microprobe is rather difficult (or even impossible), if the dimensions of the second phases are very small. In a previous work [1] it was shown that the chemical nature of the second phases responsible for the fracture can be determined by the highly surface sensitive AES. In [1] all conclusions were based on two assumptions a) the potassium atoms diffuse from the three dimensional second phases onto the free surface and form there a quasi-two-dimensional layer, b) the size and the form of the potassium second phases are the “well accepted” ones [2]. In this paper the validity of these assumptions will be investigated.

Experimental

The tungsten samples were fractured in situ in a Auger electron spectroscopy. The background pressure was lower than 10^{-8} Pa. The Auger spectra were recorded by a usual cylindrical mirror analyser (RIBER OPC 103). The beam current was generally about $1 \mu\text{A}$ with a diameter of $60 \mu\text{m}$, $E_p = 3 \text{ kV}$.

The samples were fractured at various temperatures in the range of 100–300 K. During the Auger measurements the temperature of the sample

holder could be varied from 100 K to 500 K. It was also possible to warm up the sample to room temperature in a short time (2–5 min).

The following tungsten samples were investigated:

- a) sintered rod, and wires with diameters of 0.9 and 0.3 mm in “as received” state;
- b) wires with diameter of 0.3 mm after various kinds of heat treatment (see Table I).

Table I

Annealing parameters of wires with a diameter of 0.3 mm

Sample	Annealing	
	temperature (K)	time (sec)
A	1300	300
B	2100	2400
C	3000	100

The samples were fractured perpendicular to their axis. As the “as received” wires were too ductile to fracture them in this way at room temperature, they were fractured below the ductile–brittle transition temperature. The heat treated wires and the sintered rod could be easily fractured at room temperature perpendicular to their axis, although in many cases also these samples were fractured at lower temperatures in order to limit the surface diffusion of potassium.

Results

If the samples were fractured at higher temperatures (i. e. above 220 K), the Auger signal of the potassium was constant during the measurement. On the other hand, if the samples were fractured at low enough temperatures, the surface concentration of the potassium was definitely smaller 10 minutes after the fracture (i. e. at the moment, when the first Auger spectrum could be recorded) than the corresponding “constant” signal coming from samples fractured at higher temperatures. Furthermore after low temperature fracture the Auger signal was not at all constant but it increased slowly. If, after a short measuring time (15–20 min) the fracture surface was heated up to 250 K, the surface concentration of potassium increased in a relatively short time to a constant value, which was roughly equal to the surface concentration of the wires fractured at room temperature. In Table II the “constant” surface concentrations of potassium in various states are summarized. All these data are connected with fractures at temperatures higher than 250 K.

Table II

Potassium concentration ranges on the fracture surface of tungsten samples

Sample	Potassium concentration ranges in monolayer units
Sintered rod	1.4–2.0
0,9 wire	1.9–2.7
0,3 mm wire “as received”	1.6–2.4
A	0.9–1.2
B	0.3–0.7
C	0.2–0.4

Discussion

During fracture, potassium second phases are opened up, i. e. they become connected to the free surface investigated by AES. In [1], it was suggested that at room temperatures the potassium diffuses from the inclusion opened by the fracture along the surface. In this way the surface concentration of potassium will depend, of course, on the size and form of the potassium second phases.

The size and shape of the potassium second phases varies drastically during swaging, drawing and annealing. According to the electronmicrographs the potassium second phases in the “as received” wires are elongated parallel to the axis of the wires and their length amounts to some μms . According to Fig. 1, after a slight heat treatment these elongated second phases are partially broken off and form shorter elongated parts and/or bubbles. In sample B (Fig. 2) and C there are only bubbles. In these samples the potassium Auger signal decreased as the annealing proceeded. This is in very good agreement with the Auger results and supports the belief that the fracturing path is going through the potassium second phases.

In [1] the surface diffusion data available were discussed. It was shown that the surface diffusion is generally fast enough to explain our results. In the following an experimental verification of the diffusion model will be given. The most important experimental fact supporting the diffusion model is the slow increase of the potassium signal after fracture.

At 250 K even some minutes are enough to deplete the inclusions and thus the potassium Auger signal during the AES investigation must remain constant, as observed. But at 100 K the depletion time will be longer due to the reduced diffusivity, and therefore the potassium Auger signal will increase during the measurement. Really, in the first spectrum recorded about 10 minu-

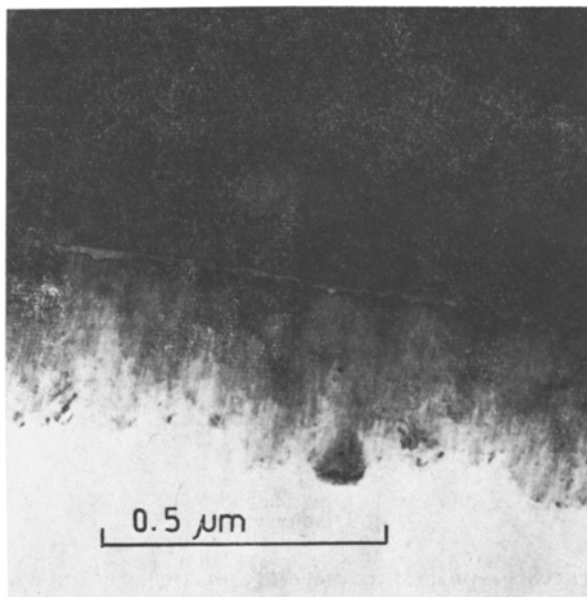


Fig. 1. Longitudinal micrograph of sample A, illustrating the bubbles and elongated rods characteristic for the partially annealed states of severely drawn doped tungsten

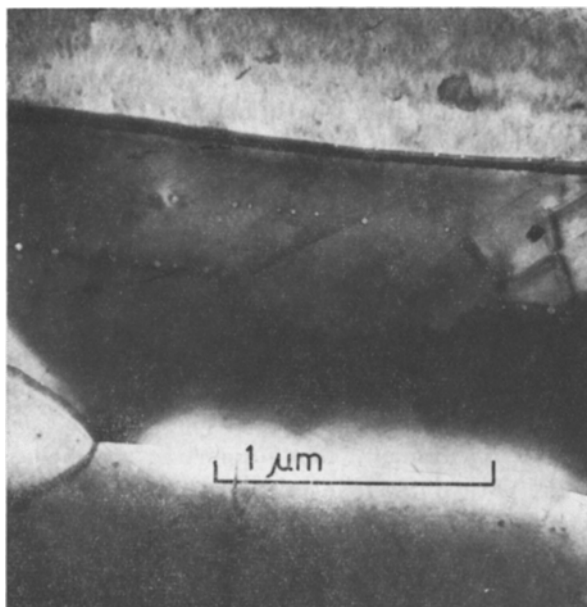


Fig. 2. Longitudinal micrograph of sample B, illustrating the bubble rows in a well annealed state

tes after the 100 K fracture the potassium Auger signal amounted only 20–40% of the Auger signal of similar samples fractured at 250 K.

Let us turn now to a more serious question: Does the total amount of the potassium detected on the surface originate from three-dimensional second phases? In principle the amount originating from three-dimensional second phases can be determined by measuring the depleting time at various temperatures. The depletion time (t_R) of bubbles with a radius of R is defined by the equation:

$$R^3 = \alpha d \cdot D_0 \cdot e^{-\frac{E}{kT}} \cdot t_R, \quad (1)$$

where d is the average thickness of the potassium surface layer, α is a constant, the value of which can be determined by the solution of the diffusion equation, D_0 and E are the unknown preexponential factor and the activation energy of the surface diffusion, respectively. The main problem is that at higher temperatures t_R is rather small and thus we have not enough measured data for fitting.

In sintered rods and in thicker wires the second phases are roughly as much larger as the diameter of the specimen [2]. According to Eq. (1), the depletion time increases very much as R increases. At any given temperature the ratio of the depletion times for the bubbles in sintered rods and in wires of 0.3. mm radius is:

$$\frac{t_{R(\text{wire})}}{t_{R'(\text{rod})}} = \left(\frac{R_{(\text{wire})}}{R_{(\text{rod})}} \right)^3 \quad (2)$$

and thus e. g. at 100 K the depletion time for a bubble in the sintered rod will be extremely large. The potassium surface concentration on the fractured surface of sintered rods (as given in Table II) is, however, higher than for the wires with a diameter of 0.3 mm. If the sintered rod was fractured at 100 K, the potassium surface concentration amounted to 25% of that after high temperature fracture. This ratio is similar to that found in the case of thin wires. This means, however, that Eq. (2) is not valid for this case; i. e. in the sintered rod only part of the potassium originates from the three-dimensional potassium second phases. The other part of potassium must be on the surface already at the very moment of the fracture.

We must conclude, therefore, that in sintered rods two kinds of potassium exist. One kind forms three-dimensional second phases, while the other builds quasi-two-dimensional second phases. This conclusion is in good agreement with the suggestion [3] that in sintered rods two kinds of potassium exist namely "active" and "non-active", if one supposes that in the sintered bodies some part of the potassium forms small bubbles, while the other part is absorbed on the surface of large voids.

Conclusions

It was experimentally verified that potassium diffusion takes place after the fracture. Comparing the potassium Auger signal on sintered rods and thin wires, we have shown that at least in sintered rods the potassium exists in two forms: in the first case potassium forms three-dimensional second phases and in the second one, it is present as an (absorbed?) layer.

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