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Grain growth of chemical vapour deposited tungsten-22 wt % rhenium alloy

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The structures of chemical vapour deposited (CVD) tungsten and a tungsten-22 wt % rhenium alloy in the as-deposited condition, were studied by scanning and transmission electron microscopy. Deposition occurs by the advancement of ledges up the {111} surfaces of four-sided pyramids. Grain growth was studied in the alloy at thirteen temperatures between 1400 and 2780°C. For annealing times of less than 1 h the apparent activation energy was 62 ± 2 kcal mol^{-1}. After several hours at temperatures above 2270°C the rate of grain growth decreased because of the development of bubbles at grain boundaries. Lamellar composition fluctuations were noted metallographically and by electron probe microanalysis. For CVD tungsten, the widening of columnar grains was studied at ten temperatures between 1290 and 2555°C. The rate of increase of columnar grain width became significant only at temperatures above 1980°C.

1. Introduction

It is of practical importance to know the microstructural response of CVD refractory materials to prolonged high-temperature exposure. An example of such an application is the use of CVD tungsten tubing as the electron emitter in thermionic emission power generation. In this case the tungsten emitter is heated by nuclear fuel fission and is also subjected to stress produced by fission gas pressure. Thus any microstructural changes are important since they directly influence the mechanical stability of the emitter.

It is of academic, as well as practical, interest to compare the annealing behaviour of unalloyed and alloyed CVD refractory metals since the former tend to deposit as columnar grains normal to the substrate, whereas alloy deposits tend to have equiaxed grains. The columnar grain-type of microstructure is rather stable thermally [1]; however, it is not as well suited to mechanical applications as is the equiaxed grain-type of microstructure.

In an earlier paper [1] CVD tungsten grain-growth data were reported which were based on observations of sections normal to the long dimension of the columnar grains. The current paper will describe grain-growth observations taken on section parallel to the long dimensions of such grians as well as on the equiaxed grain-growth of a tungsten-22 wt % rhenium alloy. The as-deposited grain structures of the tungsten and the alloy were characterized with scanning and transmission electron microscopy. Electron probe microanalysis was used with the alloy.

2. Experimental procedure

Commercially available tubular materials were utilized. The tungsten had major impurities (< 1000 ppm) of Mo, Nb and Zr and minor impurities (< 10 ppm) of F, Cr, Sr, Ti, V and Fe, and was deposited at 630°C. The tungsten-22 wt % rhenium alloy had minor impurities (< 20 pmp) of Fe, C, O_2, N_2 and H_2 and was deposited at 800°C.

Annealing was performed in an electron beam furnace at a pressure of 2×10^{-5} torr. Electropolishing and chemical etching preceded microstructural observations. Lineal analysis, checked by areal analysis, was employed to obtain alloy grain sizes. In the case of tungsten with columnar grains, the average grain widths are reported.

Electron probe microanalysis was performed using tungsten M-alpha radiation with an ammonium dihydrogen phosphate (ADP) analysing crystal and rhenium L-alpha radiation

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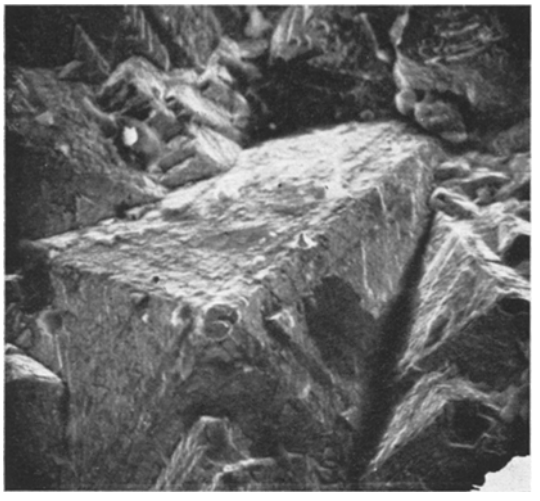

Figure 1 CVD tungsten growth surface, SEM, × 950.

with a lithium fluoride crystal.

3. Results and discussion

3.1. As-deposited structures

For CVD tungsten the appearance of the advancing deposition interface is shown in Fig. 1. This pyramidal structure is similar to the structures reported in the electrodeposition of copper single crystals [2]. The fact that long columnar grains are found in the growth direction suggests that nucleation on the deposition surface is negligible [3]. Holman and Huegel [4] have enhanced nucleation by brushing the growing deposit. Holman suggested that the pyramid faces in CVD tungsten are {111}. This would agree with our earlier pole figure results [5] which indicated a fibre axis which was largely ⟨100⟩.

There appear to be many layers of steps on the pyramid faces. It has been suggested [3] that these steps are nucleated at the grain boundaries of the columnar grains and then proceed to grow up the pyramid faces. At the top of the pyramids a matching problem occurs, as advancing steps meet and cause small cavities.

Fig. 2 reveals a rounding or smoothing of the crystallographic features of the pyramid faces on annealing at 2215° C. This is apparently a surface diffusion effect. A similar but much less distinct effect was noted [6] in CVD tungsten deposited at 700° C compared to that deposited at 500° C.

In the alloy very few dislocations and no alloy segregation effects were evident in TEM; however, electron probe microanalysis (EPMA) and scanning electron microscope (SEM) observations did suggest slight compositional fluctuations. Fig. 3 shows the lamellar segregations as observed with SEM after polishing and etching. A typical spacing between the lamellae is 1 μm and the EPMA scans for both tungsten and rhenium showed intensity fluctuations at intervals of about 1 μm, the approximate resolution of the method. The essential absence of contrast effects in TEM due to absorption is not surprising since tungsten and rhenium are adjacent in the periodic table.

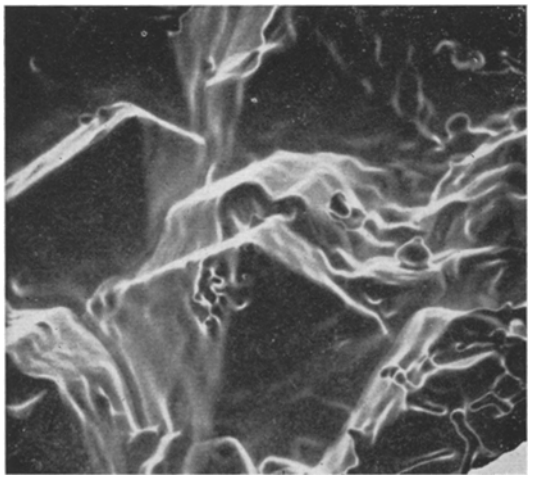

Figure 2 CVD tungsten growth surface after annealing 5 h at 2215° C, SEM, × 1000.

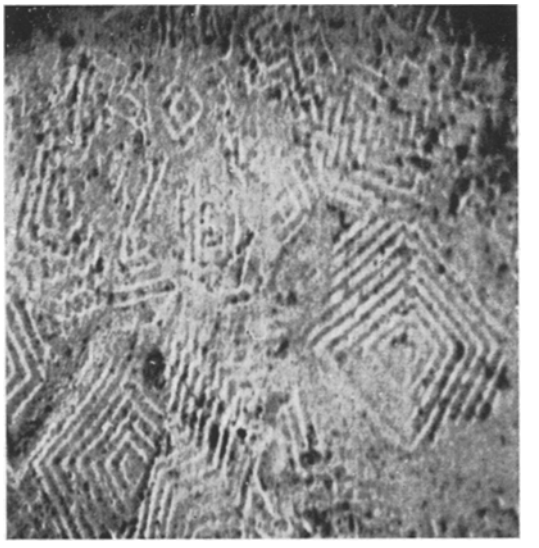

Figure 3 Segregated structure of the alloy revealed by SEM after annealing 1800° C for ½ h, electropolished and etched, × 1850.

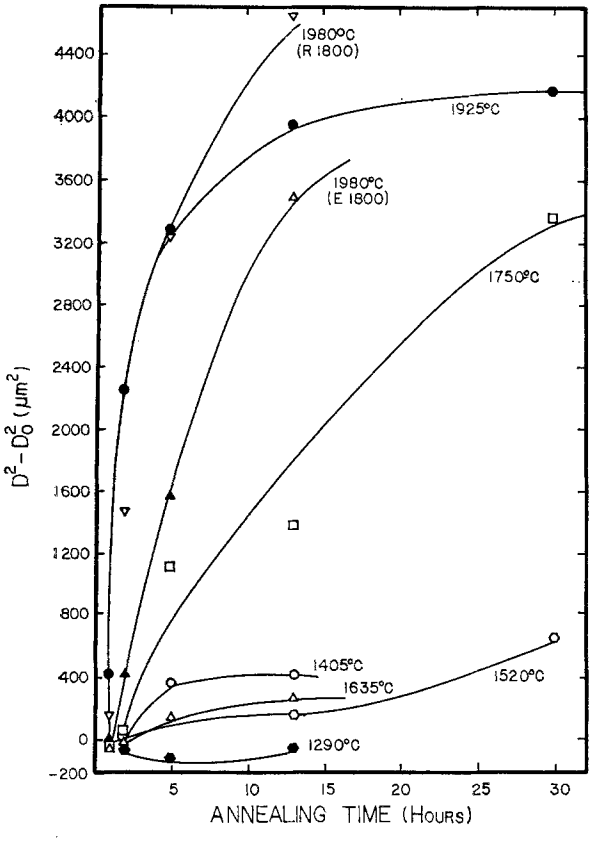

Figure 4 Alloy grain growth between 1290 and 1980°C. 1980°C (R1800) – after thermal grooving.

3.2. Grain-growth in the tungsten-22 wt % rhenium alloy

Fig. 4 describes the grain growth in the alloy up to 1980°C for times up to 30 h. The difference between the square of the instantaneous grain diameter and that of the initial grain diameter (both equiaxed) is plotted versus annealing time. The as-received material had already been annealed by the supplier for 30 min at 1800°C after which it had an average equiaxed grain size of 12 μm. Subsequent anneals below 1600°C did not produce much grain growth. Two 1980°C curves are shown; the upper curve represents measurements made after normal polishing and etching after each anneal, the lower curve represents measurements based on thermal grooving only. That is, for the thermal grooving curve, only one initial electropolish was performed. After each period of annealing a specimen was quenched to 25°C in vacuum. It is suggested that surface retardation of boundary migration occurred in the latter case. This was confirmed by the fact that lightly polished and etched surfaces yielded smaller average grain sizes than did heavily polished and etched surfaces. Grain-size distribution plots for anneals of 1, 2, and 48 h at 1980°C and for anneals of 1, 5, and 13 h at 1750°C showed fairly constant shapes, indicating that primary rather than secondary grain growth was involved.

Notice that the 1290°C curve shows an actual negative deviation. This can only mean that at 1290°C grains appear at short annealing times which are in fact smaller than the initial grain size. In an earlier paper [1], similar effects were found in CVD tungsten and meant only that new grains were being counted which earlier had been below the limit of detection. Rather than actual recrystallization, this is simply the early growth of very fine CVD nuclei. Microstructural comparisons showed that the grain size after 60 h at 1290°C was in fact less than the initial grain size. We believe that this is also responsible for the 1635 and 1520°C curves being below the 1405°C curve, i.e. in the 1520 to 1632°C

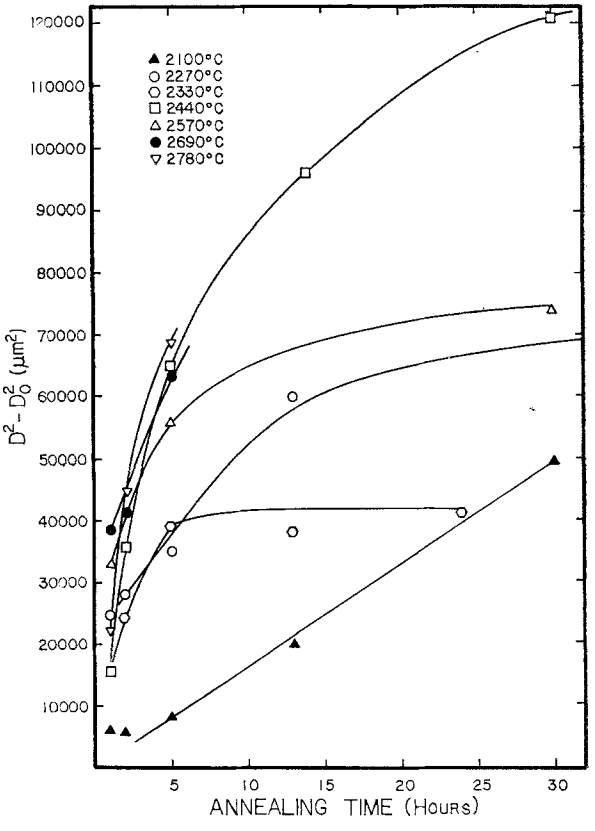

Figure 5 Alloy grain growth between 2100 and 2780°C.

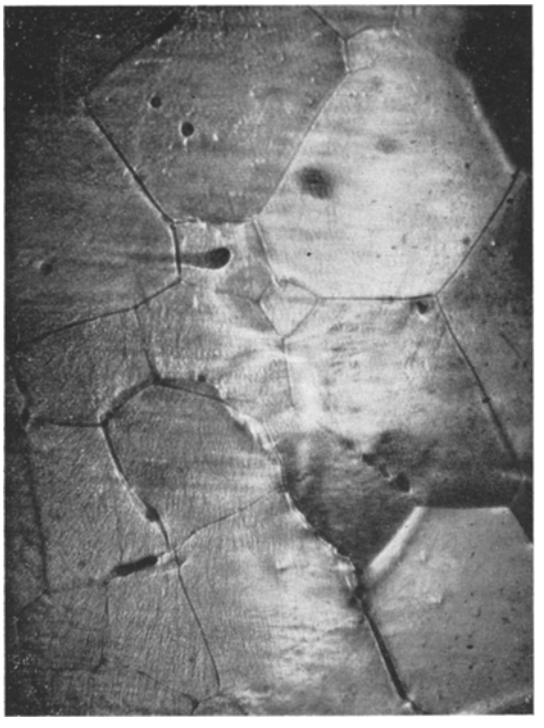

Figure 6 Optical micrograph of the alloy after annealing at 2270°C for 48 h. Electropolished and etched, × 89.

specimens new fine grains developed and lowered the average calculated grain size. By 1750°C this effect no longer occurs.

Fig. 5 shows the higher temperature annealing data. Notice that the rate of grain growth at temperatures above 2100°C is initially high and decreases sharply at times beyond approximately 5 h. This rate decrease at longer times is believed to be caused by the development of bubbles on the boundaries. The lowest temperature at which such bubbles were resolvable with optical microscopy, was 2270°C. A representative micrograph is shown in Fig. 6. The source of these bubbles is usually given as fluorine or as a combination of lattice vacancies and gaseous impurities [7, 8], particularly fluorine. We do not understand why the 2440°C curve lies above the 2570°C curve in Fig. 5. It could have been caused by a variation in fluorine content; however, this is merely speculation. Anneals were not performed beyond 5 h for 2690 and 2780°C because these temperatures were rather extreme for the equipment available. For temperatures of 1750°C and above, Figs. 4 and 5 were replotted on a basis of $\ln (D^2 - D_0^2)$ versus log time to see if this would aid in judging the fit of the data to the normal grain-growth approximation equation; $D^2 - D_0^2 = kt$. It was found that the data for specimens annealed below 2270°C for more than 2 h fell on lines with a slope of about 1, whereas above 2270°C the longer annealing time data fell approximately on lines of slope 0.3. This implies that below 2270°C the normal grain-growth approximation is fairly good (after several hours), but that above this temperature the rate of grain growth decreases. As mentioned earlier, we ascribe this behaviour to bubbles on the grain boundaries. These bubbles evidently take several hours to become effective in retarding grain growth.

An Arrhenius type plot of the rate constant k versus 10^4 T^{-1} for times up to 1 h is shown in Fig. 7. The experimental activation energy obtained for initial grain growth in the alloy was 61.7 ± 2 kcal mol^{-1}. This value is essentially the same as the value of 59 ± 2 kcal mol^{-1} reported earlier [1] for CVD tungsten. In swaged polycrystalline tungsten and in single crystals con-

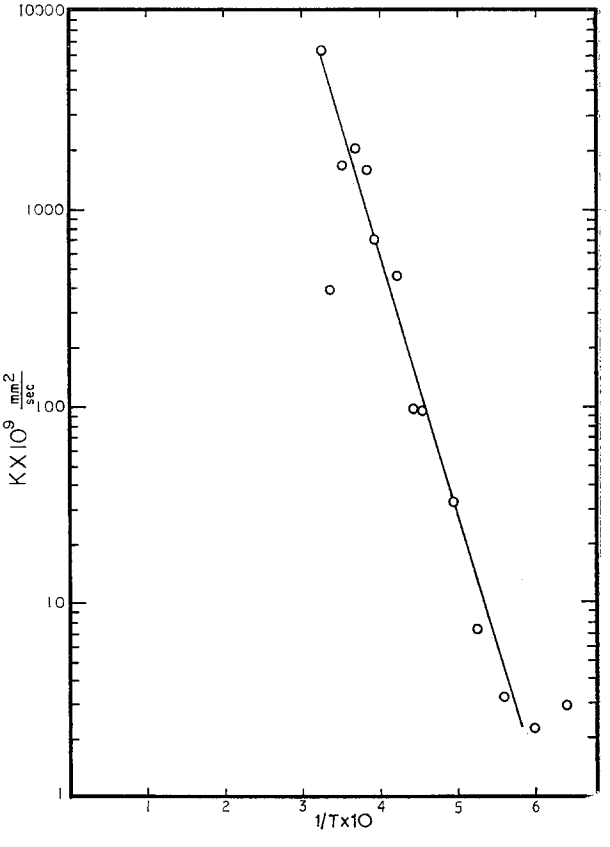

Figure 7 Arrhenius plot of $k(k = k_0 \exp(-Q/RT))$ versus $10^4/T$ for alloy grain growth at times less than 1 h.

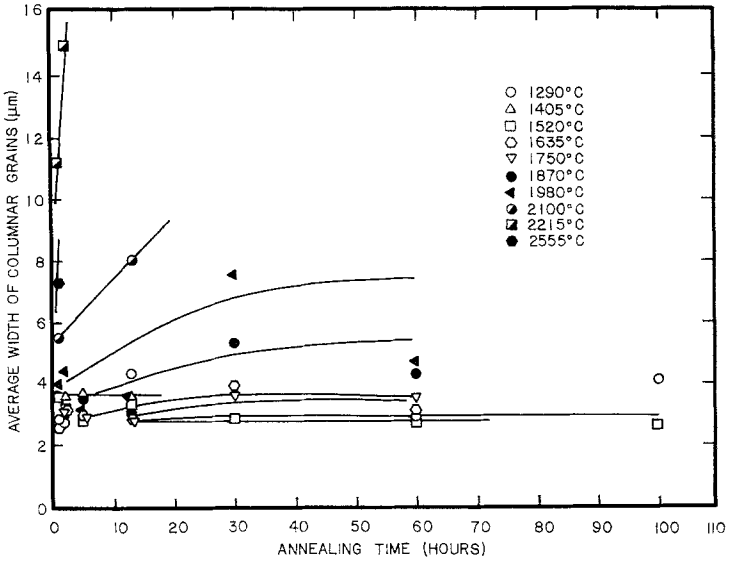

Figure 8 Average columnar grain width versus annealing time for CVD tungsten.

taining sub-boundaries with misorientations of up to 10° a grain boundary diffusion activation energy of 92 ± 2 kcal mol^{-1} has been reported [9]. Values of lattice self-diffusion are reviewed in the same paper and range from 120 to 153.1 kcal mol^{-1}. Our value of 61.7 ± 2 kcal mol^{-1} for grain growth probably represents the activation energy for grain-boundary self-diffusion in the alloy. The fact that this is lower than the 92 ± 2 kcal mol^{-1} grain-boundary diffusion value for swaged tungsten [9] suggests that boundaries in CVD materials are fundamentally different.

3.3 Grain growth of columnar grains in CVD tungsten

The lateral growth of long, relatively straight columnar grain boundaries was examined at ten temperatures between 1290 and 2555°C. Fig. 8 is a plot of the average columnar grain width versus annealing time. It is evident that very little boundary motion occurs at temperatures of less than 1980°C. Above that temperature the growth rate increases rapidly. It is not surprising that the $D^2 - D_0^2 = kt$ relation is not adequate to describe these results since virtually no boundary curvature is present to provide a driving force.

4. Conclusions

1. Tungsten-22 wt % rhenium, produced by CVD, undergoes normal grain growth during annealing below 2270°C with an experimental activation energy of approximately 61.7 ± 2 kcal mol^{-1}. At higher temperatures after several hours of annealing the rate decreases sharply due to the formation of bubbles on the boundaries. These bubbles evidently retard the motion of the boundaries.
2. EPMA revealed that solute segregation had occurred within the equiaxed grains of the alloy during deposition. This segregation was lamellar in character with a periodicity of approximately 1 μm.
3. The width of the columnar grains in CVD tungsten changes very little during annealing below 1980°C. Above this temperature this width increases rapidly.

Acknowledgements

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