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Experimental and simulated grain boundary groove profiles in tungsten

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ABSTRACT

Grain-boundary grooving has been studied on polished surfaces of polycrystalline tungsten annealed at 1350°C. Atomic force microscopy images were taken in the same area for each groove after different annealing times. Secondary oscillations next to the main groove maxima (predicted for grooving by surface diffusion) were observed, to our knowledge for the first time. The agreement between experimental and calculated groove profiles (using the surface diffusion model of Mullins (1957, *J. appl. Phys.*, **28**, 333)) improved when grain-boundary fluxes were introduced.

The theory of grain boundary grooving by surface diffusion was rigorously developed by Mullins (1957). Mullins' expressions for the width w and depth d of the grooves can be written as follows:

$$W = 4.6(Bt)^{1/4}, \tag{1}$$

$$d = 0.973m(Bt)^{1/4}, \tag{2}$$

where

$$B = \frac{\delta D_s \Omega \gamma_s}{kT}. \tag{3}$$

In these equations, t is the time of annealing, m the slope of the surface at the groove root, δD_s the product of the thickness of the layer in which surface diffusion occurs and the surface self-diffusion coefficient, respectively, Ω the atomic volume of the diffusing species, γ_s the free energy of the solid–gas interface, k the Boltzmann constant and T the absolute temperature.

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Mullins' original partial differential equation was solved numerically for general groove surfaces by Robertson (1971) and by Zhang and Schneibel (1995). These calculations show that, in addition to the main maxima on either side of a groove, a series of side maxima and minima exists. Since these oscillations decay rapidly with increasing distance from the groove root they are difficult to verify experimentally. The purpose of this letter is to show that newly developed experimental techniques are precise enough to verify the existence of secondary oscillations in addition to the main groove maxima.

Grain-boundary grooving can occur by evaporation–condensation, volume diffusion or surface diffusion (Mullins 1957, 1960). In the present experiments, grooving of tungsten was studied at 1350°C. Since the vapour pressure of tungsten at this temperature is only 2×10^{-16} Pa (Tanabe 1994), the evaporation–condensation mechanism is not thought to contribute. At 1350°C, the surface and volume diffusivities of tungsten are $\delta D_s = 1.9 \times 10^{-22}\,\mathrm{m^3\,s^{-1}}$ and $D_v = 1.4 \times 10^{-22}\,\mathrm{m^2\,s^{-1}}$, respectively (German 1996). With these values, the characteristic length $l = 2\pi\delta D_s/D_v$ derived by Shewmon (1989), above which volume diffusion dominates surface diffusion, is of the order of 8 m. Since the groove widths in our experiments were only of the order of 1 μm, grooving should have occurred exclusively by surface diffusion. Therefore Mullins' (1957) theory for surface diffusion can be used to interpret our experiments.

Polycrystalline tungsten sheets were pre-annealed at 1600°C in vacuum (10^{-4} Pa) for 61 h to obtain a stabilized grain structure and to minimize grain-boundary migration during the subsequent grooving experiments. The pre-annealed sheets were ground with 600, 800 and 1200 grit SiC papers and polished with a slurry of $\frac{1}{4}$ μm diamond powder. The polishing time had to be carefully limited to prevent overpolishing that may result in different heights of adjacent grains. Pieces of the polished sheet were placed in alumina crucibles covered with tantalum sheet and annealed in vacuum (10^{-4} Pa) at 1350°C. The anneals were periodically interrupted in order to examine the specimens. The accumulated times at 1350°C were 2, 8, 18, 28 and 98 h, respectively. After the first (2 h) anneal, grids of micro-hardness indents were placed as markers on the sample surface and approximately 20 symmetrical grooves were selected for the measurements. Using surface features such as pores, boundary curvature, etc., atomic force microscopy (AFM) images were taken in approximately the same area for each groove after different annealing times. The AFM images were taken with a Park Scientific Instruments Auto Probe M5 instrument operated in the contact mode in air. The tip and cantilever of the AFM were fabricated from highly boron-doped single-crystal silicon. The tips were symmetrical cones nominally 3 μm tall with a half cone angle of 12°. The errors due to the non-zero tip diameter were difficult to quantify because the tip wore with use. Since large dihedral angles were measured, errors due to tip rounding would be expected to be relatively small. However, to minimize this error, tips were changed periodically. A scanning rate of 0.4 Hz was chosen. The surface was always scanned in a direction perpendicular to the grooves. For chosen rectangular areas, average cross-sections were obtained using Proscan Image Processing software (Park Scientific Instruments). The data were subsequently processed using MathCad 8 software to obtain the groove parameters such as the groove depth, width and dihedral angle. To determine the dihedral angle the data points lying on approximately straight lines next to the groove root were interpolated by linear functions. Out of 20 grooves examined after annealing for 2 hours at 1350°C, five showed well developed side minima and maxima. An example is shown in figure 1.

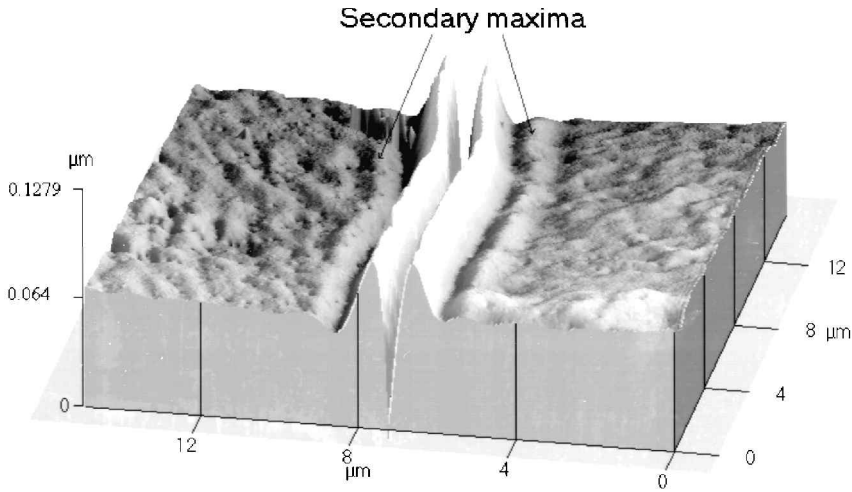

Figure 1. AFM image of a grain boundary groove in tungsten annealed at 1350°C for 2 h in vacuum. Small side maxima and minima next to the main maxima can be clearly seen.

In figure 2, an averaged profile of the groove in figure 1 is compared with numerical simulations. The simulation based on Mullins' original model (dihedral angle 142°; time $t = 0.004m^4/B$, where B is defined in equation (3)) shows lower maxima than the experiment. In a second simulation, an arbitrarily chosen flux was allowed to leave the grain boundary and to enter the surface. Also, at a chosen point in time the dihedral angle was increased during the simulation. The additional flux increased the amplitude of the maxima and minima and, as a result much better agreement with the experiment was observed.

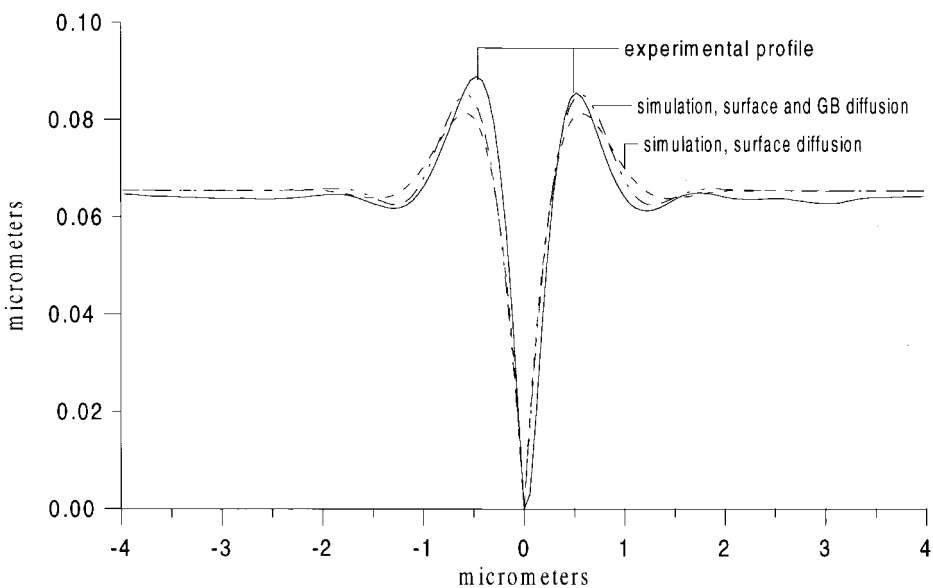

Figure 2. Comparison between measured and simulated groove profiles.

While the experimental verification of the theoretically predicted side maxima lends additional credence to Mullins' theory, several unexpected complications in the present experiments need to be pointed out. According to Mullins' model, in which the grain boundary flux is assumed to be zero, the amount of matter removed from below the original specimen surface should be exactly equal to the amount of matter deposited above this surface. In our experiments, there were many cases where more matter was deposited than removed with respect to the original specimen surface. In other words, mass conservation along the surface may not have been observed, and this is the reason why a simulation including a non-zero grain boundary flux was carried out. After annealing for times longer than 2 h, the groove growth became anomalous. The separation of the main maxima usually did not increase with time. The dihedral angle included by the surfaces on either side of the groove root showed generally a tendency to increase, and this effect was included in our simulation that included a grain boundary flux. In spite of the 1600 °C anneal prior to the grooving experiments, grain-boundary migration was often observed. Figure 3 shows an example of grain-boundary migration indicating that the grain boundary moved away from its original position during annealing. At the same time, the groove root moved up, in violation of equation (2). In similar experiments carried out in an Ar–H_2 atmosphere, the groove growth was similar to Mullins' predictions. This suggests that the environment was in some way responsible for the observed anomalies.

In summary, the side maxima and minima predicted for grain boundary grooving by surface diffusion have been observed, probably for the first time. The experiments and simulations indicate that there may be additional factors involved in the grain-boundary grooving of tungsten in vacuum which need to be identified and incorporated into the theoretical model.

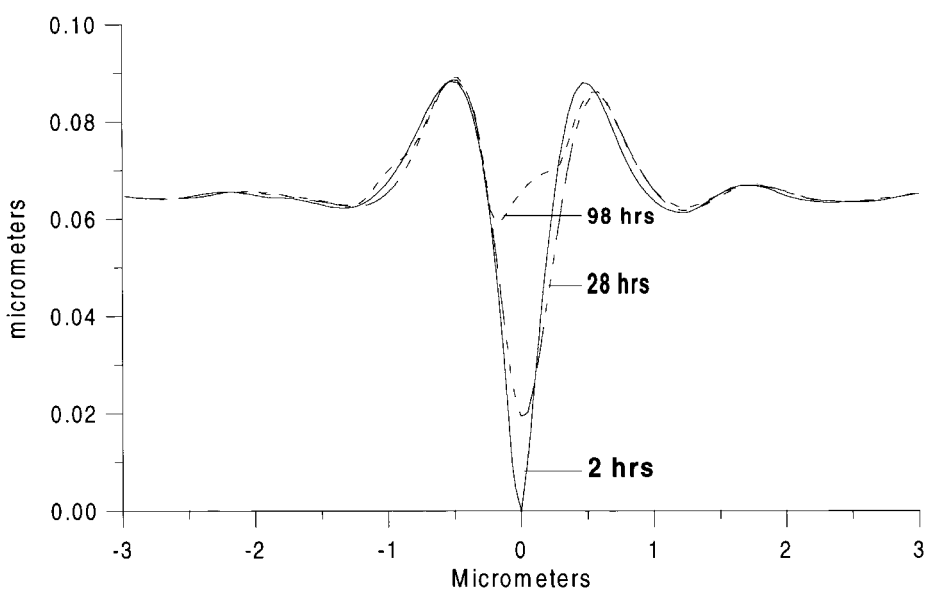

Figure 3. Averaged AFM profile illustrating grain boundary migration and groove depth reduction during annealing.

Acknowledgements

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