Full length article

Hydrogen-induced accelerated grain growth in vanadium

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ABSTRACT

Grain growth in nanocrystalline vanadium films was studied at 600 and 700 °C in vacuum and in hydrogen atmosphere with partial pressures ranging from 1 to 1000 Pa. It is shown that grain growth is significantly increased in the presence of hydrogen. Thus the expected effect of retarding grain growth either by reducing grain boundary energy due to hydrogen segregation or by hydrogen drag on the moving boundary did not occur. Two explanations are given for the accelerated grain growth. First, hydrogen reduces the formation energy of ledges, assuming these ledges are required for initiating and advancing boundary motion. Second, grain growth requires the annihilation of excess volume which may be enhanced by reducing the formation energy of vacancies in the presence of hydrogen.

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1. Introduction

Grain size control is an important aspect of materials engineering, and the use of solute additives for size control is a common technique. Grain growth is usually thought of in terms of lowering the system energy: since grain boundaries contribute energy to the system, grain growth, which reduces the total area of grain boundaries, lowers the total energy of the system. The presence of impurity atoms on the grain boundary lowers the grain boundary formation energy and, thereby reduces the driving force for grain growth, resulting in a smaller final grain size [1–5]. Some researchers propose that this energy consideration is insufficient to account for the reduced grain coarsening, and that it is the decrease of grain boundary mobility due to solute drag which accounts for the smaller final grain size [6,7]. In nanograined materials, this situation is complicated by the fact that the total number of atoms in the grain boundaries begins to approach the number of atoms in the bulk [8]. At this point, it is likely that other defects, such as grain boundary triple junctions and vacancies, play an important role in grain boundary motion, resulting in an interplay between energy considerations and mobility effects [6,9,10]. However, in the framework of a generalized Gibbs adsorption concept [11–13], the formation energy of these defects is reduced by solute segregating to the defects as well. Thus, the density of triple junctions and vacancies is increased by the segregation of solute atoms.

Hydrogen, though an interstitial solute, tends to behave differently from other impurities in metals regarding its interaction with defects. This arises from its high mobility at low temperatures, where hydrogen atoms are able to reach defects in reasonable times and the defects have not been annihilated due to recovery and/or recrystallization. This is particularly evident in its influence on dislocation behavior [14] and its creation of superabundant vacancies [15]. With respect to the influence of hydrogen on grain boundaries, research has been limited to investigations into the lowering of the grain boundary cohesion [14,16], while studies into the influence of hydrogen on grain growth in metals are missing. The present study was designed to address the issue.

The vanadium-hydrogen system is used as a model system in this study. The body-centered cubic structure of vanadium leads to a high hydrogen diffusivity, similar to iron-based ferritic alloys, though the hydrogen solubility of those alloys is much lower. With the high solubility of hydrogen in vanadium, a large range of hydrogen concentrations can be explored. Nanocrystalline films allow easy sampling of a range of temperature, time and hydrogen conditions to investigate the effect of hydrogen on grain growth with the driving force for grain growth being largely due to the small grain size.

2. Experimental procedure

Nanocrystalline films of vanadium were produced by argon ion-beam sputter deposition. The background pressure of the system

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was $p_{back} = 2x10^{-8}Pa$, while the Ar sputter pressure was $5x10^{-2}Pa$. For a substrate, 3 mm gold grids with an amorphous carbon film were used to allow observation of the film microstructure in the transmission electron microscope (TEM) without further sample preparation. The vanadium deposition rate was ~0.6 nm/min. Films with thicknesses between 90 and 120 nm were prepared, such that they are electron transparent in the TEM. The average as-grown grain size was 8 nm for the first batch of samples, and 25 nm for a second batch. This difference is likely due to small changes in the deposition parameters, due to the system being cleaned and readjusted between the batches. The complete and even rings of the diffraction pattern suggest no obvious texture to the grain orientation.

Samples were heated in a tube vacuum furnace at 600 or 700 °C for 1–2 h, with a few tests sampling longer heat times. Base pressures of 10^{-6} Pa were achieved. Hydrogen gas was added to the system during heating at pressures ranging from 1 to 1000 Pa. Before and after heating, the microstructure was investigated in a Phillips CM12 TEM operated at 120 kV. Grain size determination was carried out on bright-field TEM images by the circle-intercept method. This technique consistently gave errors on the order of ±8%.

3. Results

Grain growth in films with an initial grain size of 8 nm (Fig. 1a) starts in vacuum between 600 and 700 °C. After 1 h at 600 °C in vacuum, no grain growth is noticed, with a final grain size of 9 nm (Fig. 1b). The addition of hydrogen produces a marked change in behavior: heating at 600 °C for 1 h in 1 Pa hydrogen already produces a final grain size of 30 nm, as shown in Fig. 1c. The addition of 1 Pa H_2 corresponds to a solute concentration in vanadium of 0.013 at%, if the system is at equilibrium at 600 °C [17]. Therefore, it is evident that the presence of this small amount of hydrogen has already caused substantial grain growth. Note that the given concentration was determined for coarse grained vanadium, where any segregation of hydrogen at grain boundaries has a negligible effect on the overall hydrogen concentration. Thus the value calculated from the pressure-composition isotherms in Ref. [17] corresponds to the hydrogen concentration within the vanadium grains.

At 700 °C, grain growth visibly occurs in vacuum (Fig. 2a), with the average final grain size of that sample increasing to 16 nm, and the effect of hydrogen is even more evident. With exposure to 1 Pa of hydrogen, we again see significant grain growth (Fig. 2b). However, as visible in the same figure, the growth mode is clearly bimodal, with the large grains averaging 37 nm in diameter and the smaller grains averaging 6 nm, which is below the average starting grain size of the film, suggesting that it is the smallest grains that do not grow or are partially consumed as in a ripening process. Increasing the hydrogen pressure to 10 Pa results in faster grain growth, but it is still bimodal in nature, with average diameters of

50 and 13 nm (Fig. 2c). It is notable that the smaller grains appear to begin growing now with the addition of more hydrogen. According to Sieverts' Law and in agreement with measurements [17], the hydrogen concentration in the vanadium grains increases by a factor of square root 10, being about 0.04 at% at 10 Pa.

Higher hydrogen pressures result in increased grain growth, but reaching steady state grain sizes at 700 °C between 10 and 100 Pa hydrogen pressure. Samples heated at 700 °C for 2 h with 100 Pa and 1000 Pa hydrogen gas (which according to Sieverts' Law corresponds to 0.13 and 0.4 at% in the vanadium grains, respectively [17]) showed a similar final grain size, increasing from an initial grain size of 21 nm (Fig. 3a) to 55 and 54 nm (Fig. 3c–d, respectively). This suggests that there is a saturation point after which increasing the hydrogen pressure no longer results in an increase in the grain growth rate. Interestingly, there is also no longer a bimodal distribution. Whether this is due to the increased growth of all grains with the addition of this much hydrogen, or whether growth of selected grains occurred aggressively at the expense of smaller grains, now completely consumed, is not clear.

As heating continues for longer periods of time, the difference in behavior due to hydrogen becomes more noticeable. As shown in Fig. 4, at 700 °C, a larger final grain size of 110 nm is achieved after 6 h heating in only 1 Pa H_2 when compared with reaching a final size of 35 nm in vacuum despite a longer heating time of 18 h. This corresponds to an order of magnitude higher growth rate (Fig. 5). It is also important to note that, as expected [5], grain growth in vacuum slows down with time, with the same amount of grain growth occurring between 2 and 4 h as occurs between 4 and 18 h. In the presence of hydrogen, after 6 h, grain growth likewise appears to slow down. However, in this case, as the grain size is approaching the film thickness (~120 nm), a geometric constraint may be artificially inhibiting grain growth [18]. This is supported by the apparent sharpness in the change in the slope of the hydrogen curve compared to the vacuum curve in Fig. 5a, where, between 1 and 4 h, the vacuum data gently curves towards a steady state value (likely unaffected by geometry), while the hydrogen data displays a higher slope initially before flattening more abruptly. Also, as highlighted in Fig. 5b, where parabolic grain growth behavior is plotted as straight lines, grain growth in hydrogen appears to be initially following a parabolic behavior before abruptly flattening out, while grain growth in air does not appear follow a parabolic curve at all.

4. Discussion

The experimental results of the present study clearly demonstrate that the exposure of nanocrystalline vanadium to gaseous hydrogen produces a significant increase in grain growth rates. Even relatively low amounts of hydrogen cause a doubling in the final grain size compared to that achieved in vacuum. Higher pressures or chemical potentials of hydrogen result in further
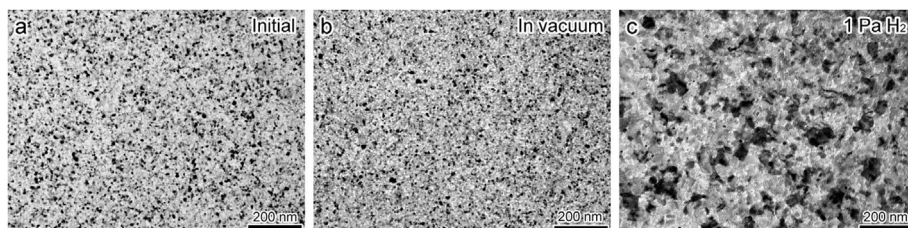
Fig. 1. TEM micrographs of grain growth in vanadium film at 600 °C for 1 h a) Starting microstructure with average grain size of 8 nm b) Microstructure after heating in vacuum with a final grain size of 9 nm c) Microstructure after heating in 1 Pa H_2 gas with a final grain size of 30 nm.