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Thermal stability of a highly-deformed warm-rolled tungsten plate in the temperature range 1100 °C to 1250 °C

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Pure tungsten is considered as armor material for the most critical parts of fusion reactors (i.e. the divertor and the first wall), among other reasons due to its high melting point (3422 °C) and recrystallization temperature. The thermal stability of a pure tungsten plate warm-rolled to a high plastic strain by 90% thickness reduction was investigated by isothermal annealing for up to 190 h in the temperature range between 1100 °C and 1250 °C. Vickers hardness testing allowed tracking the changes in mechanical properties caused by recovery and recrystallization. The hardness evolution could be rationalized in terms of a logarithmic recovery kinetics and a Johnson-Mehl-Avrami-Kolmogorov recrystallization kinetics accounting for an incubation time of recrystallization. The observed time spans for recrystallization and the corresponding recrystallization activation energy for this highly deformed plate suggest that large plastic deformations (e.g. applied during shaping) are only suitable to produce tungsten components to be used at relatively low temperatures (up to 900 °C for a 2 years lifespan). Higher operation temperatures will lead to fast degradation of the microstructure during operation.

Keywords: tungsten, annealing, recrystallization, thermal stability

1. Introduction

Pure tungsten is the material of choice for the most critical parts of fusion reactors (i.e. the armor of the divertor and the first wall). An important reason for this choice is the high melting point (3422 °C) of tungsten and therefore its high recrystallization temperature, which makes tungsten excellent to withstand the high heat fluxes (10-15 MW/m²) and temperature gradients present in operating fusion reactors [1,2]. Other important properties tungsten offers include high thermal conductivity [3], good thermo-mechanical properties (e.g. creep resistance) [4], low sputtering yield [5], and resistance to radiation damage [6]. Unavoidably, the high operation temperatures during operation in fusion reactors will induce changes in mechanical properties due to recovery, recrystallization and grain growth. These microstructural changes degrade the mechanical properties (e.g. strength) [7], and embrittle the material in case of recrystallization of tungsten [8], due to localization of internal stresses at grain boundaries [9].

The aim of this study is to characterize the thermal stability of a plate of pure tungsten warm-rolled to 90% thickness reduction. Isothermal annealing is carried out between 1100 °C and 1250 °C for up to 190 h. Vickers hardness measurements are performed to track softening during annealing related to recovery and recrystallization and analyzed in terms of Kuhlmann recovery [10] and Johnson-Mehl-Avrami-Kolmogorov recrystallization [11] kinetics. The results are compared to an earlier study of a similar tungsten plate warm-rolled to 67% thickness reduction, i.e. to a moderate plastic strain [12].

2. Experimental

A 4 mm thick warm-rolled plate of 99.95% pure tungsten was received from Advanced Technology & Materials Co., Ltd., Beijing. The plate had been manufactured from tungsten powder by cold-isostatic pressing and sintering under hydrogen atmosphere at 2300 °C for 6 h. To obtain the final thickness, the plate had been warm-rolled to a thickness reduction of 90% at a temperature of about 1000 °C. Small specimens of about 3×4×8 mm³ were cut from the plate using a diamond saw.

Isothermal annealing was performed on these specimens at six different temperatures between 1100 °C and 1250 °C using a universal high temperature tube furnace Nabertherm RHTC 80-230/15. For protection of the specimens against oxidation and formation of volatile WO₃, the specimens were encapsulated in glass ampoules (one specimen in each ampoule). The procedure consists of flushing the ampoules with Argon, creating vacuum conditions inside and finally sealing with a blowtorch. The specimens were put in the pre-heated furnace, removed after the desired annealing time and cooled to room temperature by air-cooling. Specimens which optically showed any indication of oxidation after heat treatment were discarded.

After annealing, transversal sections (comprising the rolling and the normal direction) were mechanically grinded and polished for Vickers hardness measurements. The indents were placed in the center of the specimens far from the original surface in contact with the rolls. A load of 10 kg and a dwell time of 10 s

were used. A total of 20 indents were averaged for each sample, with the standard deviation of the average reported as accuracy as well as error bars in the figures presenting the hardness evolution. Electropolishing with 3 wt.% NaOH at a constant voltage of 10 V was required for specimens investigated by electron backscatter diffraction (EBSD). Etching with 3% wt. H₂O₂ was performed on specimens for light optical microscopy.

3. Results and Discussion

3.1 Microstructural investigations

The microstructural changes during recrystallization are visualized in the light optical micrographs presented in Fig. 1 for the warm-rolled condition, a partially recrystallized state and the fully recrystallized state after annealing at 1175 °C for different times. The micrographs clearly reveal that the deformation structure with elongated grains along the rolling direction (RD) after warm-rolling (Fig. 1a) becomes replaced by recrystallizing grains (Fig. 1b) until a fully recrystallized structure with equiaxed grains is achieved (Fig. 1c).

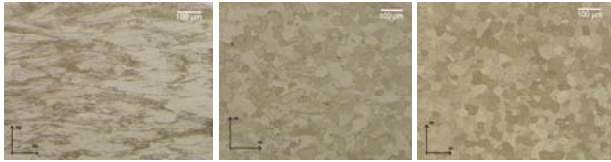


Fig. 1. Light optical micrographs for tungsten warm-rolled to 90% thickness reduction: a) as-received condition with elongated grains along RD, b) partially recrystallized sample annealed for 20 h at 1175 °C, where a mixture of equiaxed recrystallized grains and deformed elongated grains is observed, c) fully recrystallized sample annealed for 50 h at 1175 °C showing only equiaxed recrystallized grains. All sections represent the transversal plane containing the rolling and the normal direction, RD and ND, respectively; RD being horizontal.

The presence of a deformation structure in the warm-rolled condition is highlighted in the boundary map of Fig. 2 obtained by EBSD on the transversal section. An elongated grain structure along the rolling direction is clearly observable from the high angle boundaries (with misorientation angles above 15°) with a mean boundary spacing of 5.5 μm along RD. Within the deformed grains, low angle boundaries (with misorientation angles between 2° and 15°) are observed abundantly having a mean boundary spacing of 0.67 μm along RD.

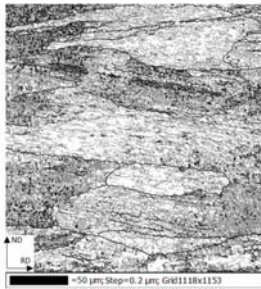


Fig. 2. Boundary map of tungsten warm-rolled to 90% thickness reduction (as-received condition) obtained by EBSD with step size 0.2 μm of an area 224×231 μm² on a transversal section containing the rolling and the normal direction, RD and ND, respectively. Grey and black lines represent low and high angle boundaries, respectively.

3.2 Hardness evolution

The evolution of the Vickers hardness with annealing time at two different temperatures is illustrated in Fig. 3. A monotonous decrease in hardness is observed from the value $HV_{def} = 434 \pm 2 HV_{10}$ of the deformed state to the value $HV_{rex} = 351 \pm 2 HV_{10}$ of the fully recrystallized state. The later hardness value being almost constant at long annealing times and common for all five temperatures indicates also the absence of any grain growth.

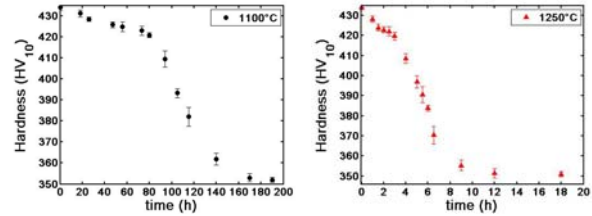


Fig. 3. Evolution of the Vickers hardness of tungsten warm-rolled to 90% thickness reduction with annealing time at different temperatures: (a) 1100 °C and (b) 1250 °C.

A simple approach to quantify the annealing kinetics and hence the thermal stability is obtained by the time span to achieve a hardness $(HV_{def} + HV_{rex})/2 = 392.5 HV_{10}$, i.e. when half of the hardness loss has been achieved. The annealing times to reach half of the hardness loss are estimated by linear interpolation from Fig. 3 (and corresponding figures for the other temperatures). As obvious from Fig. 4, the dependence of the time to half of the hardness loss on annealing temperature follows closely an Arrhenius relation

$$t_{\Delta HV/2} = t_{\Delta HV/2}^* \exp(E_{\Delta HV/2}/RT) \quad (1)$$

with prefactor $t_{\Delta HV/2}^*$, the universal gas constant R and an apparent activation energy $E_{\Delta HV/2} = 357 (1 \pm 3\%)$ kJ/mol for half of the total hardness loss.

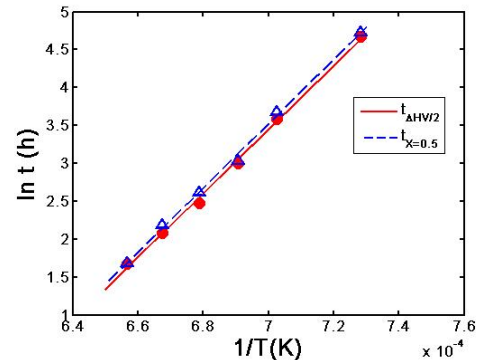


Fig. 4. Arrhenius plot of characteristic times during isothermal annealing of tungsten warm-rolled to 90% thickness reduction in dependence on temperature: time to half of the total hardness loss $t_{\Delta HV/2}$ and time to half recrystallization $t_{X=0.5}$.

Two different softening stages can be distinguished in Fig. 3 during annealing. The first stage corresponds to the initial rapid decrease of hardness which slows down over time, whereas the second stage occurring at longer annealing times entails a higher reduction in hardness following a characteristic sigmoidal shape. These stages are directly related to the microstructural changes occurring during recovery and recrystallization,

respectively, and the corresponding decrease of dislocation density they induce. The stored energy in the deformed microstructure (mainly in the form of dislocations) is the driving force for both processes [11].

3.3 Recovery

Recovery summarizes all thermally activated mechanisms by which dislocations annihilate and rearrange themselves into more stable configurations. The reduction of material strength due to dislocation rearrangement and removal causes a hardness decrease which (for not too short times) allows quantification of the progression of recovery in terms of models as the logarithmic dependence elucidated by Kuhlmann [10]

$$HV_{rec} = HV_0^* - C \ln t. \quad (2)$$

Recovery of the present material during the initial hardness decrease (from an effective value HV_0^*) is successfully described using Eq. (2) in the temperature range 1100 °C to 1250 °C (see Fig. 5) leading to a constant value $C/T = 41 \cdot 10^3 (1 \pm 4\%) \text{ Pa K}^{-1}$.

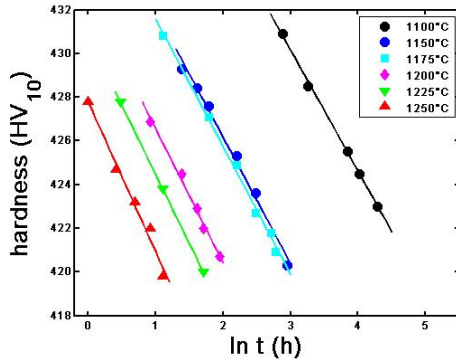


Fig. 5. Semi-logarithmic plot of the Vickers hardness of tungsten warm-rolled to 90% thickness reduction in dependence on annealing time at all studied temperatures.

3.4 Recrystallization

Recrystallization is a thermally activated process by which strain-free regions (nuclei) are generated in the deformed matrix and grow into it. Because these nuclei are dislocation-free and their growth eliminates the dislocation content, the work-hardened matrix is replaced by softer regions and recrystallization can be followed by a change in hardness. The average hardness is related to the fraction of recrystallized regions and recovered matrix according to the rule of mixtures:

$$HV = X HV_{rex} + (1 - X) HV_{rec} \quad (3)$$

with the hardness of the recrystallized regions HV_{rex} and the hardness of the recovered matrix HV_{rec} weighted by their respective volume fractions X and $1-X$. In this manner, the volume fraction X of the recrystallized regions can be determined from the measured hardness HV at any time and the hardness HV_{rec} of the recovered regions extrapolated by Eq. (2) to larger times. The recrystallized fraction can be fitted to classical Johnson-Mehl-Avrami-Kolmogorov recrystallization kinetics [11]

$$X = 1 - \exp\left(-b^n (t - t_{inc})^n\right) \quad (4)$$

where the coefficient b describes thermal activation and the exponent n is related to the nature of nucleation and the dimensionality of nuclei growth [11]. Additionally, a possible incubation time t_{inc} before the onset of recrystallization is taken into account here [13].

By combining the Kuhlmann model for recovery with the Johnson-Mehl-Avrami-Kolmogorov model for recrystallization, the entire annealing kinetics is described successfully for all temperatures as illustrated in Fig. 6 for 1175 °C: the early annealing phase can be described nicely by the recovery model alone (dashed line). A good description (solid line) of the hardness evolution during recrystallization at 1175 °C is achieved as well, when an incubation time of 16.1 h is considered; without considering incubation, Eq. (4) fails to describe the experimental data with a reasonable exponent n , as it overestimates the recrystallized fraction in the early phase of annealing. The obtained exponent n shows only minor deviations from a common average value of 2. Despite theoretical expectations of larger values up to 4, such a low value is typically found in literature, e.g. [14].

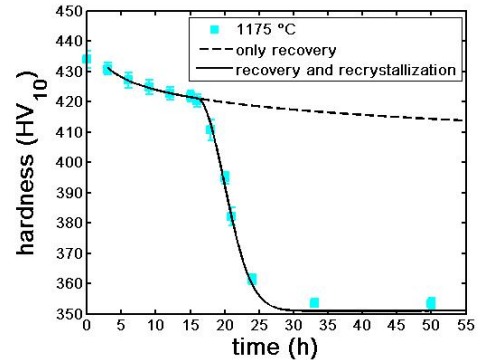


Fig. 6. Evolution of Vickers hardness of tungsten warm-rolled to 90% thickness reduction during annealing at 1175 °C. Experimental values (symbols) versus predictions by solely the recovery model of Eq. (2) (dashed line) and additionally the recrystallization model of Eqs. (3) and (4) (solid line).

The existence of an incubation time is supported by the microstructure of a sample annealed for a shorter period than the obtained incubation time. In Fig. 7 only very few nuclei (forming a recrystallized fraction of 2%) are present after annealing for 15 h at 1175 °C.

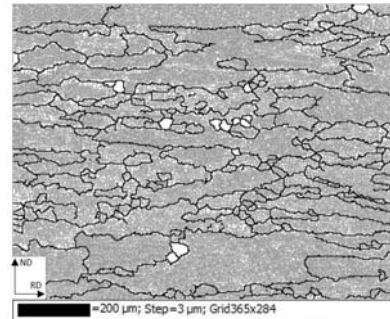


Fig. 7. Boundary map obtained by EBSD with a 3 μm step size covering an area 1095 × 852 μm² on the transversal section of a sample annealed for 15 h at 1175 °C. A few nuclei shown in white are identified (as regions with internal misorientations below 1°, partially surrounded by high angle boundaries and at least 81 μm² large) leading to a recrystallized fraction of 2%.

The activation energy for half recrystallization can be derived from an Arrhenius relationship comparable to Eq. (1) for the time to reach half recrystallization (i.e. $X=0.5$ in Eq. (4)) at each temperature. From Fig. 4, an activation energy of 352 (1±4%) kJ/mol is obtained for half recrystallization, which is slightly lower than the activation energy for half hardness loss (357 kJ/mol).

4. Discussion

For the tungsten plate warm-rolled to a large plastic strain by 90% thickness reduction, the activation energy for half recrystallization of 352 kJ/mol is significantly smaller than the value 579 kJ/mol obtained for half recrystallization in an earlier study [12] on a similar tungsten plate warm-rolled to a moderate plastic strain (by 67% thickness reduction). Such a higher value is in reasonable agreement with the activation energy of bulk self-diffusion 502-628 kJ/mol [15] and other observations in literature obtaining comparably high activation energies for recrystallization: For example, an activation energy of 544 kJ/mol is reported for recrystallization of an extruded rod of high purity tungsten [16], whereas for recrystallization of heavily-drawn wires activation energies of 502 kJ/mol and 573 kJ/mol are found when annealed under vacuum or Argon atmosphere respectively [17]. Lower values (closer to 352 kJ/mol) are less frequently reported; for instance, an activation energy of 396 kJ/mol has been found for grain growth after recrystallization of a similar plate warm-rolled to 75% thickness reduction [18].

Notably, the activation energy for half recrystallization obtained here is in the range of the activation energy of grain boundary diffusion in tungsten 377-460 kJ/mol [15,19]. One reason for the change from the high activation energy of bulk diffusion to the lower activation energy of grain boundary diffusion for the highly deformed material might be the presence of an abundance of low angle boundaries. As seen from Fig. 2, the spacing between low angle boundaries after 90% warm-rolling is only 0.67 μm , whereas after 67% warm-rolling low angle boundaries are still 2.0 μm apart, while their fraction of all boundaries is almost unaltered.

The obtained activation energy allows extrapolating the recrystallization kinetics to lower temperatures. Accordingly, at 900 °C and 800 °C (typical operation temperatures in fusion reactors) half recrystallization would not be achieved before 2.4 (1±24%) years or 71 (1±35%) years, respectively. A much longer lifetime (at least 1 million years) was obtained at 800 °C for the 67% thickness reduction plate [12], clearly demonstrating the accelerating effect that the higher stored energy and change of predominating diffusion mechanism has on the recrystallization kinetics of this highly deformed plate, and therefore on the degradation of the material.

5. Conclusion

The annealing behavior of a highly-deformed warm-rolled pure tungsten plate has been quantified in the temperature range from 1100 °C to 1250 °C. From the

loss in hardness, two characteristic annealing stages (recovery and recrystallization) are identified. The hardness loss during recovery can be nicely fit by the logarithmic time dependence rationalized by Kuhlmann. A proper description of the recrystallization behavior was obtained by the Johnson-Mehl-Avrami-Kolmogorov kinetics considering an incubation time. The obtained activation energy of recrystallization is comparable to the one of grain boundary diffusion, instead of the one of bulk self-diffusion as reported in previous studies for deformed tungsten. It is suggested, that the smaller spacing between low angle boundaries present in highly-deformed material compared to moderately-deformed tungsten [12] could be responsible for this difference in activation energy. Extrapolation of the annealing kinetics to lower temperatures based on the parameters obtained here showed that for 90% warm-rolled tungsten a lifespan of 2 years can only be expected for temperatures up to 900 °C which is too low for a potential use as armor material in a divertor. Hence, tungsten must not be deformed to such large strains, while moderately-deformed tungsten provides excellent thermal stability to ensure a longer lifetime at higher operation temperatures (e.g. 2 years at 1075 °C) [12].

Acknowledgments

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