



Full length article

Crystallite growth in nanocrystalline tungsten; rate determining mechanism and the role of contaminations

Zoltán Hegedűs^{a,*}, Sai Ramudu Meka^{a,1}, Eric J. Mittemeijer^{a,b}^a Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, D-70569 Stuttgart, Germany^b Institute for Materials Science, University of Stuttgart, Germany

ARTICLE INFO

Article history:

Received 23 July 2015

Received in revised form

22 October 2015

Accepted 6 December 2015

Available online 5 January 2016

Keywords:

Nanomaterials

Growth kinetics

Isothermal heat treatment

X-ray diffraction

Tungsten

ABSTRACT

The thermal stability of nanocrystalline tungsten was investigated by tracing the evolution of the microstructure as a function of (isothermal) annealing time at different temperatures (800–875 °C). To this end especially *in situ* X-ray diffraction and transmission electron microscopy methods were applied to ball milled tungsten powder. Initially the dislocation density and the crystallite/domain size decreased and increased rapidly, respectively. Upon prolonged annealing the crystallite growth rate decelerated and even became nil: a saturation crystallite size, increasing with increasing annealing temperature, was attained. Application of all available isothermal growth models to the experimental data resulted in very low values for the activation energy (60–120 kJ/mol) indicating that recovery of the deformed microstructure is the dominantly occurring process, leading to pronounced crystallite/domain growth. The effect on the growth kinetics of different levels of contaminations, which exert a drag force on the moving boundaries, was also investigated.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Nanocrystalline materials (grain size less than 100 nm) exhibit physical and chemical properties generally very different from those of their coarse-grained counterparts [1–12]. The unique properties of nanomaterials originate in particular from the high fraction of grain-boundary/surface atoms in a poorly ordered state and, also, from a high degree of crystal imperfection. Therefore nanocrystalline materials do not represent a state of thermodynamic equilibrium, i.e., they are metastable and thus, in particular, grain growth is possible by thermal activation. Thereby, the unique properties originating from the nanocrystalline nature get lost. Therefore, it is crucial to understand and control the grain growth process of nanocrystalline materials.

General understanding of the nature of grain growth in nanocrystalline materials lacks. Thus, often opposite results have been reported: for example in some studies the onset of grain growth was observed at lower homologous temperatures in nanocrystalline materials than in coarse-grained ones [13,14], whereas in other

studies the nanocrystalline material showed better thermal stability at higher homologous temperatures than the coarse-grained materials [15]. Also, in some studies an incubation period has been observed before the onset of grain growth [16], whereas a rapid initial grain growth has been reported elsewhere [17].

The experimentally determined activation energy of grain growth in coarse-grained polycrystalline metals has often been found to be close to the activation energy of grain-boundary diffusion [18]. The same holds for nanocrystalline metals [19–27] and therefore, the rate controlling mechanism of grain growth in nanocrystalline metals is usually claimed to be grain-boundary diffusion (e.g., for results on nanocrystalline Fe, Cu and Ni see Refs. [23,24], and [25–27], respectively).

Tungsten has been selected as the material for studying the thermal stability of nanocrystallinity against the following scientific background: (i) Grain growth in coarse-grained polycrystalline W has been investigated extensively in the past [28–34]. (ii) As a consequence of its high melting temperature, activation energies for different thermally activated processes, as diffusion and vacancy generation, are distinctly different, hereby favoring a clear identification of rate controlling mechanism(s) for grain/crystallite growth.

Tungsten is an attractive material for heat-shield coatings and as plasma-facing components, due to its high melting temperature,

* Corresponding author.

E-mail addresses: z.hegedus@is.mpg.de, zoltan885@yahoo.com (Z. Hegedűs).¹ Present address: Metallurgical and Materials Engineering Department, Indian Institute of Technology Roorkee, Roorkee 247667, India.

good heat conduction and good high temperature strength [35–37]. However, its relatively high ductile–brittle transition temperature hinders fabrication of components of W at room temperature by conventional plastic deformation processes like rolling, drawing, etc. Therefore, grain refinement, for significant improvement of the ductility of W [38,39], is important, thus emphasizing the *technological* importance of understanding and controlling the thermal stability of the microstructure.

Often a saturation value for the crystallite size is observed upon annealing. This can be ascribed to the presence of impurities hindering boundary migration. This topic has been dealt with controversially in the literature (e.g., see Ref. [18]). Therefore, in this work the effect of deliberately varying the level of oxygen and carbon contamination on growth is investigated as well.

The present project focuses on the evolution of the microstructure of W during ball milling and especially upon subsequent annealing. The microstructure was characterized detailedly by *in situ* and *ex situ* X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM).

In the current paper for presenting and discussing results the term “crystalline/domain growth” instead of “grain growth” is used predominantly. Thereby, it is recognized that a (nano)grain can be composed of a number of crystallites/domains. Diffraction methods, as XRD, via the analysis of diffraction line broadening, allow the determination of “microstrain” and “coherency length” (of diffraction), i.e., the “crystallite/domain size”. Thus changes of the microstructure can be deduced in a much more detailed way as compared to the descriptions based on grain size only [40,41].

2. Kinetic growth models

This paper deals with crystallite/subgrain growth rather than grain growth. The theoretical description of subgrain coarsening is not well developed. This is in particular because of the lack of experimental data. The few available models involve severe simplifications and provide equations mathematically similar to those for conventional grain growth [18,42]. For this reason in the current investigation, (the mathematical descriptions of) models originally developed for conventional grain growth will be adopted to describe subgrain coarsening.

Coarsening is usually attributed to the curvature induced movement of (sub)grain boundaries [18,43]. The driving force for coarsening originates from the excess Gibbs energy of the (sub) grain boundaries. If the boundary is part of a sphere of diameter R , then the release of Gibbs energy upon (sub)grain growth is given by Ref. [43]

$$\Delta G = 2\alpha V\gamma/R, \quad (1)$$

where γ is the boundary energy (assumed to be constant for all boundaries), α is a geometric constant and V is the molar volume. The velocity of a boundary is equal to the product of the released Gibbs energy (driving force) and the mobility (M) of the boundary. Therefore the rate of (sub)grain growth can be given as

$$dR(t)/dt = M\Delta G = 2M\alpha\gamma V/R(t). \quad (2)$$

Eq. (2) after integration yields:

$$R^2(t) - R_0^2 = k_1 t, \quad (3)$$

where $k_1 = 4M\alpha\gamma V$ is usually referred to as growth-rate parameter or rate constant. Eq. (3), describing the time dependence of the average (sub)grain size as a function of annealing time, represents the case of *classical parabolic growth* (with $R_0 = R(t=0)$). The case of so-called *generalized parabolic growth* is represented by:

$$R^n(t) - R_0^n = k_1 t, \quad (4)$$

where n is the growth exponent. Experimental results on coarse-grained materials revealed, that n varied between 2 and 4 [15,44] and in nanocrystalline materials even attained higher values [18,19]. The deviation of the growth exponent from the theoretically predicted value 2 is usually explained by the presence of contaminations, non-uniformity of γ , variations in the original grain size, etc. [18].

Eqs. (3) and (4) each describe growth continuous with time. Experimental results showed that, especially in nanocrystalline materials, growth ceases after attaining a limiting size, which has been attributed to the counteracting pinning forces exerted on moving boundaries by segregated contaminations (which may also change the value of γ) and/or second-phase particles at the grain boundaries.¹ This has led to the introduction of a drag term (b_2) into Eq. (2):

$$dR(t)/dt = 2M\alpha\gamma V/R(t) - b_2, \quad (5)$$

thus

$$k_2 t = \frac{R_0 - R(t)}{R_\infty} + \ln\left(\frac{R_\infty - R_0}{R_\infty - R(t)}\right), \quad (6)$$

where $k_2 = b_2^2/(2M\alpha\gamma V)$ is the rate constant of this model and $R_\infty = 2M\alpha\gamma V/b_2$ is the limiting grain size. This model is referred to as *growth model with impediment* (here GI model).²

Recognizing a possible change of the density of impurities and/or second-phase particles at the boundary during growth, a size dependent drag term ($b_3 R(t)$) was introduced into Eq. (5) [46]:

$$dR(t)/dt = 2M\alpha\gamma V/R(t) - b_3 R(t), \quad (7)$$

and thus

$$R(t) = \left[R_\infty^2 - \left(R_\infty^2 - R_0^2 \right) \exp(-k_3 t) \right]^{1/2}, \quad (8)$$

where $k_3 = 2b_3$ and $R_\infty = \sqrt{2M\alpha\gamma V/b_3}$. This model is called *growth model with size dependent impediment*, (here GSDI model).

For both growth models, involving drag effects (Eqs. (6) and (8)) the rate constants satisfy the following dependence on the absolute temperature (T), R_∞ and the involved activation energy (Q):

$$Tk_{2,3}R_\infty^2 \propto \exp\left(-\frac{Q_{2,3}}{k_B T}\right), \quad (9)$$

where k_B is the Boltzmann constant. The dependence of the left-hand side of Eq. (9) on the temperature derives from the temperature dependence of the boundary mobility. The activation energy of grain growth can thus be determined from the slope of the plot of $\ln(Tk_{2,3}R_\infty^2)$ versus T^{-1} (assuming that the boundary energy, γ , is temperature independent). It should be noted, that the temperature dependence of $k_{2,3}$ is only marginally influenced by the additional temperature term on the left-hand side of Eq. (9); it is governed by the temperature dependence of the exponential at the right-hand side of Eq. (9).

Grain boundaries in nanocrystalline materials may possess a

¹ Recent mesoscale simulations showed, that grain-boundary smoothing may provide an alternative grain growth stagnation mechanism even in the most pure materials [45].

² Eq. (5) has no explicit analytical solution for $R(t)$. Therefore this model is usually applied in the implicit form of Eq. (6).

Download English Version:

<https://daneshyari.com/en/article/7879040>

Download Persian Version:

<https://daneshyari.com/article/7879040>

[Daneshyari.com](https://daneshyari.com)