Materials Letters 65 (2011) 712–715

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Size dependency of self-diffusion and creep behavior of nanostructured metals

B. Arab [a], S. Sanjabi [b,*], A. Shokuhfar [a]

[a] Advanced Materials and Nanotechnology Research Lab, Faculty of Mechanical Engineering, K.N. Toosi University of Technology, P.O. Box: 19395-1999, Tehran, Iran
[b] Nanomaterials Group, Department of Materials Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran

ARTICLE INFO

Article history:
Received 14 July 2010
Accepted 24 November 2010
Available online 28 November 2010

Keywords:
Nanostructured materials
Diffusion creep
Size effect
Nanomaterials
Mechanical property

ABSTRACT

Grain boundary and *bulk* diffusion are two main governing processes of creep deformation in materials. Since the diffusion activation energy for nanostructured materials is lower than that for bulk, the diffusion is enhanced at the nano-scale, and nanosructured materials are expected to creep at lower temperatures and stresses. In this paper, a model has been developed to explain the effect of grain size on diffusion and creep behavior of nanostructures. Diffusion and creep phenomena have been shown to depend significantly upon size. Comparisons have been made with reported experimental results and related theoretical studies.

1. Introduction

The current scientific and technological interest in nanomaterials comes from the fact that material at the nano-scale behaves differently from that in the macroscopic world due to size, shape and quantum effects [1]. Creep of materials is classically associated with time-dependent plasticity under a fixed stress, often at an elevated temperature (e.g. greater than $0.5T_m$, where T_m is the absolute melting temperature) [2]. Creep deformation occurs principally through diffusion and dislocation motion, and the relative contributions of these processes can be different depending on temperature, stress and time-scale. Some theoretical and experimental studies have been performed recently to investigate the diffusion and creep behavior of nano-scale systems, e.g. [1,3–6]. However, the lack of a universal model for size-dependent diffusion and creep deformation in nanostructured materials, considering both grain boundary (*gb*) and bulk diffusion, motivated the current authors to develop such a comprehensive model. In this study, we develop size-dependent models of bulk and *gb* diffusion, and then modify the Nabarro–Herring and Coble relations of creep deformation to investigate the size-dependent parameters that affect the creep strain rate in nanostructures.

2. Modelling

2.1. Size-dependent self-diffusion

Diffusion in crystalline solids is mediated by different structural defects such as vacancies, interstitials, dislocations, grain boundaries, and so on. Here, we concentrate on vacancy diffusion within grains and along grain boundaries, which causes bulk and *gb* self-diffusion respectively.

Diffusion is a thermally-activated process, and can be written in the form of an Arrhenius equation,

$$D = D^0\, exp\left(-\frac{\Delta H}{RT}\right) \tag{1}$$

where D is the diffusion coefficient, ΔH is the activation enthalpy of diffusion, R is the gas constant and T is absolute temperature. D^0 is a pre-exponential or frequency factor. Physically, D^0 is almost constant because it depends on the atomic vibration frequency, ν, the lattice parameter, a, the entropy of diffusion, ΔS, and a geometric constant, ϕ. For solids with the same crystal structure and bond type, and with not too dissimilar atomic mass (which influences ν), ϕ, a, ν and ΔS are all about equal [7]. Hence D^0 is considered to be independent of the size and temperature.

Grain boundary diffusion and bulk diffusion have their own activation enthalpies and frequency factors, and consequently their diffusion coefficients will be different, with the following forms,

$$D_{gb} = D^0_{gb}\, exp\left(-\frac{\Delta H_{gb}}{RT}\right) \tag{2}$$

$$D_L = D^0_L\, exp\left(-\frac{\Delta H_L}{RT}\right) \tag{3}$$

Indices *gb* and *L* correspond to *grain boundary* and *lattice* (*bulk*) terms respectively. Experimental data, and also theoretical analyses, have revealed linear relations between activation enthalpy of self-

---

* Corresponding author. Tel./fax: +98 21 82883325.
E-mail address: sanjabi@modares.ac.ir (S. Sanjabi).

0167-577X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2010.11.060

diffusion in metals and their melting temperatures. The relations can be written as $\Delta H_{gb} \approx \alpha_1 T_m$ and $\Delta H_L \approx \alpha_2 T_m$, where, α_1 and α_2 are constants for any given classes of solids and diffusion processes. Values of α_1 and α_2 can be found in the literature [8–11].

To show the size dependency of melting temperature in nano-scale, we rewrite these linear relations in the form of $\Delta H_{gb} \approx \alpha_1 T_{m,d}$ and $\Delta H_L \approx \alpha_2 T_{m,d}$, where $T_{m,d}$ is the size-dependent melting temperature. Substitution into Eqs. (2) and (3) gives,

$$D_{gb} = D^0_{gb}\ exp\left(-\frac{\alpha_1 T_{m,d}}{RT}\right) \tag{4}$$

$$D_L = D^0_L\ exp\left(-\frac{\alpha_2 T_{m,d}}{RT}\right) \tag{5}$$

In the case of nanostructures, the size-dependent melting temperature takes the general form, [12],

$$T_{m,d} = \left(-1\frac{\beta}{d}\right)T_{m,0} \tag{6}$$

where β is a materials-dependent constant and d is the average size of grains. Values of β for different metals are reported in [12]. If $T_{m,0}$ represents *bulk* melting temperature, then substitution of Eq. (6) into Eqs. (4) and (5), gives the size-dependent *gb* and lattice self-diffusion:

$$D_{gb} = D^0_{gb}\ exp\left[\frac{\alpha_1 T_{m,0}\left(\frac{\beta}{d}-1\right)}{RT}\right] \tag{7}$$

$$D_L = D^0_L exp\left[\frac{\alpha_2 T_{m,0}\left(\frac{\beta}{d}-1\right)}{RT}\right] \tag{8}$$

Eqs. (7) and (8) will be used in the next section to model the creep behavior of nanostructured metals.

2.2. Size-dependent diffusion creep

Diffusion creep is very likely to occur in bulk materials at moderate and high temperatures [8]. However, in the case of nanostructured materials, analysis of the deformation processes suggests that diffusion creep is important at intermediate and low temperatures [3]. On the basis of creep deformation maps, diffusion creep is correlated with low stresses ($\sigma/G < 10^{-4}$ [13,14], where σ is the applied stress and G is the shear modulus). *Grain boundary* (*gb*) and *bulk (lattice)* diffusion lead to so-called *Coble creep* and *Nabarro–Herring creep* respectively [14]. The corresponding strain rates can be written as [15–17],

$$\dot{\varepsilon}_c = A_c \frac{D_{gb}\delta\sigma\Omega}{d^3 k_B T} \tag{9}$$

$$\dot{\varepsilon}_{NH} = A_{NH}\frac{D_L\sigma\Omega}{d^2 k_B T} \tag{10}$$

where, $\dot{\varepsilon}_{NH}$ and $\dot{\varepsilon}_c$ represent Nabarro–Herring and Coble creep strain rates respectively, A_{NH} and A_C are numerical factors depending on the grain shape and boundary conditions, and are equal to 10–40 and 30–50 respectively [14,15,17]. D_L and D_{gb} are the bulk and *gb* diffusion coefficients respectively, σ is imposed stress, Ω is atomic volume, and k_B is the Boltzmann constant. These two relations reveal that Nabarro–Herring creep, caused by bulk diffusion, directly depends on d^{-2}, while Coble creep, caused by *gb* diffusion, is a function of d^{-3}. This shows that a reduction of grain size leads to a considerable increase in creep strain rate. Furthermore, it is obvious that Coble creep deformation is more sensitive to size variation. Another point here is that both creep strain rates have a linear-dependence on the applied stress. Using Eqs. (7–10), expressions for size-dependent creep strain rates can be derived,

$$\dot{\varepsilon}_c = \frac{A_c\delta\sigma\Omega D^0_{gb}}{d^3 k_B T}\ exp\left[\frac{\alpha_1 T_{m,0}\left(\frac{\beta}{d}-1\right)}{RT}\right] \tag{11}$$

$$\dot{\varepsilon}_{NH} = \frac{A_{NH}\sigma\Omega D^0_L}{d^2 k_B T}\ exp\left[\frac{\alpha_2 T_{m,0}\left(\frac{\beta}{d}-1\right)}{RT}\right] \tag{12}$$

Values of δD^0_{gb} and D^0_L for different lattice structures (bcc, fcc and hcp) are reported in [9–11,18]. Using these relations, the individual effect of each parameter (stress, temperature, and particularly, grain size) on the creep strain rate can be investigated.

The total creep strain rate is the sum of these two components,

$$\dot{\varepsilon}_{total} = \frac{\sigma\Omega}{d^2 k_B T}\left\{A_c D^0_{gb}\frac{\delta}{d}\ exp\left[\frac{\alpha_1 T_{m,0}\left(\frac{\beta}{d}-1\right)}{RT}\right] + A_{NH}D^0_L\ exp\left[\frac{\alpha_2 T_{m,0}\left(\frac{\beta}{d}-1\right)}{RT}\right]\right\} \tag{13}$$

3. Results and discussion

Results of modelled diffusion in current study are consistent with results reported by Guisbiers et al. [1]. Fig. 1 illustrates the variation of $\ln(D_L/D_0)$ vs. grain size for nanostructured copper based on Eq. (8) with a temperature equal to 300 K. As can be realized, plots show an upward trend by decreasing the size, and at very small values of d (~15 nm), diffusion coefficient steeply rises.

The strain rate for diffusion creep (based on both *gb* and bulk diffusion) attained from Eq. (13) is compared to atomistic simulations performed by P.C. Millett et al. [4], for the case of nanocrystalline molybdenum with bcc structure. Four grain sizes (8, 12, 16 and

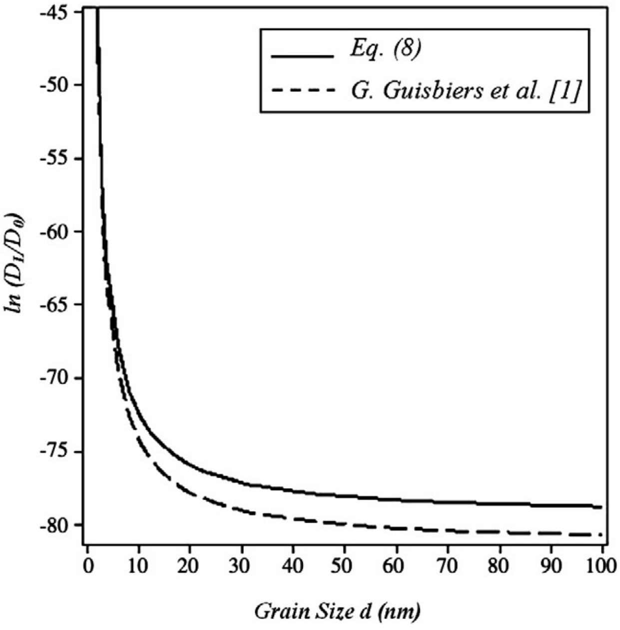

Fig. 1. Plots of $\ln(D_L/D_0)$ vs. grain size for nanocrysralline Cu at $T = 300$ K.