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Scripta Materialia 50 (2004) 993–997
Scripta MATERIALIA
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Diffusion controlled creep in nanocrystalline materials under grain growth

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Received 23 October 2003; received in revised form 23 December 2003; accepted 5 January 2004

Abstract

We consider diffusion controlled creep in nanostructured materials under the conditions when grain growth occurs concurrently. The Nabarro–Herring and Coble mechanisms are re-visited to calculate the effect of attendant vacancy generation on creep. Strain rate variation that resembles primary and secondary creep behaviour is predicted.

Keywords: Grain growth; Vacancy generation; Diffusion creep; Nabarro–Herring creep; Coble creep

1. Introduction

With the current drive for developing nanocrystalline (nc) materials for structural applications, it is remarkable that such important aspect of the mechanical response of nc materials as creep behaviour has hardly been studied. The obvious reason is a limited availability of bulk nanostructured materials required to produce creep specimens. In a paper by Markmann et al. that just appeared in a Viewpoint Set on mechanical properties of fully dense nanocrystalline materials in this Journal [1], miniaturised testing equipment was used to circumvent this difficulty. The authors report that creep of Pd with the average grain size of about 10 nm at 313 K is consistent with the Coble mechanism—in keeping with a general expectation that creep deformation of nc materials is diffusion controlled, especially at elevated temperatures. As the grain structure may be coarsening concurrently with creep deformation (which was apparently not the case in the experiment mentioned [1]), it is of interest to explore possible effects of grain growth on creep behaviour. An obvious direct effect is a deceleration of creep, as the creep rate is inversely proportional to the second or the third power of the grain size. However, there is another mechanism that acts against this trend. As was shown recently [2–4], vacancy generation due to the consumption of the total excess volume of grain boundaries, which is an integral part of the grain growth process, leads to retardation of grain growth. The effect is particularly pronounced for small grain size in the nanometer range, where the vacancy supersaturation produced inhibits grain growth. This will obviously reduce the deceleration of creep due to grain growth. Moreover, vacancy supersaturation associated with grain growth induced vacancies will act to further enhance the creep rate. In the initial stage of creep, this latter effect will be predominant, so that an overall enhancement of creep is expected. However, as will be shown below, the creep rate continuously decreases and approaches a level below the conventional Nabarro–Herring or Coble creep rate in the absence of grain growth. The aim of this communication is an investigation of the role of grain growth induced vacancy generation and a quantitative prediction of the creep behaviour of nc materials under grain growth.

2. Vacancy generation during grain growth

The approach taken in Refs. [2–4] is based on the concept that the excess free volume in the grain

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doi:10.1016/j.scriptamat.2004.01.002

boundaries is released into the bulk when the total grain boundary area is reduced during grain growth. The assumption made is that the excess free volume is released in the form of individual vacancies. It is corroborated by molecular dynamic simulations [5] in which injection of vacancies into the bulk in the wake of a shrinking grain boundary was observed. Quantitatively, the amount of vacancy supersaturation and the concomitant grain size variation can be described by a set of coupled differential equations: one expressing the balance of energy associated with an increment dR of average grain size R:

$$-\frac{d}{\mathrm{d}R}\left(\frac{3\gamma}{2R}\right)\mathrm{d}R = \frac{3}{2}\cdot\frac{1}{R}\frac{(\mathrm{d}R/\mathrm{d}t)^2}{m}\mathrm{d}t + \frac{NkT}{c^{\mathrm{eq}}}(c - c^{\mathrm{eq}})\frac{6\beta\delta}{R^2}\mathrm{d}R \tag{1}$$

and the other accounting for the evolution of the average vacancy concentration c in the bulk:

$$\dot{c} = \frac{6\beta\delta}{R^2}\cdot\frac{\mathrm{d}R}{\mathrm{d}t} - \frac{D_{\mathrm{v}}}{d^2}(c - c^{\mathrm{eq}}) \tag{2}$$

Here γ, δ, β, and m are grain boundary characteristics: surface tension, thickness, relative excess free volume (relative density difference between the bulk and the grain boundary material) and mobility, respectively. The quantities N, k, T, D_{v} and c^{eq} denote the number of atoms per unit volume, the Boltzmann constant, the absolute temperature, the vacancy diffusivity and the thermal equilibrium vacancy concentration, respectively. Finally, d stands for the characteristic vacancy sink spacing. Eq. (1) describes how the energy release associated with the reduction of the grain boundary area [LHS of Eq. (1)] is distributed between the dissipation due to the drag forces [first term in the RHS of Eq. (1)] and the vacancy sub-system [second term in the RHS of Eq. (1)]. The variation of the vacancy concentration is described by Eq. (2).

For the case of nanostructured materials of interest here, it is natural to assume that, at least initially, no vacancy sinks of the dislocation type are available in the bulk of a grain. The sink spacing d in Eq. (2) is thus to be identified with the average grain size R. This implies that vacancies generated at grain boundaries are also absorbed by grain boundaries (and further transported to a free surface via grain boundary diffusion). The main concept of the approach [2–4], *viz.* inhibition of grain growth due to vacancy generation, is still valid in this case. Indeed, an increase in the local vacancy concentration in a boundary on the way of vacancies to the free surface leads—as a result of equilibrium between the grain boundary and the adjacent bulk—to an increase of vacancy concentration in the grain interior.

The set of Eqs. (1) and (2) was solved both for the case when vacancies are annihilated at sinks within the bulk of the grain ($d < R$) and for the aforementioned case when $d = R$ [4]. For the latter case, which is of main interest here, *linear* grain growth controlled by the self-diffusion coefficient (and not by the grain boundary mobility!) was predicted:

$$R = R_0 + \frac{1}{24}\cdot\frac{\gamma D_{\mathrm{v}} c^{\mathrm{eq}}}{NkT(\beta\delta)^2}t \tag{3}$$

where t denotes the time and R_0 is the initial grain radius. This type of grain growth kinetics was, indeed, observed experimentally [6]. During linear grain growth the average vacancy concentration in the bulk is maintained at a nearly constant level above the equilibrium one. One can expect that all processes involving vacancies, such as diffusion, void formation and, notably, diffusional creep should be accelerated in this regime due to the presence of excess vacancies. A steady-state vacancy concentration maintained over the linear growth stage can be estimated from Eq. (2) (where d is now replaced with R) by setting the rate of the concentration variation, $\dot{c}$, to zero and substituting for dR/dt an expression following from Eq. (3). The resulting vacancy concentration reads

$$c = \lambda c^{\mathrm{eq}} \tag{4}$$

where

$$\lambda = \left[1 + \frac{\gamma}{4NkT(\beta\delta)}\right] \tag{5}$$

At first glance, an inverse dependence of the effect on the 'vacancy efficiency' of grain boundaries represented by the product $\beta\delta$ may appear strange. However, the level of vacancy supersaturation is a result of interplay between the number of vacancies injected in the bulk due to the shrinkage of the total volume of the boundaries and the rate of this shrinkage. While the first quantity is proportional to $\beta\delta$, the latter is inversely proportional to the *square* of $\beta\delta$, as seen from Eq. (3).

To get a feel for the magnitude of the concentration enhancement factor λ, we consider the case of Al at $T = 423$ K. With $\gamma = 1$ J/m, $N = 6\cdot 10^{28}$ m^{-3}, $\beta = 0.02$ [2–4] and $\delta = 1$ nm, an increase of the vacancy concentration by a factor of $\lambda \cong 36$ is obtained.

Linear (or nearly linear) grain growth will continue until vacancy sinks other than the grain boundaries will emerge. In an initially dislocation-free nanocrystalline material this can only happen when dislocation sources in grain boundaries will become operative. The corresponding grain size can be estimated roughly as $R_{\mathrm{c}} \cong (G/\sigma)b$, where G is the shear modulus, σ the applied stress and b the magnitude of the dislocation Burgers vector. For values of stress typical of a creep test (i.e. several MPa), R_{c} lies in the micrometer range. When R outgrows R_{c}, i.e. after a time

$$t_c = \frac{R_c}{\dot{R}} = 24\frac{NkT(\beta\delta)^2 R_c}{\gamma D_v c^{eq}} = 24\frac{NkT(\beta\delta)^2 R_c}{\gamma D_{SD}} \qquad (6)$$

where D_{SD} is the coefficient of self-diffusion in the bulk of a grain, linear grain growth will gradually revert to conventional parabolic growth and the vacancy concentration c will asymptotically approach its thermal equilibrium value. (Here $\dot{R}$ determined by Eq. (3) was substituted.) This transition occurs with a characteristic relaxation time ('incubation time' in terms of Ref. [4]) that has the same order of magnitude as t_c [4]. In other words, the grain growth vacancy enrichment effectively persists over a time of the order of $2t_c$. For the conditions and parameter values given above, an estimation of $2t_c$ yields a value of about 3 h.

3. Diffusional creep under grain growth

As follows from the considerations in the previous section, in the case of in situ grain growth the expressions for Nabarro–Herring or Coble creep need to be modified. However, if a standard textbook treatment of diffusional creep was applied, no effect of this enhancement of the vacancy concentration would follow. We therefore deem it necessary to revisit the Nabarro–Herring model [7,8] in order to establish a rigorous framework for the treatment of the problem. It is customary to attribute diffusional creep to the non uniform vacancy concentration in an inhomogeneously stressed solid. In this case the diffusion flux is determined by the gradient of the vacancy concentration, and an overall increase of the vacancy concentration, as with grain growth induced vacancies, would not affect the creep rate. This concept is physically wrong, though, because the vacancies in an inhomogeneously stressed solid are in thermodynamic equilibrium and therefore, their chemical potential is zero everywhere, even though their concentration is non uniform. As Herring [8] pointed out correctly, it is the inhomogeneous chemical potential distribution of the *atoms* that gives rise to a diffusion flux in diffusional creep. In the presence of a stress σ the chemical potential of an atom is changed by an amount $\sigma\Omega$. A uniaxial stress causes a chemical potential gradient of order $\sigma\Omega/R$ on a grain scale, which gives rise to a diffusion flux and, hence, diffusion creep. The overall vacancy concentration does affect the creep rate, since the atomic mobility is proportional to the total local vacancy concentration.

The atom flux across a grain is then given by

$$j = \frac{D}{kT} N \cdot \frac{\Omega\sigma}{R} \qquad (7)$$

where D denotes the bulk diffusivity of atoms. For the vacancy mechanism of bulk diffusion, it can be written as

$$D = D_v c \qquad (8)$$

The plastic strain rate associated with the grain shape variation is then given by

$$\dot{\varepsilon}_{NH} = A\frac{j\Omega}{R} = A\frac{\Omega\sigma}{kT}\frac{1}{R^2} D_v c \qquad (9)$$

Here A is a numerical coefficient; use was made of the relation $N\Omega = 1$ that holds for a pure material. In a similar way, an expression for the plastic strain rate can be obtained for the case when creep is controlled by diffusional mass transfer via grain boundaries (Coble creep [9]) assuming a vacancy mechanism of grain boundary diffusion:

$$\dot{\varepsilon}_{Coble} = A\pi\frac{\Omega\sigma}{kT}\frac{\delta}{R^3} D_v^{GB} c^{GB} \qquad (10)$$

Here D^{GB} is the vacancy diffusivity and $c^{GB} = Bc = c^{GB} = Bc = \lambda B c^{eq}$ is the vacancy concentration in grain boundaries, B denoting the grain boundary adsorption (segregation) coefficient. (An interesting modification of the diffusion controlled creep, in which the $1/R^2$ dependence is combined with the *grain boundary* diffusivity, was recently discussed in Refs. [10,11].)

If no grain growth induced vacancy generation is considered, the sole effect of grain growth on creep will be through an increase of R in the expressions for the creep rate, Eqs. (9) and (10), according to the *parabolic* growth law

$$R^2 = R_0^2 + 4\gamma m t \qquad (11)$$

For example, for the Nabarro–Herring creep, the modified creep rate $\dot{\varepsilon}^*_{NH}$ will assume the form

$$\dot{\varepsilon}^*_{NH} = \dot{\varepsilon}^{Ref}_{NH}/(1 + t/t^*_{parabolic}) \qquad (12)$$

where

$$\dot{\varepsilon}^{Ref}_{NH} = A\frac{\Omega\sigma}{kT}\frac{1}{R_0^2} D_v c^{eq} \qquad (13)$$

is the classical Nabarro–Herring creep rate for a constant grain radius R_0 and

$$t^*_{parabolic} = \frac{R_0^2}{4\gamma m} \qquad (14)$$

is a characteristic time. However, in the case when vacancy supersaturation due to grain growth, with $c = \lambda c^{eq}$, prevails, creep will be affected in two ways. First, the growth rate will be reduced [2–4], the grain size being represented by a linear time law, Eq. (3). Second, the *actual*, i.e. increased, vacancy concentration in the grain interior has to be substituted for c in the expressions for the creep rate. The modified creep rate for the Nabarro–Herring mechanism is then given by

$$\dot{\varepsilon}^{**}_{NH} = \dot{\varepsilon}^{Ref}_{NH} \cdot \frac{\lambda}{(1 + t/t^{**}_{linear})^2} \qquad (15)$$

where

$$t^{**}_{\text{linear}} = \frac{24NkT(\beta\delta)^2 R_0}{\gamma D_{\text{v}} c^{\text{eq}}} = \frac{24NkT(\beta\delta)^2 R_0}{\gamma D_{\text{SD}}} \tag{16}$$

For the parameters values given above and for $R_0 = 10$ nm this time can be estimated as $t^{**}_{\text{linear}} \cong 60$ s. (Of course, this estimate is very sensitive to temperature. For instance, for $T = 373$ K this time will be about 3.6 h.)

Similar considerations can be applied to Coble creep. If thermodynamic equilibrium between the grain interior and the grain boundaries is assumed to be reached quasi-instantaneously (i.e. within the time much smaller than the characteristic times t_{c} and t^{**}_{linear}), the actual vacancy concentration in the grain boundaries, c^{GB}, will be enhanced, as compared to the thermal equilibrium value, by the same factor of λ. This leads to an increased rate of Coble creep:

$$\dot{\varepsilon}^{**}_{\text{Coble}} = \dot{\varepsilon}^{\text{Ref}}_{\text{Coble}} \cdot \frac{\lambda}{(1 + t/t^{**}_{\text{linear}})^3} \tag{17}$$

with

$$\dot{\varepsilon}^{\text{Ref}}_{\text{Coble}} = A\pi \frac{\Omega\sigma}{kT} \frac{\delta}{R_0^3} D_{\text{v}}^{\text{GB}} B c^{\text{eq}} \tag{18}$$

The initial enhancement of the creep rate over the conventional (reference) creep rate can be quite significant. Indeed, as seen from Eqs. (15) and (17), it is given by the factor λ that was shown to be large (about 36 in the example considered in the previous section). Over the time of the order of $\lambda^{1/2} t^{**}_{\text{linear}}$ for the Nabarro–Herring mechanism and $\lambda^{1/3} t^{**}_{\text{linear}}$ for the Coble mechanism the initial creep rate will drop to the level of the reference creep rate, i.e. the creep rate that would be recorded in the absence of grain growth. (For the aforementioned values of parameters, it follows $\lambda^{1/2} t^{**}_{\text{linear}} \cong 360$ s and $\lambda^{1/3} t^{**}_{\text{linear}} \cong 200$ s. This corresponds to the grain sizes of 35 and 24 nm, respectively.) With further passage of time, the creep rate will continuously decrease, and at $t = t_{\text{c}}$ it will be very low as compared to that in the absence of grain growth. At that point in time, the factors modifying the conventional Nabarro–Herring and the Coble creep rates will read $\lambda/[1 + (R_{\text{c}}/R_0)^2] \cong \lambda \cdot \lambda/[1 + (R_{\text{c}}/R_0)^2] \cong \lambda \cdot (R_0/R_{\text{c}})^2$ and $\lambda/[1 + (R_{\text{c}}/R_0)^3] \cong \lambda \cdot (R_0/R_{\text{c}})^3$, respectively. An estimate of these factors yields 10^{-3} and 10^{-5}. For $R > R_{\text{c}}$, beyond the incubation regime, grain growth will slow down further, and for sufficiently large time, $t \gg 2t_{\text{c}}$, the decrease of the creep rate will be only very moderate, in accordance with the conventional, parabolic law. After a time of the order of $R_{\text{c}}^2/(4\gamma m)$, the creep rate will stay practically constant. In this sense, the scenario described mimics a pseudo primary and pseudo steady-state creep. The pseudo steady-state creep rate for the Nabarro–Herring and the Coble mechanisms is given respectively by Eqs. (13) and (18), in which R_0 is replaced with R_{c}.

4. Conclusion

The above considerations show that grain growth induced vacancy effects have a strong influence on diffusion controlled creep of nanocrystalline materials. The obvious decrease of the Nabarro–Herring and Coble creep rate due to the usual increase in grain size is partly compensated by inhibition of grain growth owing to vacancy generation. Moreover, the attendant vacancy supersaturation gives rise to a further creep enhancement. The overall effect can be described as follows. At first, the creep rate is increased over that in the absence of grain growth by a large factor λ. Creep enhancement is sustained over a time of the order of $\lambda^{1/2} t^{**}_{\text{linear}}$ and $\lambda^{1/3} t^{**}_{\text{linear}}$ for the Nabarro–Herring and the Coble creep, respectively, but the enhancement factor gradually decreases over this time. Beyond this period the creep rate will be dropping further, and at each moment it will be lower than in the absence of grain growth. However, it will be higher than what a conventional parabolic grain growth law would predict. Finally, after a time of the order of $2t_{\text{c}}$, grain growth induced vacancy effect will no longer be operative, and parabolic growth will set in. With further slowing down of the creep rate, pseudo steady-state creep, with the strain rate given by the conventional equations for the Nabarro–Herring and Coble creep (albeit with the grain size of the order of R_{c} instead of R_0) is recovered. This behaviour resembles a transition from primary to secondary creep—a fact that has not been discussed previously in the context of diffusion controlled creep.

We would like to stress that the commonly accepted approach to diffusional creep based on a vacancy concentration gradient would not have captured the effect discussed, as grain growth induced vacancy generation increases the global vacancy concentration but does not give rise to additional concentration gradients. The correct approach of Herring based on the understanding that the diffusion creep mechanism is caused by a gradient of the *chemical potential of atoms* had to be utilized instead.

We hope that the predictions made in this communication will stimulate experimental work on diffusion controlled creep under the conditions of concurrent grain growth.

Acknowledgements

Financial support from NATO through grant PST.CLG.977968 is gratefully acknowledged.

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