

On the enhancement of diffusion kinetics in nanocrystalline materials

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Abstract

It is well known that volume diffusivity in nanocrystalline materials is orders of magnitude greater than that in coarse grained materials of identical chemistry. The present study offers a theoretical explanation of this enhancement by attempting to correlate the diffusivity with the excess free volume of the grain boundary atoms in the nanocrystalline materials. Assuming a simplified geometry of the nanocrystalline aggregate, the excess free volume of the grain boundary atoms has been expressed as a function of grain size. Applying the concept of isothermal equation of state, it is shown that the effect of negative hydrostatic pressure on the diffusion kinetics in nanocrystalline materials at a given temperature is equivalent to the same obtained for coarse grained materials at an effective elevated temperature. The predicted results have been compared with the earlier published relevant experimental data from several Cu-based systems. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nanocrystals are ultrafine grained (<15–20 nm) materials with nearly up to equal proportion of atoms constituting the crystalline (grain body) and inter-crystalline (grain boundary) regions [1–3]. Experimental results based on positron annihilation spectroscopy indicate that grain boundaries in nanocrystalline materials are characterized by a relative lack of periodicity (compared to that in the grain bodies) and an excess free volume (ΔV_F) [4]. In the past, several novel properties of nanocrystals like enhanced catalysis, ductility and diffusivity have been attributed to the contribution of ΔV_F [5]. On the other hand, a number of investigations claim that the grain boundary structure in nanocrystals is no different than that of the coarse-grained polycrystals [6,7]. Recently, Pabi et al. [8] have demonstrated that the diffusion kinetics accompanying mechanical alloying in a high energy planetary ball mill, leading to the formation of nanocrystals, are best simulated assuming a volume diffusion controlled process occurring at an effective elevated temperature that could be scaled with the melting/liquidus temperature.

Subsequently, Das et al. [9] have arrived at an identical conclusion in analyzing the mechanical alloying kinetics of Cu–Al alloys. Earlier, it was predicted that the decrease in

the activation energy of diffusion during mechanical alloying due to the generation of a large population of crystal defects could be equivalent to an increase in the effective temperature of diffusion [10]. It may be noted that several studies have reported an expansion in lattice parameter/volume due to nanocrystallization [11,12]. Conceptually, this lattice expansion due to reduction in grain size is analogous to the same owing to the thermal effect. Mori and Yasuda [13] have shown that a solute film deposited on nanocrystals with less than a critical grain size (typically, 6 nm) undergoes rapid dissolution at room temperature. The absence of such a dissolution with coarse particles clearly suggests that lattice expansion/softening in nanocrystals may activate a defect aided mass transport process equivalent to diffusion at an effective elevated temperature.

Recently, we have highlighted the role of excess free volume and negative hydrostatic pressure at grain boundaries to account for a metastable bodycentered cubic (bcc) → facecentered cubic (fcc) allotropic change in nanocrystalline niobium [14] and inverse Hall–Petch behavior of nanocrystals [15] through theoretical analyses based on the isothermal equation of state for metals [16]. The mathematical analysis carried out in the present study is essentially an attempt of extending the earlier proposed equation of state for metals by Rose et al. [16] to explain an experimentally observed characteristics of nanocrystals, namely the temperature equivalence of the enhanced rate of mass transport.

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In order to do this, an attempt has been made to determine the variation of ΔV_F as a function of grain diameter (d_c). Subsequently, the negative hydrostatic pressure ($-P_h$) has been determined as a function of ΔV_F by using the equation of state for metals. Finally, the variation of the effective elevated temperature (T_e), expressed as T_e/T_m (where T_m is the melting temperature of the chosen metal), is determined as a function of $-P_h$ or in turn ΔV_F (or d_c). The theoretical predictions are compared with the relevant experimental results reported by us in the past [8,9].

2. Theoretical formulation

In order to compare the mechanism of diffusion along the grain boundary with that in the grain body, Aaron and Bolling [17] suggested that the atomic transport through a grain boundary enjoys one less degree of constraint than that in the interior of the crystal. Recently, a modeling study on the boundary structure of nanocrystalline Fe, based on the calculation of the diffused background intensity in the X-ray diffraction pattern, has demonstrated that each atom in the outer three atomic layers of a crystallite could be randomly displaced from its regular atomic site to the maximum extent of 50% of the nearest neighbor distance [18]. Subsequently, it is suggested that the atomic structure of grain boundaries virtually exhibits a complete lack of long range structural periodicity parallel to the interface [19]. Such a description of the grain boundary indicates that atoms could be marginally displaced from their regular sites along the plane parallel to the interface rather than that in a direction perpendicular to it, and thereby, gives rise to an excess volume per atom (ΔV_F) in the grain boundary plane.

Therefore, the dimensionless measure of ΔV_F may be conveniently approximated as the fractional excess surface area in the core of the grain boundary. Such a hypothesis may allow one to express ΔV_F as a function of the grain

diameter (d_c) which is an experimentally measurable quantity. To obtain such a correlation, the geometry of a grain may be approximated as a sphere of maximum diameter d_c inscribed in the tetrakaidecahedron geometry of a given crystallite (Fig. 1). In order to obtain the average value of ΔV_F of an atom in the grain boundary, the same may be considered to be located at the mean position (broken lines in Fig. 1) of the interfacial region shared by an individual grain (thick lines in Fig. 1). Therefore, ΔV_F may now be conceived as the fractional excess surface area of the grain boundary plane located at a distance of $(d_c + \Delta/2)/2$ from the center of a grain, where Δ (=1 nm) is the thickness of the interfacial boundary assumed to be independent of d_c . Therefore, the dimensionless value of ΔV_F for unit thickness may be expressed as [14,15]

$$\Delta V_F = \frac{(d_c + \Delta/2)^2 - d_c^2}{d_c^2} \quad (1)$$

Taking ΔV_F of the grain boundary atoms into account, the isothermal equation of state for a grain boundary, as stated by Fecht [5], is

$$P_h = -\frac{3B_0 [(V/V_0)^{1/3} - 1]}{(V/V_0)^{2/3}} \exp(-a^*) \times (1 - 0.15a^* + 0.05(a^*)^2) \quad (2)$$

where P_h is the excess negative hydrostatic pressure, B_0 the equilibrium bulk modulus, V_0 the equilibrium volume of the atom with equilibrium Wigner–Seitz cell radius (r_{WSE}) and V is the volume of an atom having the real Wigner–Seitz cell radius (r_{WS}) such that $\Delta V_F = (V - V_0)/V_0$. a^* is given by

$$a^* = \frac{r_{WS} - r_{WSE}}{l} \quad (3)$$

where l is the length scale characteristic of a material [16]. Such a description requires B_0 , V_0 and a^* (or l) as the input

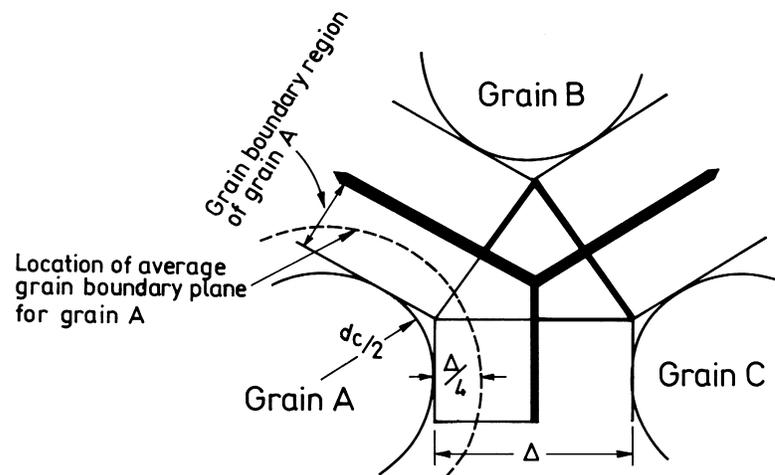


Fig. 1. Schematic representation of three adjoining tetrakaidecahedron (along the polyhedral edge) (after [23]). Superimposed on it are the approximated spherical shape of grains and location of average grain boundary plane for grain A.

parameters to be obtained from [16] to calculate P_h as per Eq. (2).

An increase in ΔV_F due to the reduction in d_c develops a negative hydrostatic pressure at the grain boundary, which may change the activation energy of the atomic transport processes in the bulk. Considering self-diffusivity (D) of the bulk as a combined function of the pressure (P) and temperature (T) as

$$D = f(P, T) \quad (4)$$

one obtains

$$\left(\frac{\partial(1/T)}{\partial P}\right)_D \left(\frac{\partial P}{\partial(\ln D)}\right)_T \left(\frac{\partial(\ln D)}{\partial(1/T)}\right)_P = -1 \quad (5)$$

For a pressure activated process occurring at a given temperature, it is known that the activation volume (ΔV_a) may be approximated as [20]

$$\Delta V_a = RT \left(\frac{\partial(\ln D)}{\partial P}\right)_T \quad (6)$$

where R is the gas constant. Similarly, the activation energy (Q) for a similar thermally activated process under isobaric condition may be expressed as [20]

$$\left(\frac{\partial(\ln D)}{\partial(1/T)}\right)_P = \left(-\frac{Q}{R}\right) \quad (7)$$

Thus, combining Eqs. (5)–(7), one arrives at

$$\left(\frac{\partial(1/T)}{\partial P}\right)_D = \frac{\Delta V_a}{QT} \quad (8)$$

The activation energy may be related to the bulk modulus (B_c) of the crystalline volume as [20]

$$\frac{\Delta V_a}{Q} = \frac{K}{B_c} \quad (9)$$

where K is a constant related to the Gruneisen parameter (γ) as

$$K = 2 \left(\gamma - \frac{1}{3}\right) \quad (10)$$

Hence, substituting the relation obtained from Eq. (9) into Eq. (8), the latter may be rewritten (for a general situation where diffusivity D is a variable) as follows:

$$\frac{\partial(1/T)}{\partial P} = \frac{K}{B_c T} \quad (11)$$

Let us assume that the initial state of the system under the equilibrium temperature T_0 is defined by a zero hydrostatic pressure (i.e. $-P_h=0$). Subsequently, a comparable level of activation may be achieved either by increasing the temperature from T_0 to T_e under isobaric condition (i.e. at $P_h=0$) or by increasing the hydrostatic pressure from $-P_h=P_0$ to

$-P_h=P_e$ (P_e is the magnitude of hydrostatic pressure corresponding to P_h) under isothermal condition (i.e. at $T=T_0$). Thus, by integration within the chosen limit, Eq. (11) yields

$$\int_{T_0}^{T_e} T \partial \left(\frac{1}{T}\right) = \frac{K}{B_c} \int_{P_0}^{-P_e} \partial P$$

or,

$$T_e = T_0 \exp\left(\frac{KP_e}{B_c}\right) \quad (12)$$

Here, the value of B_c for the respective crystal is determined at a given pressure from the variation of the pressure dependent bulk modulus expressed as [16]

$$\left[\frac{dB_c}{dP_e}\right] = 1 + \frac{2.3}{3} \frac{r_{WSE}}{l} \quad (13)$$

Therefore, Eq. (12) allows one to compare the activation obtained at a given value of P_h (say, at $-P_h=P_e$) at $T=T_0$ for nanocrystalline materials with the same obtained at a higher temperature (i.e. $T=T_e$) for a coarse grained material for which $P_h=0$.

3. Results and discussion

Fig. 2 shows the variation of the excess free volume ΔV_F as a function of grain diameter d_c obtained from Eq. (1). It is apparent that ΔV_F does not register any significant variation with a decrease in d_c up to a level of 20 nm. However, reduction in grain size below 10 nm results into a significant increase in excess free volume per atom at the boundaries of nanocrystals. Furthermore, Fig. 2 registers an asymptotic variation of ΔV_F with d_c in the lower and upper ranges of d_c . Thus, ΔV_F is insignificant for very coarse grain size, but approaches a value of unity as d_c is decreased well below say, 2 nm. In this regard, it may be mentioned that Fecht [5] has earlier predicted a mechanical instability of the grain boundary at a value of $\Delta V_F=0.44$. Eq. (1) yields that $d_c=2.5$

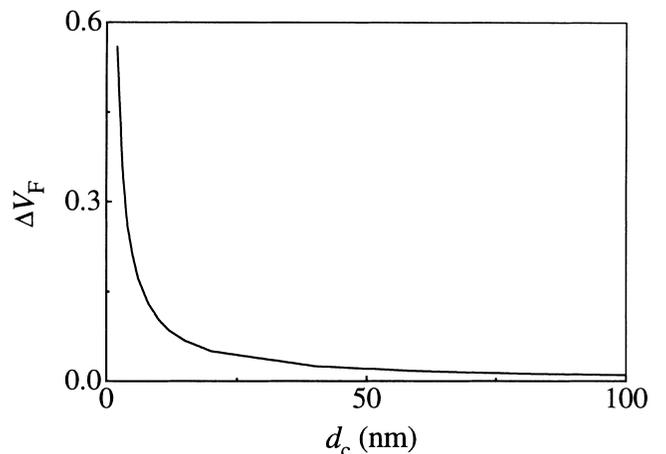


Fig. 2. Variation of excess free volume ΔV_F as a function of grain size d_c .

for $\Delta V_F=0.44$. It is interesting to note that an earlier theoretical study based on the simulation of the phonon density of states and related free energy changes has predicted that nanocrystals undergo thermodynamic instability when the grain size is reduced to typically 1.5–2 nm [21,22]. Therefore, it appears that the variation of ΔV_F as a function of d_c obtained from Eq. (1) is in reasonable agreement with the earlier predicted lower limit of mechanical instability of nanocrystals in terms ΔV_F [5] and d_c [21,22].

Fig. 3 reveals the variation of the magnitude of negative hydrostatic pressure $-P_h$ obtained as a function of excess free volume ΔV_F or in turn grain diameter d_c , for the two representative metals Cu (fcc) (continuous line) and Cr (bcc) (discontinuous line) obtained as per Eq. (2) using the necessary input parameters for the concerned elements from [16]. It may be noted here that $-P_h$ is the hydrostatic stress corresponding to the negative pressure originating due to the excess free volume in the grain boundary according to Eq. (2) [5]. It is evident from Fig. 3 that $-P_h$ increases as grain diameter d_c decreases or excess free volume ΔV_F increases. This change is significantly rapid for the coarser level of d_c , whereas it gradually levels off to approach a saturation value for d_c less than 4–5 nm. It may be noted that the variation of $-P_h$ as a function of ΔV_F predicted in the present analysis in case of Cr is in reasonable agreement with that earlier predicted by Fecht [5] for the same elements.

The effect of $-P_h$ on diffusion in nanocrystalline metals at a given temperature (T_0) may be expressed in terms of the projected diffusion kinetics at an effective elevated temperature (T_e) obtained from Eq. (13) which is comparable to the kinetics of the same taking place at $-P_h=0$, i.e. for relatively coarse grained metals. Results obtained from Eq. (12) for Cu are plotted in Fig. 4 which shows the variation of T_e , scaled with the melting temperature (T_m) of the specific metal, as a function of $-P_h$. It is apparent from Fig. 4 that

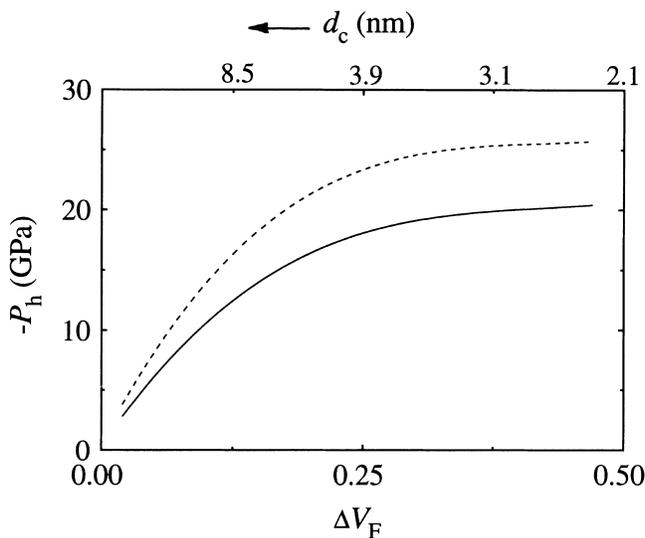


Fig. 3. Variation of $-P_h$ as a function of excess free volume ΔV_F or grain size d_c for Cu (continuous line) and Cr (discontinuous line).

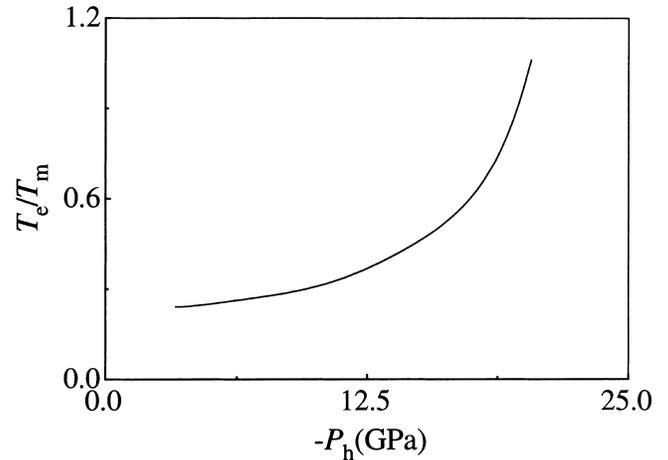


Fig. 4. Variation of T_e/T_m as a function of $-P_h$ for Cu.

the value of T_e/T_m gradually increases with the increase in $-P_h$ up to a definite level of $-P_h$, beyond which T_e/T_m shows a remarkable increment for a small change in $-P_h$, so much so that the variation of T_e/T_m approaches infinity beyond this level of $-P_h$.

Increase in the value of $-P_h$ as a result of increase in ΔV_F of the atoms in the grain boundary of nanocrystalline materials may exert a significant influence in the enhancement of bulk diffusivity. Such an enhancement may be attributed to the lattice expansion or softening occurring due to the reduction in grain size to the nanometric level. Thus, $-P_h$ in the grain boundary of nanocrystalline materials may be held responsible for the pressure induced activation of bulk diffusion at a given temperature, in analogy to the role played by temperature for the activation of a similar process taking place at a given level of pressure.

Thus, the faster diffusivity in nanocrystals (at $-P_h=P_e$ and $T=T_0$) could be equivalent to volume diffusion under equilibrium condition ($-P_h=0$) in usual polycrystals operating at an effective elevated temperature ($T=T_e$) (cf. Eq. (12)). The results from the present model in the case of Cu (Fig. 4) indicate that T_e/T_m plotted against the corresponding $-P_h$ tends to approach an infinite slope beyond an almost identical value of $T_e/T_m=0.5$. It is interesting to note that the value of T_e/T_m obtained in the present analysis is in agreement with the results obtained by us in the previous experimental studies [8,9] on several Cu-based systems as shown in Table 1. It is important to mention that a recent investigation by us [24] has evidenced a similar variation of T_e/T_m as a function of $-P_h$ in other elements like Cr, Nb, etc. as that of Cu (in Fig. 4) in spite of the significant difference in their melting points and Bravais lattices. Furthermore, Fig. 4 reveals that T_e/T_m exceeds a value of 0.5, typically known as the equi-cohesive temperature for metals, beyond a certain level of $-P_h$. Such a temperature indicates a probable softening of the grain boundary comparable to that achieved at a temperature above $0.5T_m$ in the coarse grained materials. Therefore, the results obtained from Fig. 4 indicate

Table 1
Comparison of T_e/T_m obtained from our previous studies for Cu alloys with that obtained in the present study for elemental Cu

System	T_e/T_m	Reference
Cu ₇₀ Zn ₃₀	0.43	[8]
Cu ₆₀ Zn ₄₀	0.48	[8]
Cu ₅₀ Ni ₅₀	0.48	[8]
Cu ₈₂ Al ₁₈	0.51	[9]
Cu	0.50	This study

that a thermodynamic condition may be attained in the grain boundaries beyond a certain value of $-P_h$ ($=19-21$ GPa), or in turn below a particular level of d_c (<10 nm), which is equivalent to that obtained in the grain boundary of the coarse grained materials above the equi-cohesive temperature.

4. Conclusion

The results in the present study suggests that the increase in negative hydrostatic pressure at the grain boundaries consequent upon the reduction of grain size below say, 10 nm may enhance the kinetics of atomic transport in the nanocrystalline materials. This enhancement signifies as if mass transport in nanocrystals (<10 nm grain size) occurs through bulk/volume diffusion at an effective elevated temperature.

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