



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Solid State Communications 130 (2004) 581–584

solid
state
communications

www.elsevier.com/locate/ssc

Grain size-dependent diffusion activation energy in nanomaterials

Q. Jiang*, S.H. Zhang, J.C. Li

*Department of Materials Science and Engineering, Contribution from Key Laboratory of Automobile Materials (Jilin University),
Ministry of Education, Jilin University at Nanling Campus, 142 RenMin Street, Changchun 130025, China*

Received 30 October 2003; received in revised form 13 January 2004; accepted 15 March 2004 by B. Jusserand

Abstract

We report a unified model, free of any adjustable parameter, for size-dependence of intrinsic diffusion activation energy of elements in crystals. It is found that as the size of the nanocrystals decreases, the diffusion activation energy of atoms decreases and the corresponding diffusion coefficient strongly increases due to the Arrhenius relationship between them, which leads to evident diffusion at the room temperature. The model prediction is in agreement with the experimental diffusion results of N into bcc Fe and Ag into Au nanoparticles.

© 2004 Elsevier Ltd. All rights reserved.

PACS: 66.30.Dn; 61.46 + w

Keywords: A. Nanostructures; D. Diffusion; D. Activation energy

1. Introduction

It is well known that there are lower diffusion activation energy of atoms in nanocrystals or nanostructured materials and thus larger diffusion coefficient than the corresponding bulk counterpart due to the increase of surface (interface)/volume ratio of the nanocrystals or nanostructured materials [1–3]. The potential of this phenomenon for industrial application is an evident drop of temperature for any diffusion process. The latest example is that the nitrification in bcc nanostructured Fe can be made at 573 K while this operation usually is carried out at 773 K or higher [1]. Moreover, a rapid alloying between Ag shell and Au nanocores may occur in several days at the room temperature [2]. This kinetic property of materials in return is also meaningful to consider the thermal stability of the core-shell structure when the both sizes of the core and the shell are only several nanometers or less [2,3]. The size and temperature dependent diffusion coefficient function is also an important parameter for any phase transition process through nucleation and growth where the size of the formed

nucleus is 1–2 nanometers and inoculation time and growth time are certainly related to the kinetic properties of a material [4]. The understanding of this kind of scientific problem becomes more urgent due to recent development on the nanotechnology where the full size of the materials is in nanometer size range [5,6].

Although the size-dependent properties of the kinetic parameters are so useful, a unique attempt to establish a quantitative model for describing this kind of size-dependence, based on simply the consideration on surface/volume ratio, cannot satisfactorily interpret the diffusion coefficient of Ag in Au nanoparticles [3]. Thus, it is necessary to model quantitatively the size and temperature dependence of the diffusion coefficient $D(r, T)$ with r being the radius of nanoparticles or grains and T being the temperature.

In this contribution, a model for $D(r, T)$ function without adjustable parameters is established through considering the size-dependent activation energy $E(r)$. In light of the model, it is found that when r is several nanometers, in one side, at the same T , $D(r, T)/D(\infty, T)$ could even be more than 10^{10} due to the drop of $E(r)$ where ∞ denotes the bulk size; in the other side, when a constant diffusion coefficient is needed, the diffusion temperature can decrease for several hundreds of degrees. The model predictions correspond to the

* Corresponding author. Tel.: +86-431-509-5371; fax: +86-431-509-5876.

E-mail address: jiangq@jlu.edu.cn (Q. Jiang).

experimental results of N diffusing into bcc nanostructured Fe and Ag shell diffusing into Au nanocores.

2. Model

To begin with, a well-known Arrhenius dependence for self-diffusion or intrinsic diffusion coefficient of interdiffusion $D(r, T)$ is introduced [2],

$$D(r, T) = D_0(r) \exp[-E(r)/(RT)] \quad (1)$$

where $D_0(r)$ denotes a pre-exponential constant, R is the ideal gas constant.

To establish an $E(r)$ function, $D[r, T_m(r)] = D[\infty, T_m(\infty)]$ is assumed [2] where $T_m(r)$ and $T_m(\infty)$ denote the size-dependent and the bulk melting temperature. Thus, $D[r, T_m(r)] = D_0(r) \exp\{-E(r)/[RT_m(r)]\} = D_0(\infty) \exp\{-E(\infty)/[RT_m(\infty)]\}$ in terms of Eq. (1). According to a point defect mechanism, D_0 is proportional to $\exp(\Delta S/R)$ where ΔS is the activation entropy, $\Delta H = E(r)$ is the activation enthalpy. In terms of a general thermodynamic relationship, $T[\partial \Delta S(r)/\partial T]_P = [\partial E(r)/\partial T]_P$ where $P = 2f/r$ is the internal pressure which holds for a spherical particle at a certain size. Thus, $\Delta S(r)$ varies as $E(r)$ changes. However, the change of $\Delta S(r)$ induced by vibrational frequency change due to the activation process is less than 5%, which is rather small, even if r varies from bulk to 2–3 nm [7]. This fact implies that $E(r)$ is almost temperature independent. $D_0(r)$ is thus a weak function of r while the effect of the exponential term of $\exp[-E(r)/(RT)]$ on $D(r, T)$ is much stronger. As a first order approximation, $D_0(r) \approx D_0(\infty)$ is assumed (in the following, D_0 is used as abbreviation). Therefore,

$$E(r)/E(\infty) = T_m(r)/T_m(\infty) \quad (2)$$

$T_m(r)/T_m(\infty)$ functions can be deduced by considering the averaged mean square displacement (msd) of atoms in a nanocrystal $\sigma^2(r)$ with [8],

$$\sigma^2(r) = \sigma_V^2(r) + [\sigma_S^2(r) - \sigma_V^2(r)n_S/n_V] \quad (3)$$

where the subscripts S and V denote surface and interior atoms of a particle, n is the atom number of a nanocrystal with $n_S/n_V = (4\pi r^2 h/V_0)/[(4/3)\pi r^3/V_0 - (4\pi r^2 h/V_0)] = 3h/(r - 3h)$ when the shape of the nanocrystal is considered as spherical or quasi-spherical where V_0 and h show the volume of the nanocrystal and the atomic diameter. The msd of the nanocrystal is larger than the corresponding bulk value not only on its surface, but also in its core, or the both $\sigma_V^2(r)$ and $\sigma_S^2(r)$ are size-dependent. However, it is assumed that $\sigma_S^2(r)/\sigma_V^2(r) = \sigma_S^2(\infty)/\sigma_V^2(\infty) = \alpha$ is size-independent [8]. Since the cooperative coupling between the surface region and the interior region may be important for small particles, the variation of $\sigma^2(r)$ is considered phenomenologically to be dependent on the value of $\sigma^2(r)$ itself [8],

which leads to [8],

$$\sigma^2(x + dx) - \sigma^2(x) = (\alpha - 1)\sigma^2(x)dx \quad (4)$$

where $x = n_S/n_V = r_0/(r - r_0)$ with $r_0 = 3h$. Integrating Eq. (4),

$$\int_{\infty}^r \frac{1}{\sigma^2(x)} d\sigma^2(x) = (\alpha - 1) \int_0^x dx,$$

or,

$$\sigma^2(r)/\sigma^2(\infty) = \exp[(\alpha - 1)x] = \exp[(\alpha - 1)(r/r_0 - 1)] \quad (5)$$

In Eq. (5), r_0 as a radius of a nanoparticle where almost all atoms are located on the surface has been further extended for different dimensions of all low-dimensional crystals [9–11]. Let d denote the dimension and $d = 0$ for nanoparticles where r has a usual meaning of radius, $d = 1$ for nanowires with r being taken as its radius and $d = 2$ for thin films with r denoting its half thickness. r_0 is given by (1) $r_0 = 3h$ for $d = 0$ since $4\pi r_0^2 h = 4\pi r_0^3/3$; (2) $r_0 = 2h$ for $d = 1$ since $2\pi r_0 h = \pi r_0^2$; and (3) $r_0 = h$ for $d = 2$ since $2h = 2r_0$. In short, the relationship between d and r_0 is given by [9–11],

$$r_0 = (3 - d)h. \quad (6)$$

To find a convenient means for correlating $T_m(r)$ to measurable physical properties such as σ^2 , Lindemann criterion [12–14], which says that a crystal will melt when σ/h reaches a certain fraction of c , is useful and is known to be valid qualitatively for small particles,

$$\sigma/h = c. \quad (7)$$

Although c varies a bit with crystal structure. It is 0.13 for fcc crystal and 0.18 for bcc crystal [14]. This difference is partly induced by the change of h , which depends on the coordination number of a lattice CN [15]. A smaller CN corresponds to a smaller h [16]. In order to reduce or eliminate this difference among distinct lattices or CNs , h here is calculated by atom volume that is little dependent on the lattice structure [15]. With this h , c is almost a lattice-independent.

Since $T_m(r)$ is usually higher than the bulk Debye temperature $\Theta_D(\infty)$, the high temperature approximation can be utilized [8,17,18], $\sigma^2(r, T) = f(r)T$, where $f(r)$ is a size-dependent function. Thus, at any T , $\sigma^2(r, T)/\sigma^2(\infty, T) = f(r)/f(\infty)$. Moreover, when $T = T_m(r)$, $f(r)/f(\infty) = \{\sigma^2[r, T_m(r)]/h^2\} / \{\sigma^2[\infty, T_m(\infty)]/h^2\} [T_m(\infty)/T_m(r)] = T_m(\infty)/T_m(r)$ in terms of Eq. (7). In light of the above equations, $T_m(r)/T_m(\infty) = \exp[-(\alpha - 1)(r/r_0 - 1)]$ where $\alpha = 2S_{\text{vib}}(\infty)/(3R) + 1$ for low-dimensional crystals with free surface [$S_{\text{vib}}(\infty)$ is the bulk melting entropy] [11], namely,

$$T_m(r)/T_m(\infty) = \exp\{-2S_{\text{vib}}(\infty)/[3R(r/r_0 - 1)]\}. \quad (8)$$

For metallic and organic crystals consisting of a single element or a single compound, $S_{\text{vib}}(\infty)$ is the essential contribution on the overall bulk melting entropy $S_m(\infty)$

because the contributions of the configuration term and electronic term on $S_m(\infty)$ are small [19]. Thus, $S_{vib}(\infty) \approx S_m(\infty)$ is taken.

Eq. (8) has been widely utilized to predict $T_m(r)$ functions of crystals with different chemical bonds, such as metallic [9], semiconductors [10] and organic crystals [11]. Fig. 1 gives an example to confirm the validity of Eq. (8) where the earliest [20] and the latest [2] experimental results with different experimental techniques and computer simulation results [21] of Au are shown. Eq. (8) corresponds to the experimental and computer simulation results where as r decreases, $T_m(r)$ decreases. Note that the shape of the particles affects $T_m(r)$ value through r_0 in terms of Eq. (6) where the experimental results [2,20] are predicted with $d = 1$ while the computer simulation results [21] are done with $d = 0$. This is because only the computer simulation may guarantee a free surface of nanocrystals. For both experimental results, the particles are either coated with porous silica shells [2] or deposited on substrate having an island shape [21], which leads to a quasi-dimension of one [9].

Substituting Eq. (8) into Eq. (1) through Eq. (2),

$$D(r, T) = D_0 \exp\left[\frac{-E(\infty)}{RT}\right] \exp\left[\frac{-2S_{vib}(\infty)}{3R} \frac{1}{r/r_0 - 1}\right]. \quad (9)$$

3. Results and discussion

Fig. 2 shows a comparison between Eq. (9) and experimental results for $D(r, T)$ function of N atoms diffusing into nanostructured bcc Fe [1]. Although only one experimental point shown in Fig. 2 is difficult to supply the consistency of $D(r, T)$ function in the whole range of r with the experiment, this experimental point fits the model parameters. In Fig. 2, even T decreases from 773 to 573 K,

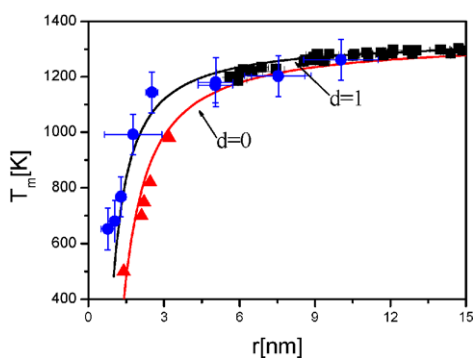


Fig. 1. $T_m(r)/T_m(\infty)$ functions of Au crystals denoted as a solid line in terms of Eq. (8). ● [2], ■ [20] and ▲ [21] show the experimental and the computer simulation results. The related parameters in Eq. (8) are: $h = 0.2884$ nm [15], $d = 1$ for experimental results [2,20] while $d = 0$ for the computer simulation results [21]. $T_m(\infty) = 1337.58$ K [22] and $S_m(\infty) = 9.3826$ Jg-atom⁻¹K⁻¹ [22].

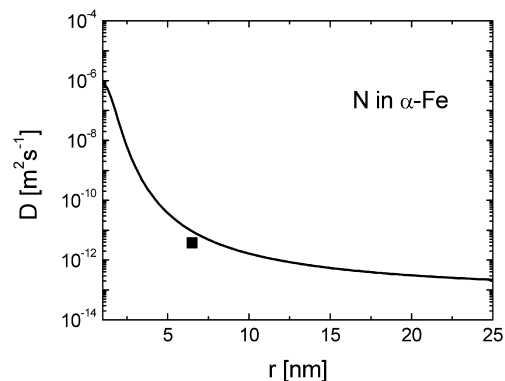


Fig. 2. $D(r, T)$ function of N diffusing into bcc nanostructured Fe shown as the solid line in terms of Eq. (9) where r is the radius of the grain size of Fe [1]. The parameters in Eq. (9) are as follows: $h = 0.2483$ nm and $d = 0$ for Fe [15], which leads to $r_0 = 0.7449$ nm. Since N in vapor state is unique diffusion element, the sublimation entropy S_c for N is used to substitute $S_m(\infty)$ with $S_c = 36.106$ Jg-atom⁻¹K⁻¹ [22]. $D_0 = 7.46 \times 10^{-7}$ m² s⁻¹ and $E_m(\infty) = 78.3$ KJg-atom⁻¹ are obtained through substituting two experimental results of $D(\infty, 573 \text{ K}) = 5.4 \times 10^{-14}$ m² s⁻¹ and $D(\infty, 773 \text{ K}) = 3.8 \times 10^{-12}$ m² s⁻¹ [23] into Eq. (1). The symbol ■ denotes the experimental results where $D(6.5, 573 \text{ K}) = D(\infty, 773 \text{ K})$ [1].

the diffusion coefficient remains constant since the grain size of bcc Fe decreases to 6.5 nm.

Fig. 3 gives the model prediction of Eq. (9) and experimental results for $D(r, T)$ functions of Ag diffusing into Au nanocores [3]. Since the size distribution of Au nanocores in Fig. 3 is $1.25 \text{ nm} \pm 20\%$ [3] while the mean size difference of two experimental points is only 0.47 nm, the experimental points overlap each other. $D(r, T)$ function

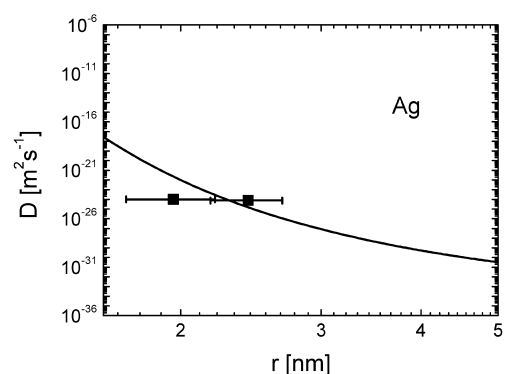


Fig. 3. $D(r, T)$ function of Ag diffusing into Au core shown as the solid line in terms of Eq. (9) where r is the total radius of the both of the Au core and the Ag shell [3]. The parameters for Au in Eq. (8) are as follows: $h = 0.2889$ nm [15] and $d = 0$, which leads to $r_0 = 0.8667$ nm. $S_m = 9.157$ Jg-atom⁻¹ K⁻¹ [22]. $D_0 = 7.2 \times 10^{-6}$ m² s⁻¹ [24] and $E_m(\infty) = 169.8$ KJg-atom⁻¹ [24]. The symbol ■ with the corresponding size error denotes the experimental results where $D(1.96, 300 \text{ K}) = 2.1 \times 10^{-24}$ m² s⁻¹ and $D(2.43, 300 \text{ K}) = 7.5 \times 10^{-25}$ m² s⁻¹ [3].

in terms of Eq. (9) is just located within them and within the size range of the experimental uncertainty [3]. Note that although the experiment itself shows a process of inter-diffusion between Ag shell and Au cores that involves Kirkendall effect. The cited data are the intrinsic diffusion coefficient of Ag into Au through some calculations [3].

Considering the different size and temperature dependences of $D(r, T)$ functions of Figs. 2 and 3 together, it could be believed that there were correspondence between the experimental results and the model predictions of Eq. (9).

In a classical approach made to model bulk diffusion through surfaces with large curvature radius r , the main term acting is $P = 2f/r$ related to the surface (or interface) stress f . The variation of $E(r)$ is then due to an activation volume $P\Delta V$ with $\Delta V = \Delta V_f + \Delta V_m$ in terms of a point defect mechanism where ΔV_f and ΔV_m are the formation and the migration volume of the point defects involved. These three quantities being positive lead to an increase of $E(r)$ as r decreases. If this consideration is applied to nanoparticles (or small grains) where there is also a large curvature on the surface, there is a reverse result of Eq. (9). However, the above consideration cannot be applied on nanocrystals. This is because the surface diffusion needs a much smaller activation enthalpy where the full free surface supply enormous room for atom diffusion with lower diffusion resistance where $\Delta V \rightarrow 0$. This results in a $1/r$ relationship of $E(r)$ in terms of a simple surface (interface)/volume ratio due to the contribution of surface diffusion. Thus, the diffusion coefficient of nanocrystals may be much larger than that of the corresponding bulk. Moreover, the essential assumption during the deduction of Eq. (8) is that the ratio of msd between the surface atoms and the interior atoms is size-independent [8,11]. Thus, the enhancement of the msd of a nanocrystal is induced by not only the large percentage of the surface atoms of the nanocrystals, but also the interior atoms of the nanocrystals, which implies that the internal energy of interior atoms of the nanocrystals is also higher than the corresponding bulk and thus the necessary activation of atoms for diffusion is easier with smaller activation energy compared with the corresponding bulk. As result, the drop of $E(r)$ is stronger than that being proportional to $1/r$ of the nanocrystals due to the additional contribution of interior atoms of nanocrystals.

The surface melting phenomena [13] have not been considered as a mechanism for the rapid increase of the diffusion coefficient of elements for nanostructured materials or nanocrystals. According to the experimental results, the surface melting could not lead to a full alloying of the core + shell structure [3] since the formation of the coherent interface between the Au core and the Ag shell can avoid any surface melting [25] while the nanostructured Fe is built by grain boundaries.

4. Conclusion

In summary, a model for $D(r, T)$ and $E(r)$ functions are established. $D(r, T)$ increase of nanocrystals is induced by the decrease of $E(r)$ due to the size effect. The model predictions for $D(r, T)$ function of N diffusing into nanostructured bcc Fe and Ag diffusing into Au nanocores are in agreement with the experimental results.

Acknowledgements

The financial support from the NNSFC (Grant No. 50025101) is acknowledged.

References

- [1] W.P. Tong, N.P. Tao, Z.B. Wang, J. Lu, K. Lu, Science 299 (2003) 686.
- [2] K. Dick, T. Dhanasekaran, Z. Zhang, D. Meisel, J. Am. Chem. Soc. 124 (2002) 2312.
- [3] T. Shibata, B.A. Bunker, Z. Zhang, D. Meisel, C.F. Vardeman II, J.D. Gezelter, J. Am. Chem. Soc. 124 (2002) 11989.
- [4] Q. Jiang, X.H. Zhou, M. Zhao, J. Chem. Phys. 117 (2002) 10269.
- [5] H. Gleiter, Acta Mater. 48 (2000) 1.
- [6] A.E. Kaloyeros, E. Eisenbraun, Annu. Rev. Mater. Sci. 30 (2000) 363.
- [7] L.H. Liang, C.M. Shen, X.P. Chen, W.M. Liu, H.J. Gao, J. Phys.: Condens. Matter 16 (2004) 267.
- [8] F.G. Shi, J. Mater. Res. 9 (1994) 1307.
- [9] Z. Zhang, J.C. Li, Q. Jiang, J. Phys. D 33 (2000) 2653.
- [10] Z. Zhang, M. Zhao, Q. Jiang, Semicond. Sci. Technol. 16 (2001) L33.
- [11] Q. Jiang, H.X. Shi, M. Zhao, J. Chem. Phys. 111 (1999) 2176.
- [12] F.A. Lindemann, Z. Phys. 11 (1910) 609.
- [13] J.G. Dash, Rev. Mod. Phys. 71 (1999) 1737.
- [14] F.H. Stillinger, Science 267 (1995) 1935.
- [15] H.W. King, in: R.W. Cahn, P. Haasen (Eds.), Physical Metallurgy, third ed., North-Holland Physics, Publishing, Amsterdam, 1983, pp. 59–63.
- [16] C.Q. Sun, Y. Wang, B.K. Tay, S. Li, H. Huang, Y.B. Zhang, J. Phys. Chem. B 106 (2002) 10701.
- [17] K. Hoshino, S. Shimamura, Philos. Mag. A 40 (1979) 137.
- [18] E. Matsushita, E. Siegel, Scripta Mater. 13 (1979) 913.
- [19] A.R. Regel, V.M. Glazov, Semiconductors 29 (1995) 405.
- [20] J.R. Sambles, Proc. R. Soc. London, Ser. A 324 (1971) 339.
- [21] F. Celestini, R.J.-M. Pellenq, P. Bordarier, B. Rousseau, Z. Phys. D 37 (1996) 49.
- [22] Table of Periodic Properties of the Elements, Sargent-Welch Scientific Company, Skokie, Illinois, 1980, p. 1.
- [23] J.D. Fast, M.B. Verrijp, J. Iron Steel Inst. 24 (1954) 176.
- [24] R.C. Weast, CRC Handbook of Chemistry and Physics, 69th ed., CRC Press, Boca Raton, FL, 1988-1989, p. F 50.
- [25] Q. Jiang, Z. Zhang, J.C. Li, Chem. Phys. Lett. 322 (2000) 549.