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Diffusion activation enthalpy of nanocrystalline metals①

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Abstract: The atomic diffusion of nanocrystalline metals showed significant difference in comparison to polycrystalline metals, this property is analyzed by considering the effect of temperature - time history on the interfacial structure. The interfacial structure is approximated by a dilated perfect crystal. Based on LeClair's diffusion theory, diffusion activation enthalpy in nanocrystalline metals was calculated. The results show that the change of diffusion activation enthalpy is closely related to the structure relaxation of the interfaces and the interfacial migration, the structure relaxation of the interfaces will increase the diffusion activation enthalpy when the crystallite growth can be negligible, whereas the migration of the interfaces will lead to the further increase of the diffusion activation enthalpy when crystallite growth proceeds rapidly. The theoretical prediction is found to be in accordance with experimental observations.

Key words: diffusion activation enthalpy; structure relaxation; interfacial migration **Document code:** A

1 INTRODUCTION

Nanocrystalline (NC) materials are polycrystals with a crystallite size on the order of nanometers. Due to the small crystallite size, NC materials consist of a high density of the interfaces. It is suggested that the structure of the crystalline component deviates little from that of the bulk, whereas the interface shows an 'extended structure' due to the existence of a large amount of free volume, which provides a high dense network of paths for fast diffusion in NC materials[1~3]. Thereby, the diffusion activation enthalpy of NC materials is expected to be very low relative to lattice and conventional grain boundary diffusion. This presumption was verified by early experimental results[4~7]. In those experiments, the experimental temperatures were relatively low (below 373 K), moreover, the diffusion activation enthalpies have rising trend with increasing temperature. The recent work of Würschum *et al*[8] indicated that at high temperatures (about 500 K) the diffusion activation enthalpies of Fe solute in NC-Pd are similar to those in conventional grain boundaries and even higher value at higher temperatures. Other authors[9] also obtained similar experimental results. It seems that the atomic diffusion in NC materials was closely related to temperature-time histories. However, there still exist discrepancies in the explanations of diffusion in NC materials. In this paper, we present theoretical studies on the atomic diffusion in NC metals by considering the effects of the temperature-time histories on the interfacial structure and the diffusion behavior.

2 CALCULATION MODEL

The diffusion coefficient for metals by the vacancy mechanism is well known to be expressed by the equation

$$D = C_v f g a^2 \gamma \exp\left(-\frac{\Delta F_2}{RT}\right) \qquad (1)$$

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where C_v is the fractional concentration of the vacancies, f is the correlation factor, g is the geometric factor, a is the lattice constant, γ is the atomic frequency of vibration on a lattice site, and ΔF_2 is the free energy change by an atom being moved from an normal site (A) to the top (B) of the potential barrier separating it from the next (A'), as shown in Fig. 1, C_v is given by

$$C_v = \exp\left(-\frac{\Delta F_1}{RT}\right) \quad (2)$$

where ΔF_1 is the free energy change of forming a vacancy. With each ΔF, there is an associated change in entropy ΔS and enthalpy ΔH, i.e.

$$\Delta F_i = \Delta H_i - T\Delta S_i \quad (3)$$

ΔH_i and ΔS_i are referred to as the enthalpy and entropy respectively, corresponding to the free energy of activation F_i. From (1), (2) and (3), D may be rewritten as

$$D = fga^2\gamma\exp\left(\frac{\Delta S_1 + \Delta S_2}{R}\right)\cdot \exp\left(-\frac{\Delta H_1 + \Delta H_2}{RT}\right) \quad (4)$$

We have

$$Q = \Delta H_1 + \Delta H_2 \quad (5)$$

where Q is the diffusion activation enthalpy.

According to LeClaire's theory[10], we can estimate ΔH_1 and ΔH_2 of the interfaces of NC metals. ΔH_1 is the change in internal energy of forming a vacancy, LeClaire suggested that it is proportional to the latent heat of sublimation, L_s, i.e.

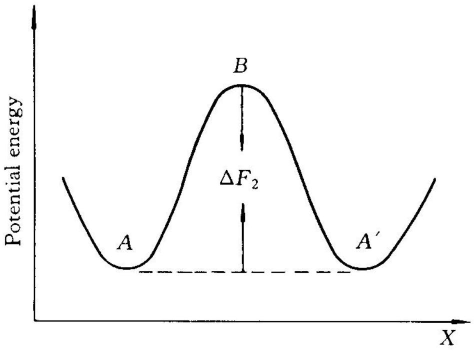

Fig. 1 Distribution of potential energy

$$\Delta H_1 = k_1 L_s \quad (6)$$

where k_1 is a correlation factor which is constant for metal of one structure ($k_1 = 0.215$ for fcc crystals[10]). The value of L_s is equal to that of the binding energy. If choosing the Morse function and regarding only the nearest-neighbor interaction, we have

$$\Delta H_1 = -6k_1NA[\exp(-2b(r-a)) - 2\exp(-b(r-a))] \quad (7)$$

where N is the number of atoms, r is the nearest-neighbor separation in the interfaces of NC metals; A, a and b are 10.4×10^{-20} J, 2.75×10^{-10} m and 1.4×10^{10} m^{-1} for NC-Pd, respectively, which can be calculated to fit the coefficient of linear thermal expansion[11].

ΔF_2 is equal to the isothermal work required to move an atom from one position to the top of the potential barrier separating it from the next. Such a movement will produce a local shear strain in the position around the diffusing atom. So, ΔF_2 can be equated to the resulting elastic strain energy:

$$\Delta F_2 = k_2 G\left(\frac{M}{\rho}\right) \quad (8)$$

where M is the atomic weight, ρ is the density of the interfaces, G is local shear modulus of the interfaces and k_2 is a correlation factor which is constant for metal of one structure. For simplifying calculation, we employ the shear modulus of the ordinary bulk materials K rather than the local value G. The value of k_2 in LeClaire's theory model needs to be recalculated, and the new value is given in Table 1. From the standard relationship, the shear modulus K is given by

$$K = \frac{3B}{2}\left(\frac{1-2\upsilon}{1+\upsilon}\right) \quad (9)$$

where B is the bulk modulus and υ is Poisson's ratio. Thereby

$$\Delta F_2 = \frac{3k_2B}{2}\left(\frac{1-2\upsilon}{1+\upsilon}\right)\left(\frac{M}{\rho}\right) \quad (10)$$

υ can be estimated by comparing the bulk modulus of the single crystal calculated from quasiharmonic Debye approximation (QDA) method[11] and shear modulus of the single crystal. With respect to NC-Pd, υ is 0.36. The density of the single crystal Pd is 12.03 g/cm^3. The interfacial

Table 1 Values of k_2(ΔS_2 is ignored in calculation[10])

Specimens	Q /(kJ·mol^{-1})	$0.215L_s$ /(kJ·mol^{-1})	M	ρ /(g·cm^{-3})	G /(kJ·cm^{-3})	k_2
Cu	203.6	73.1	63.5	8.9	46.0	0.397
Au	174.3	73.6	197	19.3	28.4	0.347
Ni	280.9	90.7	58.7	8.9	76.9	0.375
γ-Fe	283.8	86.9	55.8	7.9	80.3	0.347
Ag	179.3	61.9	108	10.5	27.1	0.420

Average $k_2 = 0.377$

bulk modulus B is the function of excess volume ΔV($\Delta V = V/V_0 - 1$, where V is the volume of the interfaces and V_0 is the volume of the corresponding crystalline state). NC metals used in most of the diffusion experiments are prepared by cluster compaction, The densities of the interfaces of such NC metals derived from the results of the experiments and the computer simulations are less than 0.85 of single crystals[12], so the excess volumes of the interfaces will be larger than 0.18.

3 RESULTS AND DISCUSSION

Experimental study of wide-angle scattering confirmed[16] that interatomic distance in the interfaces is larger than that in the crystallites. The interfacial structure can be approximated by a dilated perfect crystal[11]. The bulk modulus B decreases with increasing the excess volume ΔV, as shown in Fig. 2. There exists a critical value ΔV_c. When $\Delta V > \Delta V_c$, the interface will be mechanically unstable. If there simultaneously exists a large amount of the vacancies in the interfaces (e. g. a high concentration of the vacancies in the interfaces about 10^{-4}[3-4] is detected in the interfaces of NC metals prepared by inert gas condensation and consolidation at ambient temperature, this value is much larger than the probability of forming a vacancy from a normal site.), the probability that a particular atom has a vacancy as neighbor is proportional to the concentration of the vacancies. When an atom diffuses by the vacancy mechanism in such materials, it is unnecessary to form an new vacancy at its neighboring site, namely, ΔH_1 is equal to zero. According to equations (5) and (10), the diffusion activation enthalpy Q is equal to zero.

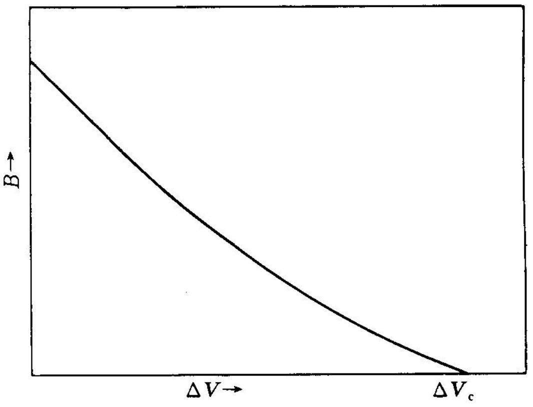

Fig.2 Change of interfacial bulk modulus B of NC metals with excess volume ΔV

In fact, structure relaxation of interfaces is inevitable in the process of diffusion experiments, so Q equals to zero is an ideal condition. The extent of relaxation is closely related to temperature and the duration of annealing. A systematic study of the thermal stability of the interfacial structure of NC-Pd by means of positron annihilation was performed by Schaefer *et al*[4] and led to the following results that in isochronal annealing, the three temperature regimes should be noticed: (a) 293~623 K. The concentration of the vacancies decreases and the vacant agglomerations aggregate; (b) 623~773 K. The vacant agglomerations disappear. (c) above 773 K. Substantial crystallite growth is observed. So, the concentration of the vacancies is closely related to temperature-time histories. If NC metals are annealed in a given temperature in which crystallite growth can be negligible, the concentration of the vacancies and the interatomic distance of the interfaces will decrease when the temperature or the duration of annealing is increased. The structure relaxation of the interfaces will impede the diffusion more and more. Assuming that the concentration of the vacancies can be considered to be little due to the structure relaxation in the interfaces when $\Delta V = 0.18$, we may use LeClair′s diffusion theory to estimate the diffusion activation enthalpy of the interfaces. Taking NC-Pd as an example, the interfacial bulk modulus of NC-Pd calculated by using QDA method[11] is 5.16×10^3 kg/mm^2. In such NC metals, before an atom may diffuse onto a neighboring site, a vacancy at neighboring site must be firstly formed. According to equation (7), the internal energy (ΔH_1) of forming a vacancy in the interfaces of NC-Pd is 77 kJ/mol. Moreover, in order that an atom diffuses onto a neighboring vacancy, it must possess a certain amount of energy to surmount the potential barrier separating it from the vacancy. The free energy change (ΔF_2), according to equation (10), is 61 kJ/mol. Comparing to ΔH_2, the contribution of the activation entropy (ΔS_2) to ΔF_2 can be negligible[10]. So, the diffusion activation enthalpy ($Q = \Delta H_1 + \Delta H_2$) in the interfaces is 138 kJ/mol for NC-Pd. This value is somewhat higher than that of self diffusion in conventional grain boundaries[13]. This result is in agreement with the experimental observations in Ref.[8].

In most of the diffusion experiments, the crystallite growth can be negligible due to the low experimental temperatures. The increase of the diffusion activation enthalpy with increasing temperature or the duration of annealing is mainly attributed to the structure relaxation of the interfaces. At higher diffusion temperatures (e.g. above 500 K for NC-Pd[4,8]), the diffusion activation enthalpy will further increase. This increase is due to the interfacial migration which is associated with the strong crystallite growth at high diffusion temperature. Between 773 K and 973 K, diffusion experiments have also been performed for Ni solute diffusion in NC-Cu[4]. The diffusivities observed are close to Ni diffusivities in single crystal Cu[13]. This can be explained by the diffusion theories of the interfacial migration well[14,15].

4 CONCLUSIONS

In nanocrystalline metals, in addition to the crystallite size, the temperature-time histories have important effects on its atomic diffusion. In the low temperature regime: diffusion occurs mainly along the interfaces, the effects of the interfacial migration on the diffusion can be considered to be negligible, the increase of activation enthalpy with increasing temperature or the duration of annealing is mainly due to the structure relaxation of the interfaces. In the high temperature regime, the interfacial migration will give rise to deviations from simple diffusion behavior, which results in the further increase of the diffusion activation enthalpy with increasing temperature.

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