Non-equilibrium grain-boundary segregation of Bi in Cu bicrystals

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Abstract: The observations of grain-boundary segregation of Bi in Cu bicrystals were analyzed. According to equilibrium grain boundary segregation (EGS) model and non-equilibrium grain-boundary segregation (NGS) model, respectively, the segregation kinetics of isothermal annealing at 500 °C and that of isochronal annealing for 24 h of Bi in Cu bicrystals were investigated. By qualitative analysis and quantitative analysis, it is concluded that the grain-boundary segregation of Bi agrees well with the theory of NGS. Based on the kinetics model of NGS, some parameters that are useful to predicting and controlling the Bi-induced embrittlement in Cu alloys are calculated as follows: the diffusion coefficient of Bi-vacancy complexes $D_c=7.8\times10^{-5}\exp[-1.46/(kT)]$; the apparent diffusion coefficient of Bi atoms $D_i^A=7.66\times10^{at+b}\exp[-1.76/(kT)]$, where $a=8.45\times10^{-8}$ and $b=-13.37$.
Key words: bismuth; copper; segregation; grain boundary; diffusion

1 Introduction

Grain-boundary (GB) segregation affects various properties of the materials, such as temper embrittlement [1−4], intermediate temperature embrittlement [5−7], tensile ductility [8−10], and GB corrosion resistance [5,11,12]. Therefore, particular attention is paid to this phenomenon by many researchers. It is well known that GB segregation is classified into equilibrium segregation and non-equilibrium segregation [13,14]. The kinetic behavior of equilibrium grain-boundary segregation (EGS) was analyzed by MCLEAN [15] using diffusion theory. The non-equilibrium grain-boundary segregation (NGS) theory was proposed by AUST et al [16] and ANTHONY [17]. The kinetic model of NGS was given by FAULKNER [18] and XU et al [13,19].

In 1985, FRACZKIEWICZ and BISCONDI [20] studied the GB segregation of Bi in Cu bicrystals (containing 0.005% Bi, mole fraction). The isotherm at 500 °C revealed that the Bi content at GB gradually increased, reaching its maximum after annealing for 24 h and then decreased slowly (Fig. 1(a)). They [20] considered that the EGS of Bi occurred and the decrease in Bi content at GB was caused by precipitation.

However, they also confirmed that intergranular particles were observed by the scanning electron microscope only in the samples annealing for 10 d. Therefore, the decrease in Bi content at GB after annealing for 24 h cannot be attributed to the formation of intergranular precipitates which was observed after annealing for 10 d. Besides, the isochrone of Bi segregation for 24 h showed that with the elevation of temperature, GB segregation of Bi increased gradually, reaching its maximum at around 500 °C and then decreased slowly (Fig. 1(b)). Based on EGS theory, they [20] considered that the heat treatment time was too short to achieve the maximum segregation at temperatures below 500 °C while it seemed to be enough to achieve a level close to the maximum in the temperature range of 500−650 °C. It is noteworthy that the NGS theory was successfully applied to explaining the maximum of embrittling isochrone of steels [1,13]. Therefore, the explanation of FRACZKIEWICZ and BISCONDI [20] by EGS theory seems to be invalid. In these cases, the segregating behavior of Bi in Cu bicrystals needs to be verified.

The present work is thus carried out to determine the segregating behavior of Bi in Cu bicrystals by the experimental results of FRACZKIEWICZ and BISCONDI [20]. It is found that the grain boundary
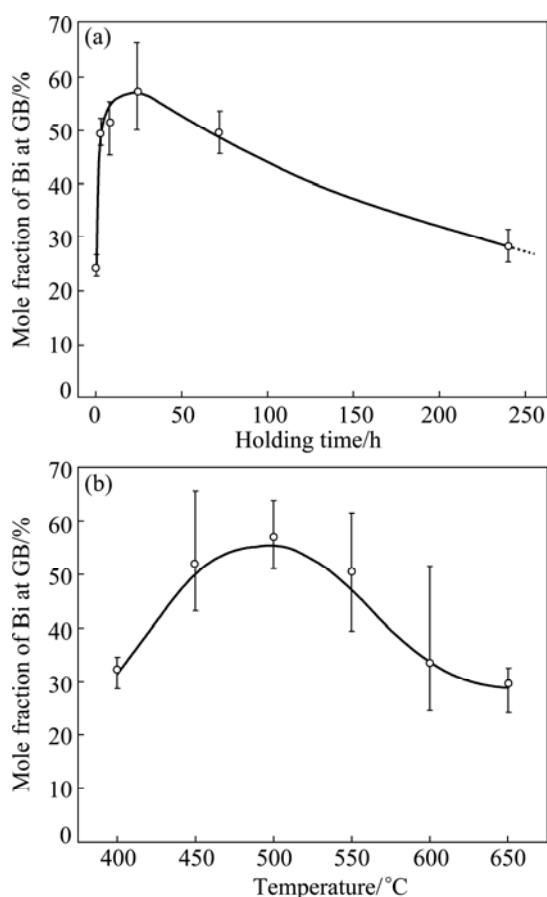
Fig. 1 Isothermal curve of Bi segregation in Cu bicrystals annealing at 500 °C (a) and isochronal curve annealing for 24 h (b) [20]

segregation of Bi agrees well with the theory of NGS. On this basis, the diffusion coefficients of Bi-vacancy complexes and Bi atoms are calculated, which are helpful to predicting and controlling the Bi-induced embrittlement in Cu alloys.

2 Kinetic models of GB segregation

2.1 Kinetic model of EGS

MCLEAN [15] proposed a model for EGS and derived thermodynamic and dynamic equations. The thermodynamic equation is

$$\frac{C_\Phi}{1-C_\Phi}=\frac{C_B}{1-C_B}\exp\left(-\frac{\Delta G}{RT}\right) \tag{1}$$

where C_Φ is the equilibrium concentration of solute atoms at GB; C_B is the bulk concentration of solute atom; ΔG is the molar Gibbs energy of GB segregation of solute atom. The dynamic equation of EGS is

$$\frac{C_\Phi(t)-C_\Phi(0)}{C_\Phi-C_\Phi(0)}=1-\exp\left(\frac{4D_i t}{\alpha^2 d_e^2}\right)\cdot\mathrm{erfc}\left(\frac{2\sqrt{D_i t}}{\alpha d_e}\right) \tag{2}$$

where $C_\Phi(t)$ is the GB concentration after time t at a

certain temperature T; $C_\Phi(0)$ is the initial GB concentration; D_i is the diffusion coefficient of the solute at a certain temperature; α is the equilibrium ratio C_Φ/C_B; d_e is the GB thickness. From Eq. (2) it is clear that the GB concentration increases gradually from an initial concentration $C_\Phi(0)$ to a final equilibrium concentration C_Φ as time extends.

2.2 Kinetic model of NGS

The NGS is considered to result from the formation of solute−vacancy atom complexes in the matrix, where solute atom, vacancy and their recombined complex are in local equilibrium [13,19]. When a sample is hold at a higher temperature T_i and then annealed isothermally at a certain lower temperature T_{i+1} at once, the diffusion of complexes toward the GB and the reverse diffusion of solute atoms from the GB will be induced. At a critical time, these two diffusions balance with each other and the solute atom content at GB reaches a maximum. When the holding time is shorter than the critical time, the diffusion of complexes to the GB will be the dominant process and is referred as the segregation process. When the holding time is longer than the critical time, the reverse diffusion of solute atoms will be the dominant process and is referred as the de-segregation process. The critical time is the most characteristic aspect of NGS and the basic criterion to distinguish NGS from EGS [1,8,13]. A formula for the critical time, t_c, is given by FAULKNER [18] and XU et al [13,19] as

$$t_c=\frac{r^2\ln(D_c/D_i)}{\delta(D_c-D_i)} \tag{3}$$

where r is the grain radius; D_c represents the diffusion coefficient of the complex; δ denotes the critical time constant.

XU et al [13,19,21] established the isothermal kinetic model of NGS for two processes. For the segregation process ($t<t_c$), the NGS kinetic equation is given as [13,19,21]

$$\frac{C_b(t)-C_m(T_i)}{C_m(T_{i+1})-C_m(T_i)}=1-\exp\left(\frac{4D_c t}{\alpha_{i+1}^2 d^2}\right)\cdot\mathrm{erfc}\left(\frac{2\sqrt{D_c t}}{\alpha_{i+1}d}\right) \tag{4}$$

For the de-segregation process ($t>t_c$), the NGS kinetic equation is given as [13,19,21]

$$C_b(t)=C_B+\frac{C_b(t_c)-C_B}{2}\cdot\left\{\mathrm{erf}\left[\frac{d/2}{\sqrt{4D_i(t-t_c)}}\right]-\right.$$

$$\left.\mathrm{erf}\left[\frac{-d/2}{\sqrt{4D_i(t-t_c)}}\right]\right\} \tag{5}$$

where $C_b(t)$ is the solute atom content at the GB as a function of t at temperature T_{i+1}; $C_m(T_i)$ is the maximum

solute content at the GB at temperature T_i; d is the width of the concentrated layer; $\alpha_{i+1}=C_m(T_{i+1})/C_B$; $C_b(t_c)$ is the solute content at the GB at critical time t_c and temperature T_{i+1}.

3 Discussion

### 3.1 Verification of segregating behavior of Bi in Cu bicrystals

According to EGS theory, the isothermal kinetics and isochronal kinetic curves of Bi segregation in Cu bicrystals were calculated and shown in Fig. 2. The parameters used for the calculation are listed in Tables 1 and 2. It can be seen from Fig. 2(a) that during isothermal annealing at 500 °C the content of Bi at the GB gradually approaches an equilibrium value $C_\Phi=$ 64.4% as time goes to infinity. On the contrary, the experimental results show a definite maximum. Thus, the trend of the calculated curve does not fit to the experimental results. From Fig. 2(b) it can also be seen that during isochronal annealing for 24 h the Bi segregation decreases progressively as the temperature increases, which obviously deviates from the experimental data in the temperature range of 400−

Table 1 Parameters and corresponding values used for calculations by EGS theory

Parameter	Value	Ref.
ΔG/eV	0.7	[20]
C_B/%	0.005	[20]
D_i/(m$^2\cdot$s^{-1})	$7.66\times10^{-5}\exp[-1.76/(kT)]$	[22,23]
d_e/m	1×10^{-9}	[24]

Table 2 Parameters and corresponding values used for calculations by NGS theory

Parameter	Value	Ref.
T_{i+1}/K	773	[20]
$C_m(T_{i+1})$/%	57.1	[20]
$t_c(T_{i+1})$/h	24	[20]
d/m	1×10^{-9}	[24]
D_{c0}/(m$^2\cdot$s^{-1})	7.8×10^{-5}	[25]
Q_i/eV	1.76	[22,23]
Q/eV	2.19	[25]
E_f/eV	1.03	[26]
E_b/eV	0.63	[18]
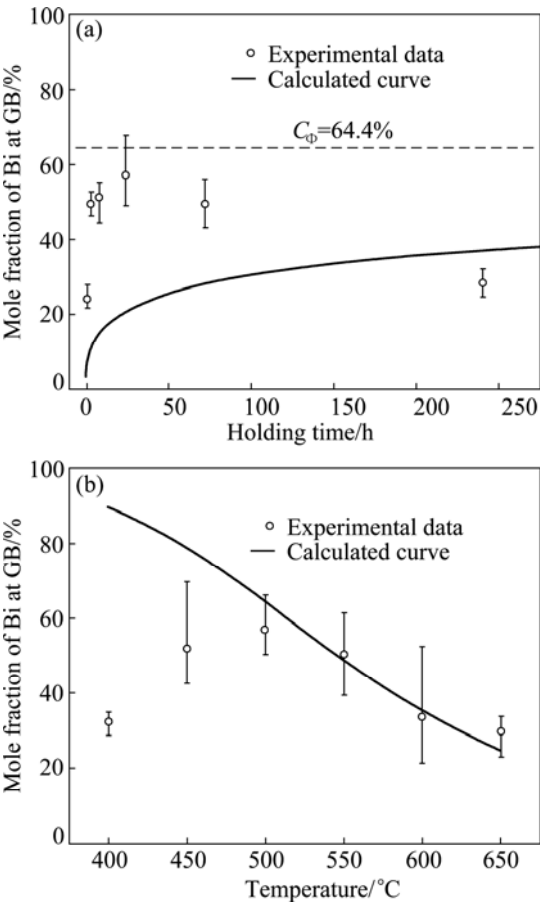
500 °C. Based on Fig. 2, it can be reasonably concluded that EGS of Bi in Cu bicrystals does not occur.

It is noteworthy that the critical time is the most characteristic aspect of NGS and the basic criterion to distinguish NGS from EGS. At the critical time, the GB segregation reaches the maximum. Thus, if NGS occurs, the GB segregation will increase first, reach the maximum at critical time, decrease gradually, and approach to thermodynamic level finally. Clearly, the isothermal kinetic curve of Bi segregation in Fig. 1(a) shows the same tendency and gives the support to the occurrence of NGS of Bi in Cu bicrystals. Besides, the NGS of Bi can induce not only the isothermal maximum, but also the isochronal one. According to Eq. (3), the critical time for the maximum GB segregation of Bi decreases when the temperature is elevated [1,8,13]. At a rather low temperature, the critical time can be much longer than the fixed annealing time of 24 h. As a consequence, the diffusion of complexes towards GBs is dominant and the Bi content at the GB is far from the maximum. So, the Bi content at the GB is low. As the temperature increases, both diffusion processes become accelerated, and therefore the critical time becomes shorter. At 500 °C, the critical time equals the annealing time of 24 h (Fig. 1(a)). Thus, the content of Bi at the GB reaches its maximum. With further increase in temperature, the critical time becomes even shorter than 24 h. Thus, the reverse diffusion of Bi becomes already dominant during the fixed holding time of 24 h. In consequence, segregation of Bi at the GB decreases. From the qualitative analysis of both isothermal and isochronal kinetics of Bi segregation, it can be confirmed

Fig. 2 Isothermal curve of Bi segregation annealing at 500 °C (a) and isochronal curve annealing for 24 h (b) calculated with EGS theory

that the segregating behavior of Bi in Cu bicrystals is NGS.

3.2 Calculation of isotherm of NGS of Bi

Since the segregation of Bi at GB in Cu bicrystals is NGS, the detailed knowledge of NGS of Bi must be helpful to predicting and controlling the Bi-induced embrittlement in Cu alloys, for example, intermediate temperature embrittlement [27].

In the experiment of FRACZKIEWICZ and BISCONDI [20], the samples were quenched at solution temperature of 950 °C. Here, it is considered that the content of Bi at the GB reaches the equilibrium during solution treatment at temperature T_i. Consequently, $C_m(T_i)$ (equal to C_Φ) can be obtained by Eq. (1). As for the maximum content of Bi at temperature T_{i+1}, $C_m(T_{i+1})$, it can be assumed to be equal to $C_b(t_c)$ which is the content of Bi at the GB at the critical time [28,29]. According to the experimental results, the critical time t_c at 500 °C can be determined as 24 h. All parameters are listed in Tables 1 and 2. Substituting these parameters into Eqs. (4) and (5), the diffusion coefficients of Bi−vacancy complex and Bi atoms at different isothermal holding time were simulated and shown in Table 3. It is worth mentioning that the simulated diffusion coefficients in Table 3 are not the real diffusion coefficients of the complexes or the solute in the matrix. Actually, they are apparent diffusion coefficients according to the NGS model since diffusions of complexes towards the GB and solute atoms towards grain interiors occur simultaneously [13].

Table 3 Simulated values of diffusion coefficients of Bi−vacancy complex and Bi atoms

Holding time/h	Mole fraction of Bi segregation/%	Diffusion coefficient/(m²·s⁻¹)
0.5	24.2	$4.4×10^{-14}$
3	49.6	$2.9×10^{-14}$
8	51.4	$1.6×10^{-14}$
24	57.1	−
72	49.6	$3.2×10^{-25}$
240	28.4	$3.6×10^{-25}$

3.2.1 Segregation process of NGS of Bi

It is well known that the diffusion coefficient of the complex, D_c, is the most important parameter to characterize the NGS. However, its value of Bi−vacancy complex in Cu alloy has not been determined so far. Theoretically, the apparent diffusion coefficient of complexes will decrease as annealing time extends in the segregation process since diffusions of complexes and solute atoms occur simultaneously. Whereas, the diffusion of Bi atoms towards grain interiors is far slower than that of complexes towards GB, the apparent diffusion coefficient of complexes can be assumed to be

nearly constant and as the real one [13,29,30]. In this case, the average value, $D_c=2.97×10^{-14}$ m²/s, of the apparent diffusion coefficients (see Table 3) can be taken as the real diffusion coefficient of Bi−vacancy complexes in Cu alloys. By using this value, the kinetic curve of NGS of Bi in segregation process was calculated (Curve I in Fig. 3). It can be seen from Fig. 3 that Curve I fits well with the experimental data, which confirms the reliability of this assumption.
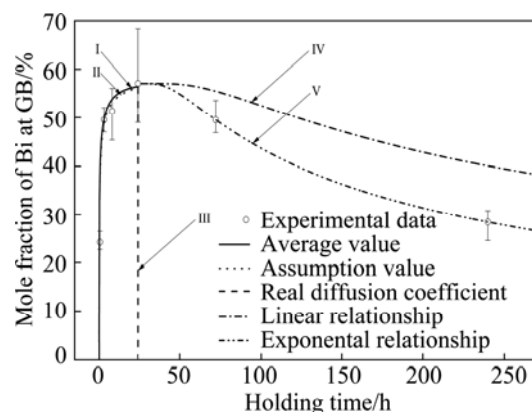
Fig. 3 Isothermal kinetics curves of Bi segregation in Cu bicrystals at 500 °C calculated by NGS theory (For segregation process, Curve I and Curve II were obtained by averaging simulated values of D_c in Table 3 and by Eq. (9), respectively. For de-segregation process, Curve III was calculated by the real diffusion coefficient D_i of Bi in Cu bicrystals; Curve IV and Curve V were calculated by assuming relationship between D_i and t to be linear and to be exponent, respectively)

Although the diffusion coefficient of Bi−vacancy complexes, D_c, is determined, it is only a specified value at 500 °C. A general formula for D_c in Cu alloys at any given temperature is still in demand. According to Arrehenius equation,

$$D_c=D_{c0}\exp[-Q_c/(RT)] \tag{6}$$

the diffusion coefficient of solute−vacancy complex depends on the activation energy Q_c and the frequency factor D_{c0}. XU et al [21] assumed that Q_c can be estimated by

$$Q_c=(Q_i+E_m)/2 \tag{7}$$

where Q_i and E_m are the activation energies of solute diffusion and vacancy migration, respectively. Since vacancies are formed when the samples are maintained at the higher temperature, E_m can be considered as

$$E_m=Q-E_f \tag{8}$$

where Q is the activation energy for self-diffusion of solute; E_f is the vacancy formation energy [31]. XU et al [21] assumed that D_{c0} is approximately replaced by the frequency factor of self-diffusion. In this case, the diffusion coefficient of Bi−vacancy complex is expressed

as

$$D_c = D_{c0}\exp[-(Q_i + Q - E_f)/(2RT)] \qquad (9)$$

Substituting the parameters listed in Tables 1 and 2 into Eqs. (4) and (9), it is obtained that

$$D_c = 7.8 \times 10^{-5}\exp[-1.46/(kT)] \qquad (10)$$

By Eq. (10), the kinetic data of segregation process of Bi were calculated (Curve II in Fig. 3). It is clear that Curve II also fits well with the experimental results, which confirms the reliability of the assumption of XU et al [21]. Thus, the Arrehenius equation for the diffusion coefficient of Bi−vacancy complex in Cu alloy is obtained.

3.2.2 De-segregation process of NGS of Bi

According to the NGS model, the reverse diffusion of Bi atoms to grain interior dominates the de-segregation process, and the apparent diffusion coefficient will be equal to the real diffusion coefficient finally. Therefore, the preferred way to calculate the kinetics of de-segregation process of the NGS of Bi is to replace the apparent diffusion coefficient D_i^A by the real diffusion coefficient D_i (Table 1). On this basis, the kinetic curve of NGS of Bi in the de-segregation process is calculated (Curve III in Fig. 3). It is seen that the calculated segregation level (Curve III in Fig. 3) drops dramatically to nearly zero. Therefore, the real diffusion coefficient is quite different from the apparent one and cannot be used for the whole de-segregation process.

It can be known from the NGS model that the apparent diffusion coefficient of solute atoms D_i^A will increase as annealing time t extends in the de-segregation process. The simulated values of D_i^A of Bi in Table 3 indicate this trend. In order to get a formula to quantify the increasing trend of the D_i^A, the simplest way is to assume the relationship between D_i^A and t to be linear, i.e. $D_i^A = (0.571t/t_c + 1.487) \times 10^{-25}$. On this basis, the kinetic data of NGS of Bi in the de-segregation process are calculated (Curve IV in Fig. 3). It is seen that the calculated segregation level (i.e. Curve IV) is higher than the measured values. Therefore, the assumption of liner relationship is inappropriate.

According to Refs. [13,29,30], the relationship between D_i and t is exponential. Therefore, the relationship can be formulated as

$$D_i^A = 7.66 \times 10^{at+b}\exp[-1.76/(kT)] \qquad (11)$$

Substituting the two simulated values of D_i^A (shown in Table 3) into Eq. (11), it can be obtained that $a = 8.45 \times 10^{-8}$ and $b = -13.37$. For the real diffusion coefficient of Bi in Cu bicrystal, D_i (shown in Table 1), the exponent parameter $(at+b)$ is −5. It implies that when the annealing time t is 9.9×10^7 s (i.e. $t > 1146.5t_c$), D_i^A approaches D_i of Bi in Cu bicrystal. On the basis of Eqs. (5) and (11), the kinetic data of NGS of Bi in the

de-segregation process are calculated (Curve V in Fig. 3). It is seen that the calculated segregation level (i.e. Curve V) fits quite well with the measured values. Therefore, the exponential relationship is applicable.

3.3 Calculation of isochrone of NGS of Bi

Based on the NGS model, the GB segregation of solute atoms will reach the maximum at the critical time during isothermal annealing. A formula for the maximum solute GB concentration $C_m(T_{i+1})$ at annealing temperature T_{i+1} after quenching from temperature T_i is given by [13,19]

$$C_m(T_{i+1}) = C_B \cdot \frac{E_b}{E_f} \cdot \exp\left(\frac{E_b - E_f}{kT_i} - \frac{E_b - E_f}{kT_{i+1}} \right) \qquad (12)$$

where E_b represents the vacancy–impurity binding energy. Substituting the parameters (Table 2) into Eq. (12), it is obtained that the values of $C_m(T_{i+1})$ fall between 0.01% and 0.07% (mole fraction) at holding temperatures between 400 and 650 °C. According to Section 3.2, the maximum content of Bi at GB at T_i is $C_m(T_i) = 3.67\%$ (mole fraction). It is clear that the calculated values of $C_m(T_{i+1})$ are far less than those of $C_m(T_i)$, which does not conform to the kinetic model of NGS. Therefore, Eq. (12) cannot effectively express the maximum solute content at the GB ($C_m(T_{i+1})$). Up to the present, there is no reliable expression for the maximum content of NGS which can be used to predict the $C_m(T_{i+1})$ quantitatively. Thus, the isochronal kinetic data of Bi segregation are unable to be calculated. Further studies should be carried out to setup a reliable equation for the maximum content $C_m(T_{i+1})$ of NGS.

4 Conclusions

1) For the Cu bicrystals containing 0.005% Bi aging at 500 °C after quenching at solution temperature of 950 °C, the GB segregation of Bi is verified with EGS model and NGS model, respectively. It is concluded that both the isothermal kinetics and isochronal kinetics of Bi segregation agree well with the theory of NGS.

2) Some important parameters characterizing the NGS of Bi in Cu bicrystal are obtained: diffusion coefficient of Bi−vacancy complexes $D_c = 7.8 \times 10^{-5} \times \exp[-1.46/(kT)]$, apparent diffusion coefficient of Bi atoms $D_i^A = 7.66 \times 10^{at+b}\exp[-1.76/(kT)]$, where $a = 8.45 \times 10^{-8}$, $b = -13.37$.

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Bi 在 Cu 双晶中的非平衡晶界偏聚

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摘 要：对 Bi 在 Cu 双晶中的晶界偏聚实验观察结果进行分析。利用平衡晶界偏聚(EGS)模型和非平衡晶界偏聚 (NGS)模型，分别对 500 °C 时 Bi 在 Cu 双晶中的等温偏聚动力学和退火 24 h 的等时偏聚动力学进行研究。从定性 分析和定量计算分析两方面推断出 Bi 的晶界偏聚特征与非平衡偏聚理论十分符合。根据非平衡晶界偏聚理论动 力学模型，计算得到 Bi−空位复合体扩散系数 D_c=7.8×10^{-5}exp[−1.46/(kT)]，以及 Bi 原子的表观扩散系数 D_i^A=7.66×10^{at+b}exp[−1.76/(kT)]，其中，a=8.45×10^{-8}，b=−13.37。这些数据有助于对 Cu 合金中 Bi 所导致的脆化进 行预测和控制的研究。

关键词：铋；铜；偏聚；晶界；扩散

(Edited by Wei-ping CHEN)