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Arrhenius relationship and two-step scheme in AF hyperdynamics simulation of diffusion of Mg/Zn interface

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Abstract: The accelerating factor (AF) method is a simple and appropriate way to investigate the atomic long-time deep diffusion at solid−solid interface. In the framework of AF hyperdynamics (HD) simulation, the relationship between the diffusion coefficient along the direction of *z*-axis which is normal to the Mg/Zn interface and temperature was investigated, and the AF's impact on the diffusion constant (D_0) and activation energy (Q^*) was studied. Then, two steps were taken to simulate the atomic diffusion process and the formation of new phases: one for acceleration and the other for equilibration. The results show that: the Arrhenius equation works well for the description of D_z with different accelerating factors; the AF has no effect on the diffusion constant D_0 in the case of no phase transition; and the relationship between Q^* and Q conforms to $Q^*=Q/A$. Then, the new Arrhenius equation for AFHD is successfully constructed as $D_z=D_0\exp[-Q/(ART)]$. Meanwhile, the authentic equilibrium conformations at any dynamic moment can only be reproduced by the equilibration simulation of the HD-simulated configurations.

Key words: accelerating factor method; Arrhenius equation; two-steps scheme; Mg/Zn interface; hyperdynamic simulation

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1 Introduction

Atomic diffusion is the fundamental alloying mechanism of the hot galvanization technique, which is very flourishing recently [1−5]. Whereas, the molecular dynamics simulation is one of the techniques most widely used for the kinetic process study due, in part, to its simplicity and ability to accurately sample the conformational space of some kinetic processes [6−8]. However, diffusion process in the solid metallic interface is of long time scale of second to hour relative to the nanosecond time scale limitation of the traditional molecular dynamics (MD) and almost impossible to be studied using the traditional MD simulation. Several methods, aimed at addressing this problem, have been introduced [9−11]. These include the accelerated molecular dynamics approach, named hyperdynamics method, based on the pioneering work of VOTER et al [12−14] that simulates infrequent events of metallic systems without preconceived notion of potential energy wells and barriers. This method eases the transition between energy basins by modifying the potential landscape. They proposed this hyperdynamics method to speed up MD simulations of long-time behavior by decreasing the amount of computational time spent in potential energy minima. The scheme modifies the potential energy surface, $V(r)$, by adding a bias potential, $\Delta V(r)$, to the true potential such that the potential surfaces near the minima are raised and those near the barrier or saddle point are left unaffected. Statistics sampled on the biased potential are then corrected to remove the effect of the bias.

Based on VOTER's framework of hyperdynamics [13,14], a new method, the accelerating factor (AF) method, was proposed to construct the bias potential effectively, and was applied to simulating the atomic diffusion at Mg/Zn interface with various accelerating factors [15]. As a result, when the accelerating factor A=5, the interfacial atoms have diffused completely, and the longstanding problem of simulating the atomic diffusion process at solid-solid interface by molecular

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dynamics was successfully solved.

Therewith, the relationship between the diffusion coefficient and temperature is the basic principle in studying the atomic diffusion at interface. For an atomic diffusion mechanism, the diffusion coefficient is required to meet the Arrhenius equation [16], which masters the relationship between the diffusion coefficient with the diffusion energy barrier Q and the diffusion constant D_0. Wherein, the diffusion constant is determined by the diffusion mechanism [17,18], containing diffusion paths, geometric factors and vibration frequency, etc. If the diffusion mechanism remains unchanged, the diffusion coefficient depends only on the energy barrier. However, the introduction of bias potential changes the original characteristics of the potential energy surface in AF hyperdynamics simulation. Although AF method fully retains the original characteristics of the potential energy surface, it is necessary to explore whether the relationship of atomic diffusion coefficient and temperature is still in accordance with Arrhenius equation, which implies that the AF method can truly reproduce the interfacial diffusion process. In the AF hyperdynamics simulations, the value of the acceleration factor can not be accurately determined to obtain the desired rate of diffusion. In other words, the quantitative relationship among the acceleration factor, the diffusion activation energy and the diffusion coefficient remains unclear. Therefore, the study of these problems helps better application of AF hyperdynamics simulation, and sheds new light on analyzing the atomic diffusion process in AF hyperdynamics simulations.

Moreover, the weakness of AF method, which has been pointed out previously [15], is that the system in AF molecular dynamics (AFMD) simulation is in transition rather than in equilibrium state. This is because the introduction of bias potential not only accelerates the diffusion of atoms, but also changes the interatomic potentials in the system. This will cause deviations from classical MD simulation in terms of configuration and energy. In order to obtain the microstructure and energy accurately, it is necessary to include the relaxation process of classical MD simulation behind each AFMD simulation to obtain the equilibrium state and energy. This procedure is termed two- or multi-step scheme.

In this work, AF method was applied to accelerating MD simulation of atomic diffusion at Mg/Zn metal interface. The relationship between one-dimensional diffusion coefficient along z-axis direction, denoted as D_z, and temperature was investigated, and the validation of Arrhenius equation and the relationship between AF, diffusion constant and activation energy was discussed. The phase distribution tendency of interface and the impact of two-step scheme on microstructure in the system were investigated.

2 Basic principle of AF hyperdynamics method

According to VOTER’s theory [13], the main idea of hyperdynamics is adding an bias potential on the original potential function, which raises the potential well and improves the atomic transition probability and thus speeds up the atomic diffusion, as shown in the following formula [13,14]:

$$V^*(r)=V(r)+\Delta V(r) \tag{1}$$

where $V^*(r)$ is the modified potential, $V(r)$ is the original potential, and $\Delta V(r)$ is the bias potential.

The bias potential increases in the probability for an atom to escape from a potential well. The relationship of HD simulation time t_{HD} and MD simulation time t_{MD} is

$$t_{\mathrm{HD}}=t_{\mathrm{MD}}\langle\exp[\beta\Delta V(r)]\rangle \tag{2}$$

where $\beta=1/kT$, k is Boltzmann's constant and T is temperature. The ensemble average $\langle\exp[\beta\Delta V(r)]\rangle$ represents the acceleration degree of HD, which is directly determined by the bias potential $\Delta V(r)$.

Previous studies [10,13,19] have proved theoretically that the HD simulation can obtain the canonical ensemble average by reweighting each sampling point in the phase space of HD simulation. The weight coefficient $\exp[\beta\Delta V(r)]$ is the Boltzmann factor of the bias potential.

AF method [15] constructs a set of bias potential within the framework of HD:

$$\Delta V(r)=\frac{(1-A)}{A}V(r) \tag{3}$$

$$V^*(r)=V(r)+\Delta V(r)=V(r)+\frac{(1-A)}{A}V(r)=\frac{V(r)}{A} \tag{4}$$

where the accelerating factor A represents the degree of acceleration. As A increases, the degree of acceleration increases. A is positive, and $A\geq1$. As shown in Eqs. (3) and (4), when $A=1$, the bias potential is zero. That is returning to the traditional MD simulations.

3 Test of Arrhenius relationship in AF hyperdynamics simulation

In this work, Lennard-Jones (LJ) potential is used to describe the Mg/Zn interfacial system. LJ potential parameters of Mg, Zn and other alloys were proposed in previous works [15].

The initial interfacial model of Mg (0001)/Zn (0001) is shown in Fig. 1(a). In this model Mg and Zn have 26 and 32 layers respectively. Each Mg layer contains 16×16=256 atoms while each Zn layer contains 20×20=400 atoms. This is mainly based on the consideration of the matching degree of the selected crystal plane. The total number of atoms in the system is 19456. The top and bottom two layers are fixed respectively, the periodic boundary conditions is only performed along *x*-axis and *y*-axis directions, the NVT ensemble is applied, and the time step Δt_{MD} is set 0.005 ps. Figure 1 (b) shows atomic number density $\rho(z)$ along the *z*-axis direction of the initial interface system, and the ordered distribution of Mg and Zn atoms along *z*-axis direction.

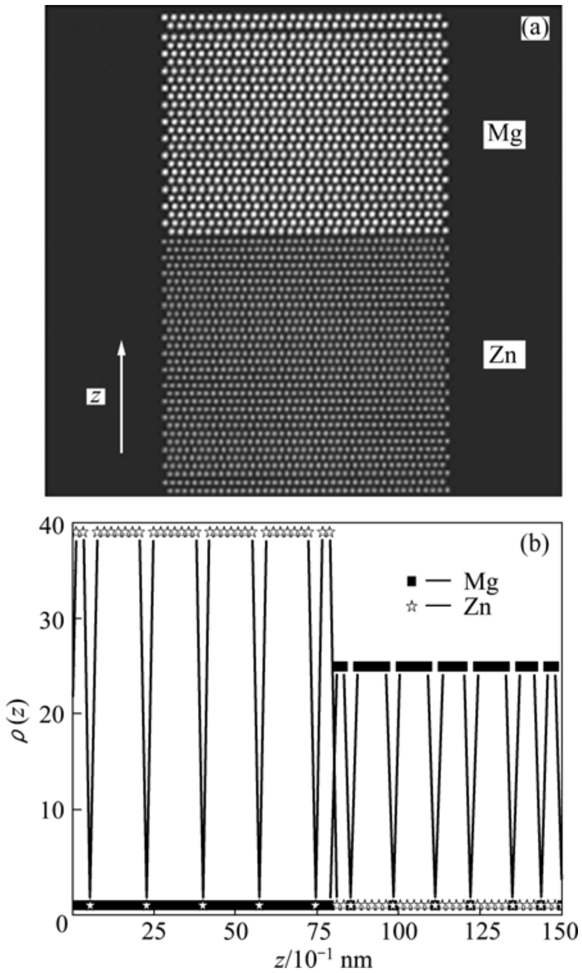

Fig. 1 Initial configuration of Mg(0001)/Zn(0001) interface (a) and its number density along *z*-axis direction (b)

As mentioned in the previous work [15], when the accelerating factor A<5, the interfacial atoms thermally vibrate in their equilibrium positions, and are difficult to escape from the potential wells to diffuse along the *z*-axis direction; when A=5, the interfacial diffusion is significant after 1×10^5 MD steps. For the convenience of studying the relationship between diffusion coefficient D and A, A takes 5−10 in this work for temperature T= 500, 600, 700 and 800 K, respectively.

The interfacial atomic 1D diffusion coefficient D_z along *z* direction is estimated according to the following EINSTEIN's diffusion equation:

$$D_z = \lim_{t\to\infty} \frac{\partial \left\langle z^2(t) \right\rangle}{2\partial t} \tag{5}$$

$$\left\langle z^2(t) \right\rangle = \left\langle [z_i(t) - z_i(0)]^2 \right\rangle$$

where $\langle z^2(t)\rangle$ is the mean square displacement (MSD).

In Eq. (5), D_z is equal to the slope of MSD—*t* curves. Only if the MSD curve is always close to a straight line, in cases of various temperatures and accelerating factors, D_z can be accurately calculated by approximating the slope of the straight line. For a system with relatively small A (A=5 or 6) and low temperature (~500 K), the simulation time should be extended due to the slow diffusion. When A=5, t_{MD} reaches 1225 ps, and when A=6, t_{MD} reaches 900 ps, and the results are shown in Fig. 2. It is found that when A=5, the MSD curve of Mg is nearly linear after t_{MD}>850 ps, and when A=6, MSD-Mg curve is nearly linear after t_{MD}>650 ps. Compared to Mg, the MSD curve of Zn is more linear because the lower melting point of Zn (~693 K relative to ~923 K of Mg) implies its stronger diffusibility. For the system with temperature and A higher than 500 K and 6, respectively, the atomic diffusion becomes faster and the MSD curve changes to a line more quickly (in 500 ps) and thus the D_z calculated will be more accurate.

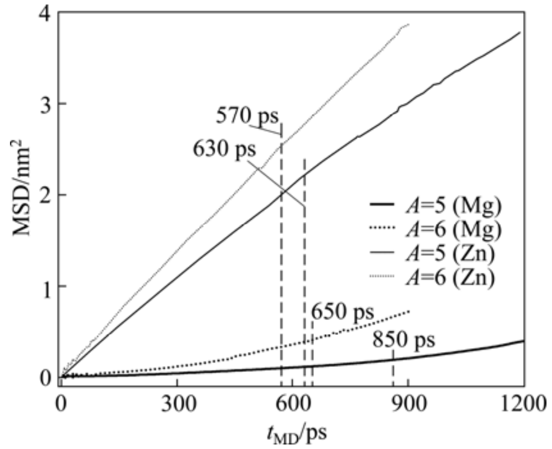

Fig. 2 MSDs of Mg and Zn at different accelerating factors at T=500 K

The famous Arrhenius equation is expressed as [17,18]

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \tag{6}$$

where D_0 is the diffusion constant, Q is the diffusion activation energy, and R is the gas constant. Taking the logarithm of both sides of Eq. (6), one can get the following relationship:

$$\ln D = \ln D_0 - \frac{Q}{RT} \tag{7}$$

It is generally believed that D_0 and Q are independent of temperature and only related to the diffusion mechanism and the nature of materials. In this case, if AF method simulation system obeys the Arrhenius equation, there should be a good linear relationship between $\ln D$ and $1/T$.

The linear relationships of $\ln D_z$ and $1/T$ for Mg and Zn with accelerating factors ranging from 5 to 10 are presented in Fig. 3, which strongly supports that the atomic 1D diffusion coefficient D_z is in accordance with the Arrhenius equation in AF hyperdynamics simulations.

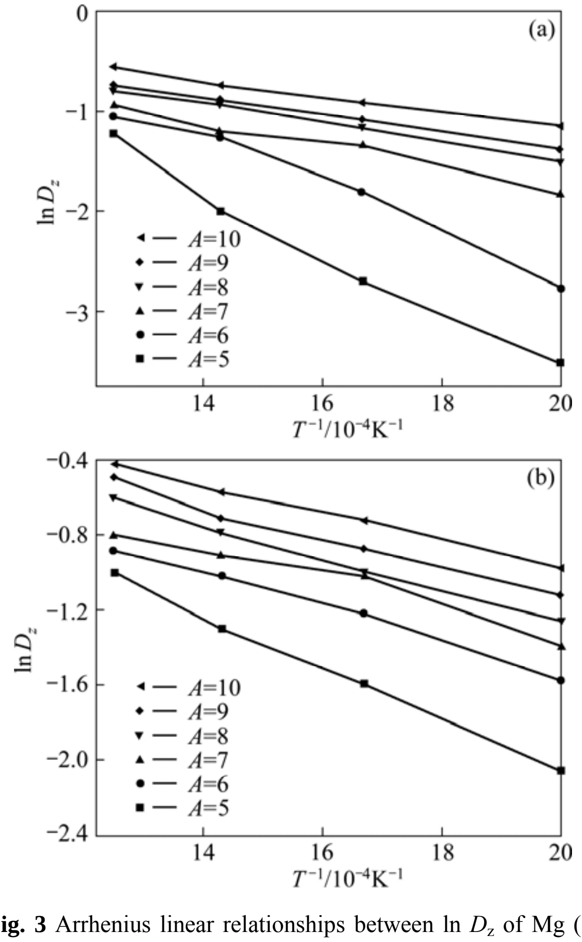

Fig. 3 Arrhenius linear relationships between $\ln D_z$ of Mg (a) and Zn (b) and $1/T$ at different accelerating factors from AF method

As mentioned above, when the diffusion mechanism is determined, D_0 is only related to the nature of materials and is independent of temperature. The prerequisite of this work, however, is that no phase transition happens in the course of heating, e.g. melting. The properties of material may change, which will cause the disturbance or even a drastic change of D_0. The role of the accelerating factor A is to lower the energy barrier to accelerate atomic jumping, while the role of heating system is to increase the kinetic energy of atoms to similarly accelerate atomic jumping. The roles of accelerating factor and heating are obviously different, but their effects are same. Thus, the phase transition may take place when we increase the accelerating factor or heat the system. We call this phenomenon the pseudo phase transition. The melting point of Mg is higher than that of Zn, so when the temperature is fixed, the increase of accelerating factor A will first induce the phase transition in Zn layers at Mg/Zn interfacial system. And the fact is in accordance with our expectation. When the temperature is 600 K, which is lower than the melting point of Zn and Mg, and A is increased to 3, the degree of disorder in Zn layers will suddenly rise in the course of simulation, which implies that the melting process takes place while the degree of disorder in Mg layers maintains low. In other word, A=3 is not high enough to make the Mg layers.

By fitting the data in Fig. 3 to Eq. (7), the values of $\ln D_0$ and Q/R at different A are obtained. The relationship of $\ln D_0$ and A is shown in Fig. 4. Figure 4 obviously implies that the value of $\ln D_0$ of Mg significantly decreases with the increase of A. But when the accelerating factor A≥7, the variation of $\ln D_0$ is small and the curve tends to be level. Meanwhile, the $\ln D_0$ of Zn changes little within the range of A. Considering the results of previous work and analyzing our results carefully, we conclude that: Zn layer is completely in a molten state in the range of A in this work, and thus its $\ln D_0$ changes little. $\ln D_0$ of Mg changes significantly due to the pseudo phase transition in Mg layers. By the results of the previous paper, it is found that when A=5, Mg layers which undergo a phase transition still partially maintain order. And thus, increasing A will further continue the pseudo phase transition in Mg layers. That is, in the variation range of A in this work, Mg is in a process of pseudo phase transition, so the value of $\ln D_0$ changes dramatically.

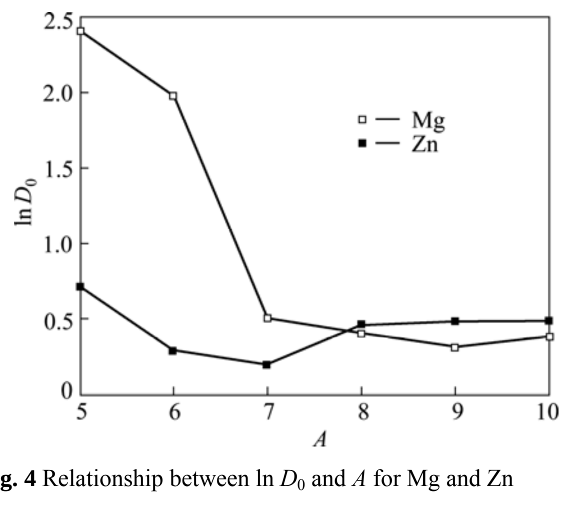

Fig. 4 Relationship between $\ln D_0$ and A for Mg and Zn

When $A \geq 7$, ln D_0 changes little, which can be considered as the end of pseudo phase transition of Mg, and the Mg layers are in a completely melted state. Therefore, without phase transition, the diffusion mechanism is certain, and thus the value of D_0 is only related with the nature of material and is independent of temperature and A.

According to the idea of HAMELBERG et al [20], the modified potential of AF method is $V^*(r) = V(r)/A$, so the barrier height H^* of the modified potential has the same relationship with the height H of the original potential, which is $H^* = H/A$. From this, it is inferred that the atomic diffusion activation energy Q^* and activation energy Q should have a similar relationship at AF hyperdynamics simulation as

$$Q^* = \frac{1}{A} Q \tag{8}$$

To examine this relationship, the Q^*/R of Mg and Zn are fitted with A to the form of time function $y = a/x^b$, in which x represents A and y represents Q^*/R. The results of the simulation with AF method are in accordance with Eq. (8) if parameter $b \approx 1$. Figure 4 implies that when A=5 or 6, pseudo phase transition of Mg does not finish, and when A=6 or 7, the fluctuation of ln D_0 is too large and Q^*/R can not fit other results well. After discarding these four points Fig. 5 is obtained and it is proved that Q^*/R and A fit well to Eq. (8) as b_{Mg}=1.1792 (~1) and b_{Zn}=0.9335 (~1).

Thus, the Arrhenius equation of 1D diffusion coefficient D_z and A in AF hyperdynamics simulation is eventually obtained as

$$D_z = D_0 \exp\left(-\frac{Q}{ART}\right) \tag{9}$$

where the effect of acceleration factor A on diffusion coefficient is obtained by the scaling of the diffusion activation energy while D_0 maintains no change.

4 Two-step scheme and its application to Mg/Zn metal interface

Mg(0001)/Zn(0001) interface, as shown in Fig. 1, is investigated at T=800 K within the two-step scheme. The first step, which is defined as accelerating step, is the simulation of diffusion process with AF acceleration method. In this step, the atomic interfacial diffusion process at Mg/Zn interface is simulated with AF method and the interfacial system is obtained in different stages of diffusion process. The second step, which is defined as equilibrium step, is the classical MD simulations of the previous stages for relaxation and equilibrium. We can just take every stage interfacial system going traditional MD simulation to make the structure and energy stabilized.

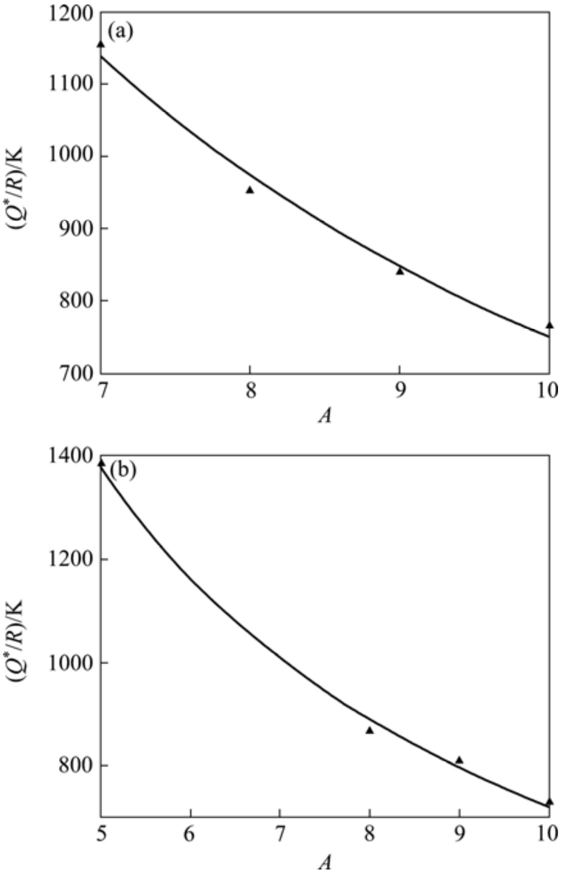

Fig. 5 Relationship between Q^*/R and A for Mg (a) and Zn (b)

Figure 6 exhibits phase diagram of Mg−Zn binary alloy [21]. There exist 5 stable alloys: $Mg_{51}Zn_{20}$, MgZn, Mg_2Zn_9, $MgZn_2$ and Mg_2Zn_{11}, of which $Mg_{51}Zn_{20}$ is stable in a very narrow range of temperature. The common characteristic of the later 4 alloys is that the number of magnesium atom is always not greater than the number of zinc atoms. So it can be defined that possible stable phases in Mg−Zn interface system have the same characteristics: the number of magnesium atom is always not greater than the number of zinc atom. On the contrary, the unstable region is defined that the

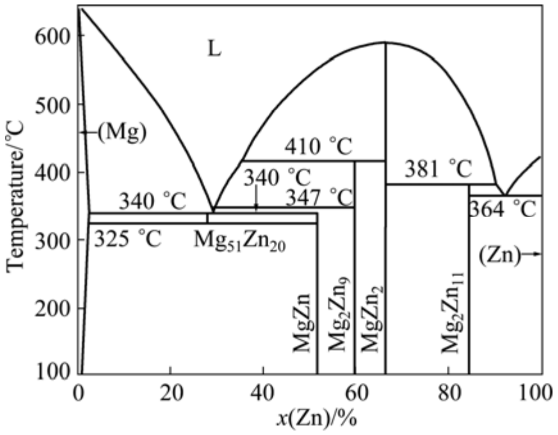

Fig. 6 Mg−Zn binary alloy phase diagram [21]

number of Mg exceeds that of Zn.

During the first step, i.e. accelerating step, an AF hyperdynamics simulation of total 700000 MD steps is made, corresponding to t_{HD}=3.5 ns, and the accelerating factor A is set to 10. Figure 7(a) exhibits the $\rho(z)$ curve at 2.0 ns, where the ellipsoid represents the unstable region defined above from Mg−Zn phase diagram. With diffusion time prolonging, unstable phase is gradually shrinking until it disappears at t_{HD}=3.5 ns, as shown in Figs. 7(b−e). Meanwhile, with diffusion going for a period of time, an area with equal Mg and Zn atom number is formed (the box marked in Fig. 7(b)), which doesn't appear early in Fig. 7(a). The phase diagram implies that the equilibrium phase with Mg/Zn atomic number ratio of 1:1 is MgZn [21]. In our simulation, once the diffusion is complete, the MgZn phase will always emerge, no matter of the accelerating factor or temperature. This implies that the MgZn phase region is symbolic for the stable or metastable diffusion process. This study also shows the trend of MgZn phase region

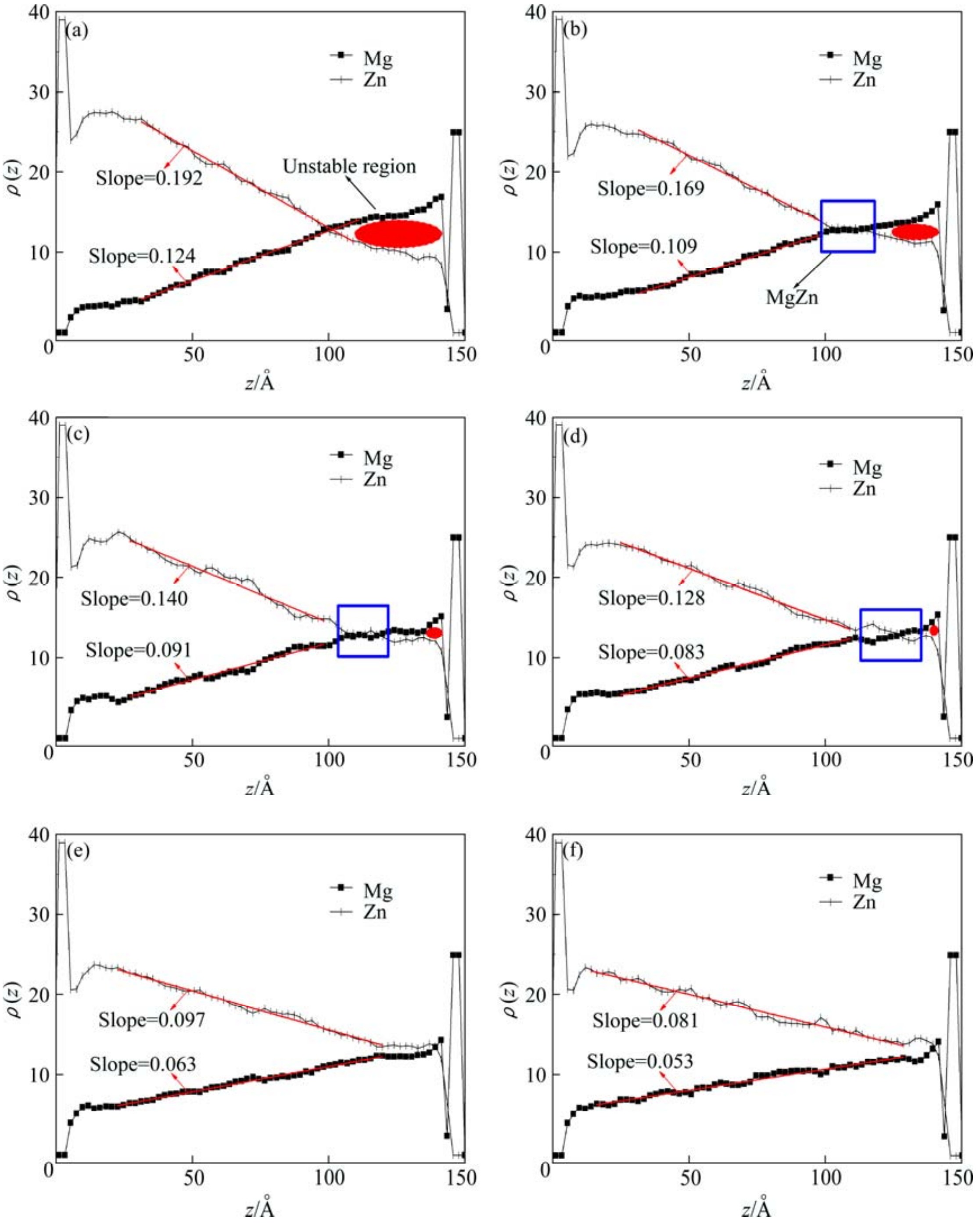

Fig. 7 z-axis direction atomic number density $\rho(z)$ change with time t_{HD} (T=800 K, A=10): (a) t_{HD}=2.0 ns; (b) t_{HD}=2.5 ns; (c) t_{HD}=2.75 ns; (d) t_{HD}=3.0 ns; (e) t_{HD}=3.5 ns; (f) t_{HD}=3.75 ns

propagating along Zn→Mg direction. When t_{HD}=3.0 ns, the region of MgZn phase begins to shrink (Fig. 7(d)) until t_{HD}=3.5 ns (Fig. 7(e)), MgZn phase disappeared completely. When t_{HD}=3.75 ns, the density of Mg is less than the density of Zn within the whole region. Therefore, from t_{HD}=3.0 ns, system dynamics process is a homogeneous process, that is, the system tends to form a single phase. Then, the whole diffusion process can be divided into three steps: unstable fast diffusion, stable even diffusion and homogeneous diffusion, while the three steps are separated by the appearance and disappearance of MgZn phase. The appearance of MgZn phase implies the end of the first step of unstable fast diffusion as well as the beginning of the second step of even diffusion. Similarly, the disappearance of MgZn implies the end of even diffusion and the beginning of the homogeneous diffusion. Figure 7 also exhibits the quantities of $\rho(z)$—z curve slopes for comparison and their curves are plotted in Fig. 8. First of all, the slope of the curve of Zn is always larger than that of Mg, which means the higher diffusion speed of Zn relative to that of Mg. Secondly, with the diffusion processing the slope decreases synchronously for both Zn and Mg. That is to say, this inter-diffusion requires the unchangeable diffusion coefficient ratio of Mg/Zn, ~1.54±0.01 in this work.

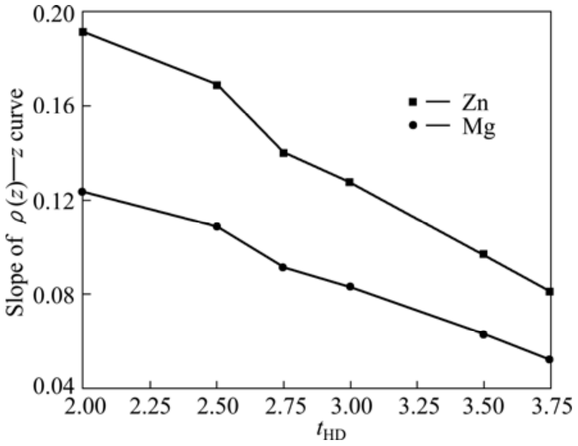

Fig. 8 Slopes of $\rho(z)$—z curves vs t_{HD}

Then, the configuration obtained from previous accelerating step at t_{HD}=3.5 ns is used as the initial configuration in the second step for equilibrium relaxation, in which the accelerating factor A is adjusted back to 1 and the simulation is performed for 100000 steps, corresponding to 500 ps.

Figure 9 presents the radial distribution functions (RDF) of both steps. Comparison of the RDFs between two steps shows that the first peak of step 2 is obviously sharper than that of step 1, and the second and third

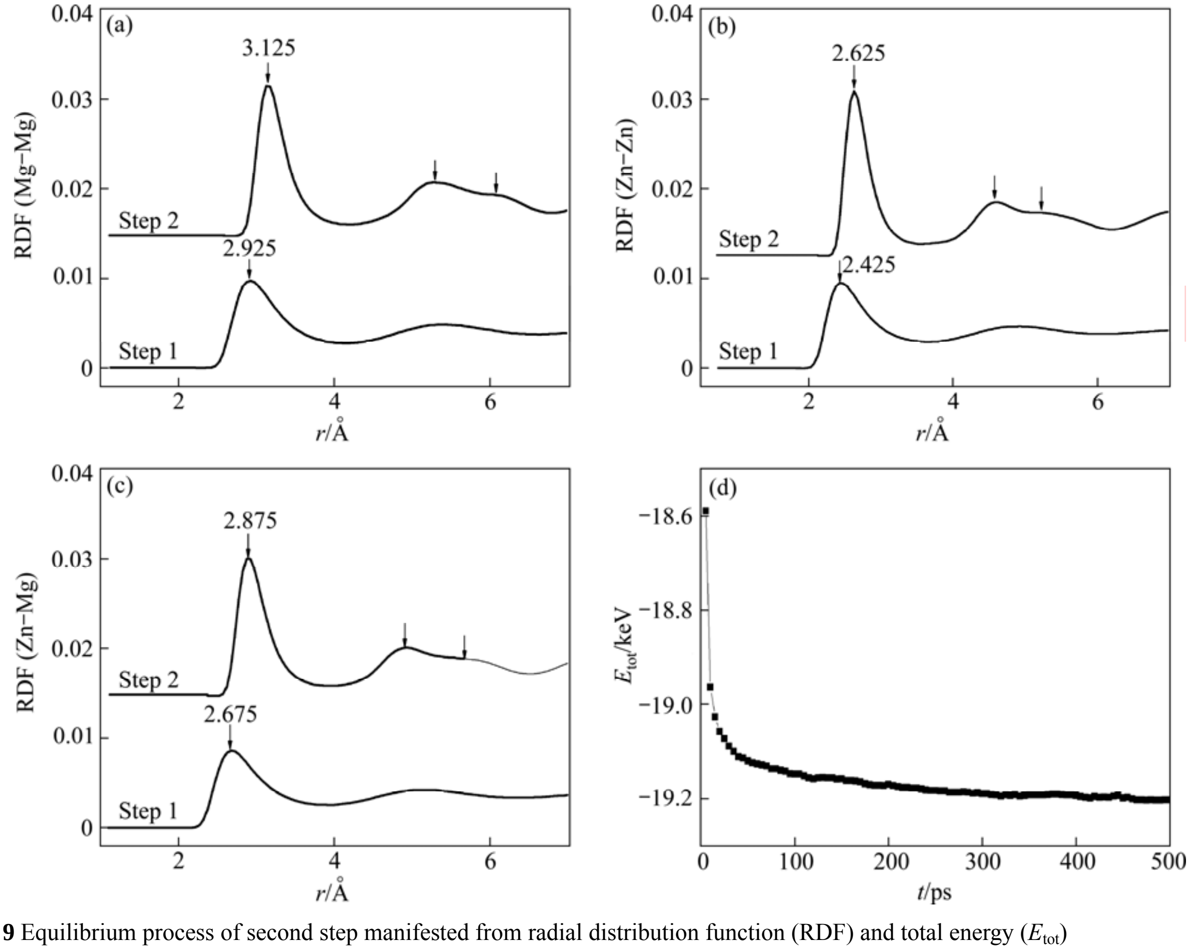

Fig. 9 Equilibrium process of second step manifested from radial distribution function (RDF) and total energy (E_{tot})

peaks emerge in the RDFs of step 2, which means the significant ordering of the structure in step 2. This ordering process signifies the decrease of the total energy, as shown in Fig. 9(d). As we know, the position of first peak, donated as r_1, represents the nearest neighbor distance. In Fig. 9, all r_1 are marked in the corresponding positions and also listed in Table 1 with experimental counterparts of $MgZn_2$ and Mg_2Zn_{11} alloys for comparison. The experimental data are from NIMS material database [22]. From Table 1, it can be clearly seen that the data of equilibrium step are much closer to the experimental result than those of accelerating step. All three distances after equilibrium process are very close to those of Mg_2Zn_{11}, so it can be deduced that the phase of Mg_2Zn_{11} should appear massively in the interface system after equilibrium step.

Table 1 Comparison of atomic nearest distances (r_1, corresponding to the first peaks of RDFs) of Zn−Zn, Mg−Mg and Zn−Mg between calculated and experimental values

Item	r_1(Zn−Zn)/ nm	r_1(Zn−Mg)/ nm	r_1(Mg−Mg)/ nm
End of accelerating step	0.243	0.268	0.293
End of equilibrium sep	0.263	0.288	0.313
$MgZn_2$ [22]	0.263	0.306	0.338
Mg_2Zn_{11} [22]	0.265	0.291	0.308

The variance of energy in the equilibrium step was also studied. Figure 9(d) implies that the total energy decreases significantly at first and then decrease gradually. After 400 ps, the system is close to equilibrium.

5 Conclusions

1) The diffusion coefficient D_z with different accelerating factors is in accordance with Arrhenius equation. In the case of no phase transition, when the diffusion mechanism is constant, D_0 is only associated with the nature of material, and independent of temperature and A. Thereby, the relationship between the atomic diffusion activation energy Q^* and the original activation energy Q is $Q^*=Q/A$, and the eventual Arrhenius relationship is $D_z=D_0\exp[-Q/(ART)]$ at the AF hyperdynamics simulation.

2) AF method can not only be applied to large scale simulation, but also predict the formation of new phase. In the simulation process of Mg/Zn interface, the entire dynamic process of the interfacial diffusion can be divided into three stages: unstable fast diffusion, stable even diffusion and homogeneous diffusion.

3) After the accelerated simulation, some equilibrium stages need to be investigated in the molecular dynamics simulation, which can lower the energy of the simulation system, and the system becomes more stable, and the microstructure is more close to the experimental results. So the two-step method has been proved that it is necessary in the dynamic simulation of acceleration.

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Mg/Zn 界面的 AF 超动力学中的阿累尼乌斯方程及两步法模拟机制

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摘 要：加速因子(AF)法是解决固体界面原子深层扩散简单且适用的方法。在 AF 超动力学模拟的框架内，以 Mg/Zn 界面为例，首先研究原子沿界面 z 轴方向上的一维扩散系数 D_z 与温度的关系，进而探讨加速因子 A 对扩散常数、扩散激活能的影响；然后，在 AF 法的基础上，通过两步法对 Mg/Zn 界面的原子扩散及相形成过程进行模拟。结果表明，不同加速因子下的扩散系数 D_z 均较好地遵循 Arrhenius 方程；在没有发生相变的情况下，当扩散机制一定时，扩散常数 D_0 的值与 A 无关；采用 AF 超动力学模拟时原子的扩散激活能 Q^* 与原激活能 Q 的关系符合 $Q^*=Q/A$。据此，构建了 AF 超动力学模拟下的一维阿累尼乌斯方程：$D_z=D_0\exp[-Q/(ART)]$。同时，AF 法可以对界面相形成过程及其变化趋势作预测，且只有两步法才能确切得到不同传质阶段的体系平衡结构及平衡能量。

关键词：加速因子法；阿累尼乌斯方程；两步法；Mg/Zn 界面；超动力学模拟

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