The effect of deposition temperature on the intermixing and microstructure of Fe/Ni thin film*

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(Received 16 December 2009; revised manuscript received 16 March 2010)

The physical vapour deposition of Ni atoms on α-Fe(001) surface under different deposition temperatures were simulated by molecular dynamics to study the intermixing and microstructure of the interfacial region. The results indicate that Ni atoms hardly penetrate into Fe substrate while Fe atoms easily diffuse into Ni deposition layers. The thickness of the intermixing region is temperature-dependent, with high temperatures yielding larger thicknesses. The deposited layers are mainly composed of amorphous phase due to the abnormal deposition behaviour of Ni and Fe. In the deposited Ni-rich phase, the relatively stable metallic compound B_2 structured FeNi is found under high deposition temperature conditions.

Keywords: molecular dynamics, physical vapour deposition, Ni/Fe thin film, temperature effect

PACC: 6855, 6120J

1. Introduction

The interfacial properties of metallic multilayers have been the subject of intense study in recent years. Since the structural and compositional variation at the interface is, eventually, going to have effect on the coating materials, the interface failure and precaution is still a puzzling problem.[1] Steel sheet with nickel coating formed by depositing nickel atoms on low-carbon steel sheet is widely used as an important type of structure-function material due to good corrosion resistance, attractive toughness and excellent plasticity. On this account, a considerable number of studies have been focused on the mechanical properties and corrosion resistance of this material.[2−6] Ma *et al.*[2] reviewed the tensile strain properties of the steel sheet with nickel coating. They found that the surface of these types of materials became unsmooth with micro-holes and was accompanied by cracks in the case of the tensile test. Quantitative investigation of the atomic structure and composition of the thin films is still a challenging issue due to the limitations of experimental analysis. However, molecular dynamics (MD) simulation using valid interatomic potentials provides abundant information at atomic scale of deposition about intermixing and mechanical properties. Thin film growth behaviours, such as MgO/MgO,[7] Fe/NiO,[8] Cu/Cu,[9,10] Cu/Ta,[11] and Co/Al[12] and microstructure evolutions[13,14] in metallic systems were successfully investigated by MD simulations. The simulation results contributed to understand the interface phenomena of the metallic multilayer and suggest a kinetic model to explain the experimental results. In the present work, we consider the temperature effect on the intermixing properties and microstructure of the deposited multilayer for Ni/Fe system.

2. Simulation methodology

Interatomic potentials play an important role in MD simulations, thus, considerable progress has been made by researchers in the development of empirical and semi-empirical many-body potentials. The embedded atom method (EAM), originally developed by Daw and Baskes, has been successfully used in analysing elastic properties, defect formation energy and fracture mechanism of various close-packed bulk metals.[15,16] In the present work, the modified EAM

*Project supported by the National Natural Science Foundation for Young Scientists of China (Grant No. 10702058) and the China Postdoctoral Science Foundation (Grant No. 20090451100).

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potential by Mishin *et al.*[17] for α-Fe/Ni system is adopted. In this method, the total energy $E_{\rm tot}$ of a collection of atoms is defined by the expression

$$E_{\rm tot} = \frac{1}{2}\sum_{i,j(i\neq j)} \Phi_{s_i s_j}(\boldsymbol{r}_{ij}) + \sum_i F_{s_i}(\boldsymbol{\rho}_i) + \frac{1}{2}\sum_{i,\alpha}(\mu_i^\alpha)^2 + \frac{1}{2}\sum_{i,\alpha,\beta}(\lambda_i^{\alpha\beta})^2 - \frac{1}{6}\sum_i v_i^2, \quad (1)$$

where indices i and j enumerate atoms and the superscripts α, $\beta = 1, 2, 3$ refer to the Cartesian directions. In this equation, the first two terms correspond to the general EAM potential and the last three terms introduce the contribution of the non-central components of bonding in order to describe the Fe–Fe, Fe–Ni and Ni–Ni interactions more accurately.

Before the simulations are performed, there are small differences of the substrate size in X, Y and Z directions due to the lattice constants of Fe and Ni changing with the deposition temperatures. The calculated lattice constants of Fe and Ni under different deposition temperatures are listed in Table 1. Since the ratio of the calculated lattice constants of Fe and Ni are very close to 13/16, the size of the substrate is set at 16 $a_{\rm Fe}$ ($a_{\rm Fe}$ is the lattice constant of Fe corresponding to certain deposition temperature) in X and Y directions and the ideal BCC structured α-Fe is created (as shown in Fig. 1). The deposition direction is perpendicular to the X–Y plane and periodic boundary conditions were implemented in the two transverse directions to eliminate the size effect. Three layers of atoms at the bottom of the substrate were fixed. The simulations were performed under constant temperature, which was kept at a desired value by scaling the atomic momentum. The Ni atoms were randomly placed on X–Y plane at a distance sufficiently far away from the top surface of the substrate and the time interval of two consecutive deposition atoms is set to 3 picoseconds (ps), that is, the deposition rate is 1.97 monolayer (ML) per nanosecond (ns). The kinetic energy of the deposited Ni atoms was set to 0.1 eV, which is the typical energy in vapour deposition or molecular beam epitaxial growth. Before the deposition, the substrate was relaxed to the stable deposition temperature.

Table 1. The calculated lattice constants of Fe and Ni under various deposition temperatures.

	100 K	300 K	500 K	700 K
Fe	2.869	2.876	2.884	2.892
Ni	3.522	3.526	3.529	3.532

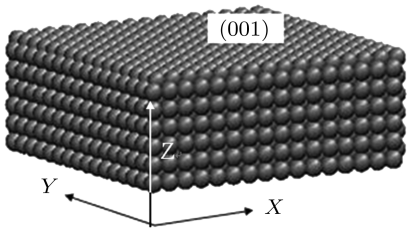


Fig. 1. The configuration of the α-Fe substrate, the (001) surface is perpendicular to Z direction.

3. Results and analysis

3.1. Effect on the intermixing character

Simulations were carried out under various deposition temperatures at a constant incident energy of 0.1 eV. Figures 2(a)–2(d) are composition variation across the interface after 10-ML Ni atoms were deposited on Fe substrate under the deposition temperatures of 100 K, 300 K, 500 K and 700 K, respectively. The dashed line is the original position of the substrate surface. Figure 2(a) shows that the interface region between the deposited Ni atom layer and the substrate is very sharp, which indicates that there was no obvious intermixing under low temperature. From Figs. 2(b)–2(d), it can be seen that there was an obvious intermixing region when the temperature was higher than 300 K. In addition, figure 2 also shows that the intermixing region consisted of Fe-rich and Ni-rich phases, and the thickness of Ni-rich phase is larger than that of Fe-rich phase. This indicates that the main diffusion was from Fe to Ni during the interface intermixing. The surface energy criteria[12] are proposed to explain this phenomenon. From the surface energy criteria, it is suggested that if the surface energy of the deposited element is larger than the sum of the surface energy of the substrate element and the interfacial energy between deposited and substrate elements, deposited atoms will penetrate into the substrate to minimize the total energy of the system. The calculated and other theoretical surface energies of α-Fe (001) and Ni (001), (110) and (111) surfaces are listed in Table 2. According to our calculations, Fe (001)/Ni (110) has the lowest interface energy of 0.98 J/m^2, it means that in the Ni (110) case, it has the highest surface energy and lowest interface energy. Thus the deposited Ni atoms can hardly penetrate into Fe (001) substrate according to surface energy criteria. The diffusion activation energy of Ni in α-Fe substrate is 2.934 eV,[20] which is much larger than the deposition energy of Ni atoms of 0.1 eV. In addition, it is

known that when the deposited atom is reaching the surface of the substrate, owing to the atomic interaction, there is a local acceleration of the deposited atom to enhance the kinetic energy of the deposited atom. Figure 3 shows the evolution of the kinetic energy when Ni atoms are deposited on Fe (001) surface, in which the peaks represent the maximum value of the Ni atom's kinetic energy due to the local acceleration. From Fig. 3, it can be seen that the maximum kinetic energy of the deposited Ni atoms can reach 2.64 eV when the deposition temperature is 100 K. Even so, the kinetic energy is still smaller than the diffusion activation energy of Ni in α-Fe substrate, so the deposited Ni atoms can hardly penetrate into α-Fe substrate.

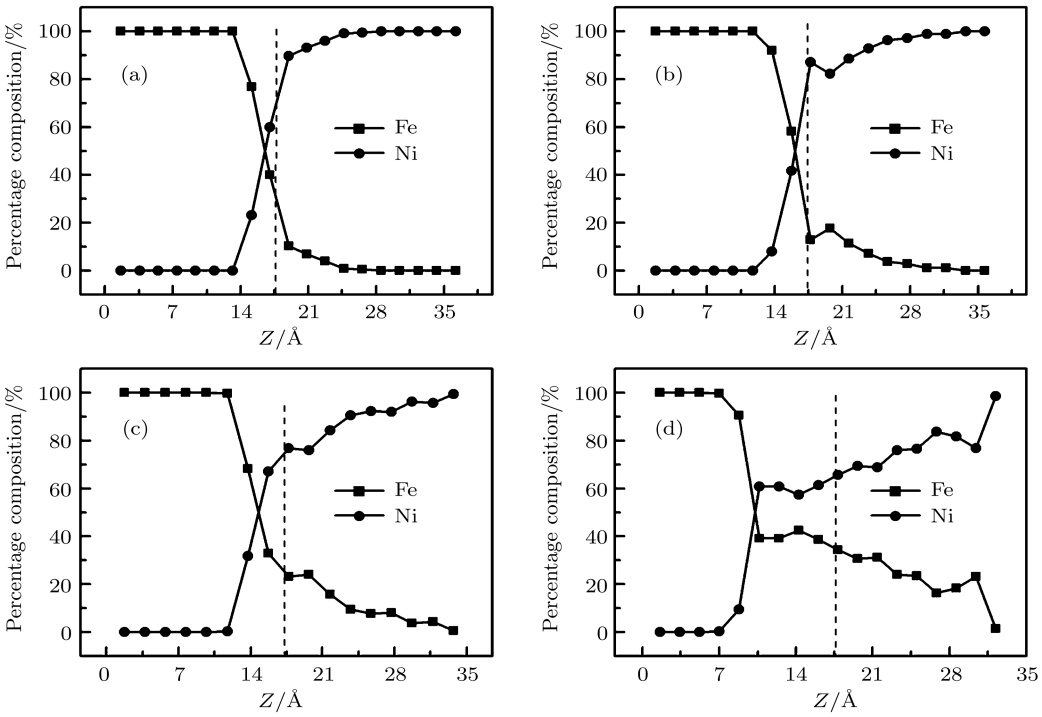


Fig. 2. Composition variations across the interface (a) 100 K, (b) 300 K, (c) 500 K and (d) 700 K. The dashed line represents the original surface position of Fe substrate (1 Å = 0.1 nm).

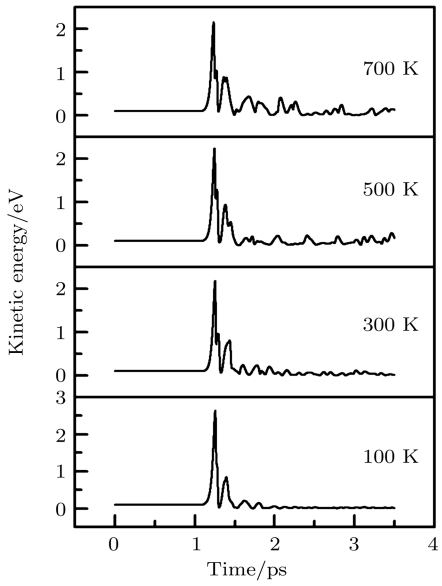


Fig. 3. The evolution of kinetic energy of the Ni atom deposited onto the Fe substrate.

Table 2. Surface energy of Fe (100), Ni (100), (110) and (111) in unit J/m^2.

	surface	calculated	others
Fe	(100)	1.561	1.625[18]
Ni	(100)	1.934	1.75[19]
	(110)	2.085	1.97[19]
	(111)	1.688	1.62[19]

Figure 4 shows the thickness of intermixing region under different temperatures, it clearly shows the linear relationship of diffusion thickness versus the deposition temperature. The thickness of the intermixing region was determined to be only approximately 8 Å when the temperature was 100 K, which indicates that there was no obvious intermixing. The thicknesses of intermixing region were approximately 14 Å, 18 Å and 25 Å under 300 K, 500 K and 700 K, respectively. This indicates the thickness of intermixing region depends

on the temperature, i.e., the higher the temperature, the thicker the intermixing region.

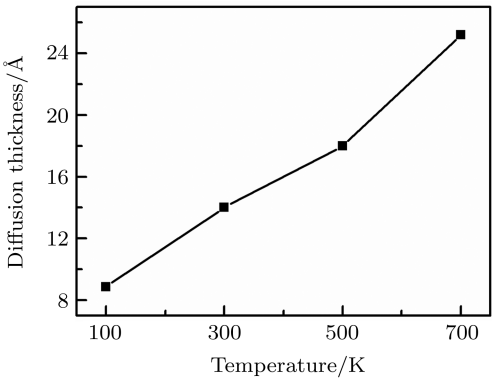


Fig. 4. The relationship of the diffusion thickness and the deposition temperature.

3.2. Effect on the microstructure

The radial distribution function (RDF) is employed to study the microstructure of the deposited Ni layers. Figure 5 is the RDF of the deposited Ni layers under different deposition temperatures. From Fig. 5, it can be seen that the deposition layers are mainly amorphous. Since the Ni atoms were randomly inserted on X–Y plane from the top of surface, the deposited Ni atoms should be disordered. In addition, the recrystallization can hardly be achieved at low temperature. Thus the deposited layers are amorphous when the temperatures were 100 K and 300 K. Electrodeposition experiments[21−23] show that Fe–Ni alloy is easy to achieve an amorphous structure. Since the deposited layers are mainly intermixing region when the deposition temperatures are 500 K and 700 K, the deposited layers are still amorphous even if recrystallization occurred.

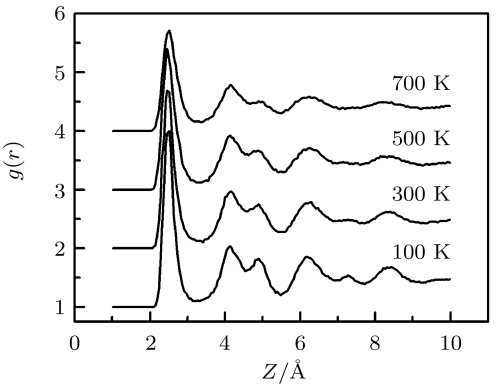


Fig. 5. The radial distribution function $g(r)$ of deposited Ni layers under 100 K, 300 K, 500 K and 700 K.

The pair analysis (PA) technique proposed by Honeycutt and Andersen[24] has been widely used in recent years to examine local structure features. In this technique, bond pairs are distinguished by four parameters, namely, i, j, m and n. i represents whether or not the two selected atoms are near-neighbours, j is the number of near-neighbours they have, m is the number of the near-neighbours they have in common, n is used to distinguish the type of the bonds. Two atoms are said to be near-neighbours if they are within a specified cutoff distance to each other. In the present work, the cutoff of Fe–Fe, Ni–Fe and Ni–Ni are proposed as 1.4σ, (1.12σ represents the equilibrium position of their pair interaction potentials).

Figure 6 shows the relative fraction of the various PA pair types versus temperature. It can be seen that under the four conditions, the sum percentage of the 1551 pair, 1431 pair and 1541 pair almost exceeds a percentage of 90, the percentage composition of 1431 pair and 1541 pair is relatively stable under these conditions, and that of 1551 pair falls down a little. The 1551 pair, 1431 pair, and 1541 pair all represent the amorphous phase. Figure 6 clearly indicates that the deposited Ni layer is mainly composed of the amorphous phase, which just matches the results of the radial distribution function analysis.

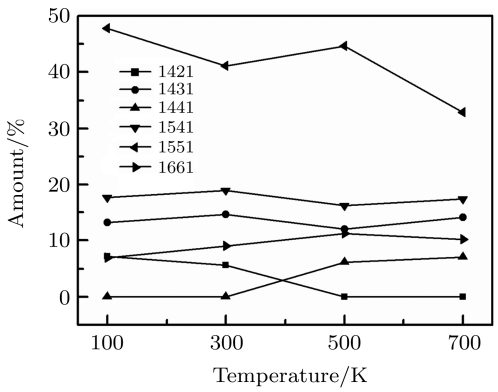


Fig. 6. The amount of the pair bonds in percentage at various deposition temperatures.

There is another phenomenon which is worth while mentioning. At higher deposition temperatures, the percentage composition of 1421 bond corresponding to the A_1 structure of Ni is decreased in the intermixing region. This kind of bond can hardly be found in the 500 K and 700 K cases, while the percentage composition of 1441 pair and 1661 pair, which represent the B_2 structure FeNi, is increased. It can be inferred that the clusters of B_2 FeNi are formed in Ni-rich phase at high deposition temperature. Bilayer Ni/Fe films grown using vacuum deposition[25]

show that the composition of FeNi increases with the annealing temperature, and starting from about $T = 920$ K upwards the samples consist of NiFe phase only. On the contrary, the composition of $FeNi_3$ decreases and disappears at $T = 920$ K with the increase of the annealing temperature. Our simulations are consistent with this result. B_2–FeNi is one of Fe/Ni metallic compounds that have relatively low formation energy. The intermixing region is amorphous-mixed with microcrystalline clusters in structure.

4. Conclusions

The physical vapour depositions of Ni atoms on α-Fe(001) surface at various temperatures were studied by molecular dynamics simulation. The atomic intermixing characters at the interface region of Fe(001)/Ni were studied and microstructure of the deposited layer was quantitatively analysed. The results are summarized as follows:

(i) There is obvious intermixing at the interface at high deposition temperature. The higher the temperature, the thicker the intermixing region. Ni atoms hardly penetrate into Fe substrate while Fe atoms easily diffuse into Ni deposition layers.

(ii) The deposited layers are mainly composed of amorphous phase due to the abnormal deposition behaviour of Ni and Fe.

(iii) In the deposited Ni-rich phase, a type of relatively low formation energy metallic compounds of B_2 structure FeNi is found at high deposition temperatures.

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