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Research on the Diffusion Behavior of Cu in Low-Carbon Steel under High Temperatures

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Abstract: The effective diffusion of Cu in Fe is the key to forming a stable transition layer between copper and low-carbon steel, but it is seriously affected by several factors, especially temperature, and the diffusion of Cu can only be completed at high temperatures. In order to analyze the diffusion coefficient of Cu in low-carbon steel under high temperatures, and to obtain the best diffusion temperature range of Cu in steel, the electrodeposition method was used to prepare the diffusion couple of copper and low-carbon steel, which would be annealed under different temperatures for 6 h; meanwhile, the MD models were also used to analyze the diffusion behavior of Cu in Fe at different temperatures. The results show that the diffusion of Cu in low-carbon steel could be realized by high-temperature annealing, and as the temperature increases, the thickness of the Cu/low-carbon steel transition layer shows an increasing trend. When the annealing temperature is between 900 °C and 1000 °C, the thickness of the transition layer increases the fastest. The results of the MD models show that, when the temperature is in the phase transition zone, the main restrictive link for the diffusion of Cu in Fe is the phase transition process of Fe; additionally, when the temperature is higher, the main restrictive link for the diffusion of Cu in Fe is the activity of the atom.

Keywords: Cu; low-carbon steel; diffusion coefficient; molecular dynamics; high-temperature annealing

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1. Introduction

Due to its excellent comprehensive mechanical properties and relatively low production cost, low-carbon steel has become the most widely used structural functional material. However, when it is exposed to the air, Fe, the main component of steel, easily reacts with oxygen to form iron oxides, resulting in corrosion of the surface of the steel. Especially in humid environment, the presence of H₂O promotes the formation of Fe(OH)₃, and accelerates the corrosion [1–3].

On a micro perspective, the corrosion of the steel mainly originates from the grain boundaries and the defects of the steel microstructure. Therefore, to avoid corrosion of steel, the corrosion of the grain boundaries and the defects should be prevented first. With corrosion tests, the American Society for Testing and Materials (ASTM) found that, when the Cu content in steel reached 0.04 wt%, the corrosion rate of the steel in the atmosphere was significantly reduced. The reason is mainly that the Cu is the corrosion-resistant element, and it is easy to segregate at the grain boundaries and the defects of the steel, thereby effectively playing a role in preventing the corrosion of the grain boundaries and the defects [4–6]. As the Cu content in steel increases, the corrosion resistance of steel would increase too, but it also brings a huge challenge to continuous casting for Cu-containing steel [7,8]. Because the Cu–Fe binary system is a typical mutual insoluble system [9], when the temperature is below 600 °C, the solubility of Cu in Fe is close to zero. The increase in Cu content in steel means that the Cu segregation would intensify also, and the crack defect rate of Cu-containing steel would increase significantly.

However, if the surface of the steel was coated with a layer of Cu, the corrosion of the steel would also be fundamentally inhibited, and this is a simple and efficient solution. Based on this concept, the simple processes of copper coating on steel, such as electrodeposition, hot dipping, and mechanical extrusion cladding, have been used to protect the steel [10–17]. However, these processes have a fatal flaw. Due to the low interface bonding force between the copper-clad layer and the steel surface, problems such as cracking of the bonding layer, partial damage, or peeling of the plating layer are likely occur in the subsequent processing or use, which would result in O₂ and H₂O entering from the breach and corroding the steel. A good copper–steel bonding layer can not only prevent the peeling of the copper plating layer, but also effectively prevent excessive deformation and cracking of the plating layer by the mechanical drag force of the bonding layer. Therefore, obtaining a stable copper–steel bonding layer is the core problem that the copper coating process needs to solve.

The key to the formation of stable bonding layer between copper and steel relies on the effective interdiffusion of Fe and Cu [18–20]. Since below 600 °C, the solubility of Cu in Fe is close to zero, the diffusion between Cu and Fe should be accomplished under high temperature. For the diffusion coefficient of Cu in Fe or steel, researchers have carried out a lot of work. Although the results have not been completely consistent due to the different experimental conditions, they all found that the diffusion coefficient of Cu in Fe did not show a single increasing or decreasing trend as the temperature rose, and the biggest influencing factor was the phase transformation of the steel.

Speich et al. analyzed the diffusion coefficient of Cu in Fe at different temperatures by the Cambridge microanalyzer [21]. They found that when the temperature was between 776 °C and 859 °C, $D = 8.6 \exp(-59,700/RT)$, and when the temperature was between 929 °C and 1020 °C, $D = 1.8 \exp(-70,500/RT)$. Lazarev et al. analyzed it by an activity measurement method. They found that when the temperature was between 707 °C and 850 °C, $D = 0.5.9 \exp(-59,000/RT)$, and when the temperature was between 920 °C and 1020 °C, $D = 92.0 \exp(-72,000/RT)$. G. Salje et al. analyzed it by the camera microanalyzer method, and they found that, when the temperature was between 772 °C and 880 °C, $D = 300 \exp(-67,800/RT)$, and when the temperature was between 925 °C and 1050 °C, $D = 0.19 \exp(-65,100/RT)$. Although there are some differences in the above results, most of the researchers found that the diffusion coefficient of Cu in Fe was significantly greater when the temperature is in the phase transition zone. However, there also some researchers had obtained the different results. For example, Anand et al. also analyzed the diffusion coefficient of Cu in Fe at different temperatures by the activity measurement method, but they obtained the different results [21]. They found that, when the temperature was between 650 °C and 750 °C, $D = 0.47 \exp(-58,380/RT)$, and when the temperature was between 800 °C and 1050 °C, $D = 0.57 \exp(-57,000/RT)$.

The different diffusion coefficients of Cu, described above, were affected by the experimental conditions and the composition of the experimental materials. Some researchers found that certain elements in Fe or steel have a greater impact on the outcome. ESMA Rassoul et al. studied the effect of carbon content in steel with the temperature higher than 900 °C [22]. They found that, in the austenite temperature range of steel, as the temperature increased, the diffusion coefficient of Cu would gradually increase too, but the carbon content in the steel had a great influence. Additionally, at any temperature, as the carbon content in the steel increased, the diffusion coefficient of Cu in the steel showed a gradually decreasing trend. M. Perek-Nowak et al. studied the influence of oxygen on the diffusion between Cu and Fe at 600–700 °C under the action of 20 N extrusion force [23]. They found that oxygen appeared to have great effect on formation of the connection, and for the microstructure, the dark-grey layer consisted of iron oxide with small addition of copper atoms (below 2 at. %), while light-grey irregular phase was made from copper (at least 70 at. %), iron, and oxygen. Peiyao Xu et al. studied the influence of sulfur on the diffusion between Cu and Fe by MS with first principles [24]. They found that the substitution energy

of sulfur at the Cu/Fe interface was the lowest, which would reduce the stability of the Cu/Fe interface and increase the diffusion coefficient.

Molecular dynamics analysis technology is widely used in the field of computational materials science, and it should be relatively sufficient in characterizing the atomic-scale structure and atomic diffusion behavior of materials [25,26]. Ouyang Yifang et al. used molecular dynamics model to analyze the atomic structure of an Fe/Al system and the interdiffusion behavior of Al and Fe, their results indicated that molecular dynamics model could also be used to analyze Cu/Fe system [27,28].

For the diffusion coefficient of Cu in Fe or steel, researchers have carried out a lot of studies, but the steel itself is also a complex alloy, and the elements in it have a great influence on the diffusion coefficient of Cu, so the results could hardly be used to solve the effective diffusion of Cu in the surface of low-carbon steel involved in this study directly. For this reason, this research used an electrodeposition method to plate copper on the surface of low-carbon steel, and performed diffusion annealing at different temperatures. Then, we analyzed the composition changes of Cu and Fe elements in the transition layer, and calculated the diffusion coefficient of Cu in low-carbon steel. At last, molecular dynamics analysis were also used to study the diffusion behavior of Cu in the surface of the low-carbon steel.

2. Experimental

2.1. Preparation of Diffusion Couple

In this research, the Cu/low-carbon steel diffusion couples were prepared by electrodeposition method. The cathode was the low-carbon, rolled steel plate; the anode was the pure copper plate. The composition of the low-carbon steel plate and the pure copper plate are shown in Tables 1 and 2, respectively. The size dimension of the steel plate was 30 mm × 15 mm × 3 mm.

Table 1. The composition of the low-carbon steel.

Composition	C	Si	Mn	P	S	Fe
Content %	0.15	0.10	1.20	0.02	0.02	others

Table 2. The composition of the pure copper.

Composition	Cu	Bi	Sb	As	Fe	Pb	S
Content %	99.90	0.001	0.002	0.002	0.005	0.005	0.005

The Ac1 and Ac3 temperatures of the steel were calculated by the computational formulas in [29]—the Ac1 temperature was 710 °C, the Ac3 temperature was 902 °C.

The main components of the electrodeposition solution are shown in Table 3, and all reagents were of analytical grade.

Table 3. Component of electrodeposition solution.

Reagent	Concentration (g/L)
Copper sulfate	30 g/L
Sodium citrate	147 g/L
Potassium sodium tartrate	45 g/L
Sodium bicarbonate	20 g/L
Potassium Nitrate	8 g/L

The device of electrodeposition is shown in Figure 1, and the volume of the beaker as the electrolytic cell was 500 mL.

Figure 1. Schematic diagram of electrodeposition device.

The specific parameters of the electrodeposition experiment were as follows: pH of solution was 11, solution temperature was 70 °C, current density was 5 A/dm², electrodeposition time was 30 min.

2.2. Diffusion Annealing Experiment

The SK-G06163 type horizontal tubular annealing furnace was used in this experiment, its rated power was 4 KW. The tube of the furnace was made of quartz, its total length was 1000 mm, and its constant temperature zone was 200 mm long, which is the middle of the tube and the temperature measurement zone. During the experiment, high-purity argon was used as the protective gas throughout. The diffusion annealing process used is shown in Figure 2.

Figure 2. Chart of diffusion annealing process.

Section 0~a: the heating stage, the heating rate was 5 °C/min. At this stage, the sample was placed at the cold end of the annealing furnace.

Section a~b: the heat preservation stage, the sample was placed in the constant temperature zone for diffusion annealing for 6 h.

Section b~c: the cooling stage, the sample was placed at the cold end of the annealing furnace, the cooling rate was 5 °C/min. When the furnace tube temperature reached room temperature, the sample was taken out for metallographic analysis and transition layer composition change analysis.

3. Results

The stability of a transition layer between copper and low-carbon steel is decided by the diffusion behavior of Cu in low-carbon steel, which also has a great influence on the microstructure of the surface of the steel. In this research, the microstructure of the cross-section of the transition layer was analyzed first, and the corrosive solution was nitric acid alcohol.

Figure 3a,b show the comparison of the microstructures of the cross-section of the transition layer before and after diffusion annealing at 1000 °C for 6 h. As shown in Figure 3a, the amount of diffusion of Cu in the surface area of the steel before diffusion annealing was very small, and it was difficult to find obvious diffusion areas in the results by optical microscopy, but the grains in the surface area of the steel became smaller.

Figure 3. Comparison of microstructure before and after diffusion annealing at 1000 °C: (a) before annealing; (b) after annealing.

As shown in Figure 3b, after diffusion annealing, an obvious transition layer appeared between the copper and the steel. Because the annealing temperature exceeded the austenite transformation temperature of low-carbon steel, the microstructure of the steel became coarser. However, for the copper–steel transition layer, due to the diffusion and infiltration of Cu, the microstructure of the transition layer was not significantly coarsened. On the one hand, the segregation and precipitation of Cu is good for the formation of the new phases of the steel; on the other hand, the new steady phases of Cu–Fe would be the cores to induce and generate more small grains during the cooling process.

Figure 4 shows the area scanning results of the distribution of Cu and Fe in the transition layer of the sample after diffusion annealing at 1000 °C. As shown in Figure 4, with diffusion annealing, Cu was mainly concentrated in the copper–steel contact area, and the content of Cu in other areas was extremely low. It is shown that the effective diffusion distance of Cu in steel was not very deep, and its distribution was not uniform. Taking into account the characteristics of Cu being easy to precipitate at the grain boundaries, the line scan analysis of the composition changes at the grain boundaries of the microstructure of the above sample were carried out, and the results are shown in Figure 5a,b.

Figure 4. The area scanning of the sample at 1000 °C.

Figure 5. The line scanning of the sample at 1000 °C: (a) the grain near to the copper coating area; (b) the grain not near to the copper coating area.

As shown in Figure 5a—for the grains near to the copper coating area—the closer to the copper coating area, the higher the Cu content in the grain, and the Cu content at the grain boundary was generally higher too; however, for the grains not near to the copper area, the Cu content at the grain boundary was significantly higher than that in the grain, as shown in Figure 5b. It is shown that the Cu content does not simply decrease with the increase in the diffusion distance. Therefore, in order to analyze the change of Cu content in the transition layer of the copper–steel composite material more accurately, the glow discharge apparatus was used to analyze the composition changing of Cu and Fe in the transition layer at different diffusion annealing temperatures.

Since the calculation of the diffusion coefficient of Cu in low-carbon steel requires the molar concentration of Cu, while the result of glow discharge apparatus is expressed by the mass concentration, the mass concentration of Cu should be converted to the molar concentration by using Equation (1).

$$C_{\text{Cu}} = \frac{P_{\text{Fe}}P_{\text{Cu}}}{W_{\text{Cu}}P_{\text{Fe}} + W_{\text{Fe}}P_{\text{Cu}}} \frac{W_{\text{Cu}}}{M_{\text{Cu}}} \quad (1)$$

where:

C_{Cu} —the molar concentration of Cu, mol/cm³;

M_{Cu} —the molar mass of Cu, g/mol;

W_{Cu} —mass concentration of Cu, %;

$P_{\text{Fe}}, P_{\text{Cu}}$ —the density of Fe and Cu, g/cm³.

The molar concentrations distribution of Cu and Fe of the diffusion-annealed samples at different temperatures are shown in Figure 4.

The molar concentration of Cu and Fe of the transition layer for different diffusion annealing temperatures of 750 °C, 800 °C, 850 °C, 900 °C, 950 °C, 980 °C, 1000 °C, and 1050 °C are shown in Figure 6a–h. In Figure 6, the Cu/Fe transition layer areas have been marked with vertical lines. In order to analyze the change trend of Cu and Fe concentration better, the left side of the intersection of Cu and Fe mass concentration curves was defined as the Cu area, and the right was defined as the Fe area, in this study.

As shown in Figure 6, as the diffusion annealing temperature rose, the thickness of the Cu/Fe transition layer increased gradually; when the temperature was between 800 °C and 850 °C, the thickness of the transition layer increased insignificantly; when the temperature was higher than 900 °C, the thickness of the transition layer started to increase rapidly; when the temperature reached 1000 °C, the growth of the thickness of the diffusion transition layer slowed down, even slightly slower than at 980 °C; when the temperature continued to rise, the thickness of the diffusion layer continued to increase, especially when the temperature reached 1050 °C, which is close to the melting point of Cu, and the thickness of the diffusion transition layer also reached the maximum value in this study, which exceeded 36 μm.

Figure 6. The molar concentration distribution of Cu and Fe in samples at different diffusion annealing temperatures; (a) 750 °C; (b) 800 °C; (c) 850 °C; (d) 900 °C; (e) 950 °C; (f) 980 °C; (g) 1000 °C; (h) 1050 °C.

As shown in Figure 6a–h, for the mass concentration distribution of Cu and Fe at different positions of the transition layer, the diffusion of Cu in Fe area was clearly weaker than that of Fe in Cu area at 750 °C. When the temperature was higher than 800 °C, as the temperature rose, the diffusion of Cu in Fe area and the diffusion of Fe in Cu area began to be similar; when the temperature continued to rise, Cu diffused more and more deeply into the Fe area, and the proportion of Cu area in the transition layer also increased. For the change of the initial mass concentration of Cu and Fe, as shown in Figure 6, as the annealing temperature rose, especially when the temperature was higher than 950 °C, the initial mass concentration of Cu decreased gradually, and the initial mass concentration of Fe began to increase. This shows that the solubility of Fe in the copper layer was gradually increasing. Taking into account the dissolution characteristics of Cu/Fe binary system at different temperatures, the gradual decrease in the diffusion layer width of Fe in Cu area at high temperatures was most likely due to the solubility of Fe in the copper layer. When the solubility of Fe in Cu gradually reached saturation, its diffusion coefficient was affected and gradually slowed down. As can be seen from Figure 6h, when the temperature reached 1050 °C, the concentration curves of Cu and Fe in the Cu area started to change slowly, and there were also some fluctuations. These are the results of the combined effect of the solubility of Fe in Cu and the diffusion of Fe in Cu.

4. Discussion

The results of the molar concentration of the Cu and Fe in the transition layer at different diffusion annealing temperatures shows that, due to the thin copper plating layer, the solubility of Fe in copper easily reached its saturation, and solubility had a great influence on its diffusion. This is also the reason why the proportion of Cu area in the transition layer gradually decreased with the increase in temperature, and even the molar concentration of Cu and Fe fluctuated in the Cu area under higher temperature.

In this study, since the diffusion of Fe in Cu is restricted by the thickness of the copper layer—and with Fe as the high temperature phase and Cu as the low temperature phase—in the question of whether a stable transition layer could be formed between copper and low-carbon steel, the diffusion of Cu in low-carbon steel had been proved to be the more critical factor. Therefore, in this study, the Cu content, accounting for 50% of the mass percentage of the system, was the starting point for researching the diffusion behavior of Cu in low-carbon steel.

4.1. Analysis of the Diffusion Coefficient

Based on the molar concentrations distribution of Cu and Fe of the samples at different diffusion annealing temperatures, as shown in Figure 6, and considering that the molar volume of the samples did not change much during diffusion annealing process, the den Broeder method was used to calculate the diffusion coefficient of Cu in low-carbon steel for different temperatures [30]. The calculation formula is shown as Equation (2).

$$D = \frac{1}{2t(\partial C/\partial x)_{x_0}} \left[\frac{C_1 - C_0}{C_1 - C_2} \int_{-\infty}^{x_0} (C - C_2) dx + \frac{C_0 - C_2}{C_1 - C_2} \int_{x_0}^{+\infty} (C_1 - C) dx \right] \quad (2)$$

where:

t —annealing time, s;

C_1, C_2 —maximum and minimum concentration, mol/m^{−3};

x_0 —the position where its concentration is C_0 , m.

The diffusion coefficient of Cu in low-carbon steel at different diffusion annealing temperatures was calculated, and the results are shown in Figure 7. As can be seen from Figure 7, except for 1000 °C, as the Cu concentration increases, the diffusion coefficient of Cu in low-carbon steel shows a gradually increasing trend, but their increase rates are different. When the temperature was below 900 °C, the concentration of Cu had little effect on the diffusion coefficient of Cu in low-carbon steel.

Figure 7. The relationship between the diffusion coefficient of Cu in low-carbon steel and the mass concentration of Cu at different diffusion annealing temperatures.

For the position where the mass concentration of Cu was 15%, when the diffusion annealing temperature was 1000 °C, the diffusion coefficient was the largest, the value for 900 °C was the second largest, and the value for 980 °C was the third largest. With the increase in the Cu concentration, the diffusion coefficient of Cu for 1050 °C had the biggest increase, the diffusion coefficient of Cu for 900 °C had the smallest increase, and its value was significantly lower than the corresponding results for 850 °C and 980 °C. When the mass concentration of Cu was 50% and the diffusion annealing temperature was 1050 °C, the diffusion coefficient was much larger than the corresponding values under other conditions.

Compared with other annealing temperatures, the diffusion coefficient of Cu for 1000 °C did not increase much with the increase in Cu concentration, and even when the Cu concentration exceeded 40%, the diffusion coefficient showed a downward trend. Considering that the initial diffusion coefficient of Cu was the highest at 1000 °C, it is easier to approach the solubility of Cu in low-carbon steel, with its diffusion behavior being affected. At 1050 °C, the temperature was close to the melting temperature of Cu, and had a higher transition energy. On the other hand, compared with other annealing temperatures, the solubility of Cu in low-carbon steel also increased rapidly, and this had a great effect on the diffusion of Cu in low-carbon steel.

4.2. Analysis of Diffusion Activation Energy

The relationship between the diffusion coefficient of Cu in low-carbon steel and the diffusion annealing temperature could be described by the Arrhenius formula [31], shown as follows in Equation (3):

$$D = D_0 \exp(-Q/RT) \quad (3)$$

where:

D —the diffusion coefficient of Cu in low-carbon steel, m^2/s ;

D_0 —frequency factor, m^2/s ;

Q —diffusion activation energy, J/mol ;

R —gas constant, $8.314 \text{ J}/\text{mol} \cdot \text{K}^{-1}$;

T —temperature, K .

Taking the logarithm for both sides of Equation (3), the result is shown as follows, in Equation (4):

$$\ln D = \ln D_0 - \frac{Q}{RT} \quad (4)$$

According to Equation (4), the relationship between $\ln D$ and $1/T$ at different temperatures with different Cu concentrations was calculated, and the results are shown in Figure 8.

Figure 8. The changing of $\ln D$ with Cu concentration at different temperatures: (a) phase transition zone; (b) austenite phase zone.

Figure 8a,b are the relationship between $\ln D$ and $1/T$ in phase transformation zone and austenite phase zone separately. The relationships have been linearly fitted, and the diffusion activation energy for different Cu concentrations were calculated by the slope of the straight line, and the result are shown in Figure 9.

Figure 9. The diffusion activation energy for different Cu concentrations.

As shown in Figure 8, whether in the phase transformation zone or the austenite phase zone, with the increase in Cu concentration, the value of $\ln D$ gradually increased. The changing trend of the fitted straight lines is relatively consistent, and there is no crossover. However, the slope of fitted lines for the phase transformation zone have a larger changing range than for the austenite phase zone.

As shown in Figure 9, when the Cu mass concentration was less than 20%, the diffusion activation energy of the phase transformation zone was greater than that of the austenite phase zone, but when the Cu mass concentration was higher than 20%, the diffusion activation energy of the austenite phase zone was significantly greater than that in the phase transformation zone; especially, as the Cu concentration increased, the difference between the two phase zones increased gradually.

The diffusion activation energy for different Cu concentrations in the phase transformation zone and the austenite phase zone were averaged, the value for the phase transformation zone was 159.5 kJ/mol, and the value for austenite phase zone was 172.1 kJ/mol. The diffusion activation energy of the austenite phase zone was relatively larger, meaning that the diffusion of Cu in the austenite phase zone was more difficult than in the phase transformation zone.

4.3. Analysis of Cu/Fe Diffusion Behavior with the MD Method

For the crystallographic characters, the structure density of FCC was 0.74, but the value of BCC was 0.68 [32,33], meaning that the diffusion of Cu in the austenite phase zone of low-carbon steel would be more difficult than in phase transition zone. However, it would be undeniable that the temperature of the austenite phase zone was significantly higher than that of the phase transition zone. High temperature would provide more energy for the diffusion to overcome the restriction of diffusion activation energy, which would also allow Cu in the austenite phase zone to obtain a higher diffusion coefficient in γ_{Fe} . In order to analyze the diffusion behavior of Cu/Fe further for different diffusion annealing temperatures, the MD method, by lamps, has been used in this research.

In consideration of the fact that the diffusion annealing temperature contains the phase transition zone (having both of the FCC and BCC structure at the same time) and the austenite phase zone of γ_{Fe} (only having the FCC structure), and given that there are a large number of vacancy defects in real low-carbon steel, the MD model both of α_{Fe} with BCC structure and Cu with FCC structure were used to analyze the diffusion behavior in the temperature zone from 750 °C to 900 °C, and the MD model both of γ_{Fe} with FCC structure and Cu with FCC structure were used to analyze the diffusion behavior in the temperature zone from 750 °C to 1050 °C, as shown in Figure 10a,b, respectively—the upper half is the Cu atoms and the lower half is the Fe atoms. In Figure 10a, the model contains 6743 Cu atoms and 6912 Fe atoms, and in Figure 10b, the model contains 6905 Cu atoms and 6912 Fe atoms. Both of the models had a 0.1% vacancy and the simulation time of the model was 200 ns.

Figure 10. The structure of the molecular dynamic models: (a) BCC Fe + FCC Cu; (b) FCC Fe + FCC Cu.

The calculation results of model with BCC α_{Fe} and FCC Cu after 200 ns for temperature from 750 °C to 900 °C are shown in Figure 11a–d. As shown in Figure 11, due to the different structure between Cu and Fe, with the increase in temperature, the stacking density and the clusters of Cu atoms at the Cu/ α_{Fe} interface increased significantly, meaning that the Cu/ α_{Fe} interface—the most active area—was greatly influenced by the increasing temperature. Because of the difference of the melting temperature, the activity of Cu atoms was greater than the activity of Fe atoms. It also means that the different structures of Cu and α_{Fe} provided more Cu atoms into the Cu/ α_{Fe} interface, if there were good chance for the diffusion of Cu, it would allow more Cu atoms to pass through the Cu/ α_{Fe} interface, and would be better for the diffusion of Cu.

Figure 11. The calculated results of the model with BCC α_{Fe} and FCC Cu: (a) 750 °C; (b) 800 °C; (c) 850 °C; (d) 900 °C.

The calculation results of model with FCC γ_{Fe} and FCC Cu after 200 ns for temperature from 750 °C to 1050 °C are shown in Figure 12a–h. As shown in Figure 12, when the temperature was lower than 900 °C, the structure of FCC γ_{Fe} was more stable. Compared with the γ_{Fe} area, the clusters in the Cu area increased more as the temperature rose. This meant that the activity of Cu gradually increased with the increase in temperature. When the temperature was higher than 950 °C, the activities of Cu and Fe atoms, especially the Fe atoms, were greatly enhanced, the distance between Cu atoms or between Fe atoms began to increase, and some Fe atoms were concentrated somewhere. However, it could be seen from Figure 12 that there was no obvious atom stacking or clusters at the Cu/Fe interfaces, meaning that the diffusion between Cu and γ_{Fe} with the same FCC structure should be mainly accomplished by Vacant-guided substitution. Considering the calculation results in Figure 11, the phase transition from BCC to FCC would provide the chance for the diffusion of Cu; if there were a lot of Cu atoms near the Cu/Fe interface, the diffusion of Cu would be enhanced. This means that the phase transition and higher temperature would be better for the diffusion of Cu.

The diffusion of Cu in Fe is the key for the forming of the stable transition layer. For the MD model in this research, the diffusion coefficient of Cu in the Cu/Fe system could be calculated by Equation (5).

$$D^* = \lim_{t \rightarrow \infty} \frac{1}{2Nt} \langle |r(t) - r(0)|^2 \rangle \quad (5)$$

where:

N —dimension of the simulation system, Z direction had been chosen in this research, $N = 1$;

t —simulation time, ns;

$r(t), r(0)$ —the atom position when the time is t and its initial position.

The calculation results of the MD model contain the mean square displacement data (MSD) of the atom and have been stored in the MSD file, the MSD could also be expressed by Equation (6) [34,35].

$$MSD = \langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle |r(t) - r(0)|^2 \rangle \quad (6)$$

Combining Equations (5) and (6) allows us to obtain Equation (7), as follows:

$$D^* = \frac{MSD}{6t} \quad (7)$$

Figure 12. The calculated results of the model with FCC γ_{Fe} and FCC Cu: (a) 750 °C; (b) 800 °C; (c) 850 °C; (d) 900 °C; (e) 950 °C; (f) 980 °C; (g) 1000 °C; (h) 1050 °C.

Based on Equation (7), combined with the MSD results at different temperatures, calculated by the above two molecular dynamics models, the diffusion coefficients at different temperatures were linearly fitted, and the results are shown in Figure 13.

As shown in Figure 13, when the temperature was less than 850 °C, the diffusion coefficient calculated by the annealing experiment was closer to the value calculated by the MD model with BCC α_{Fe} and FCC Cu; when the temperature was higher than 980 °C, the diffusion coefficient calculated by the annealing experiment was closer to the value calculated by the MD model with FCC γ_{Fe} and FCC Cu. For the calculation results of the MD models and the experimental analysis at 900 °C and 950 °C, although there are certain differences, the results could still reflect the decreasing trend of the diffusion coefficient of Cu in γ_{Fe} when the temperature rose from 900 °C to 950 °C. Since the diffusion of the element is driven by the concentration at corresponding position, the diffusion behavior of the element is closely related to the concentration difference of the element and the temperature. The calculation results of the MD model did not fully consider the effect of the element concentration, so there is a certain difference of the diffusion coefficient of Cu between the MD model and the annealing experiment. The experimental results of G. Salje have also been listed in Figure 13; it is shown that the results of G. Salje are significantly higher than the experimental analysis results and MD model calculation results involved in this study. This is mainly due to the solubility of Cu in Fe; the solubility is also the restrictive link for the diffusion of Cu in Fe. However, it is worth noting that, with the increase in temperature, the change trend of the diffusion coefficient measured by G. Salje is basically consistent with the results of this research.

Figure 13. The comparison of diffusion coefficients at different temperatures.

When the temperature was lower than 900 °C, Fe was in the process of phase transition from BCC α_{Fe} to FCC γ_{Fe} , but from the analysis results of the diffusion coefficients of Cu by the MD models with BCC α_{Fe} + FCC Cu and FCC γ_{Fe} + FCC Cu, the numerical value and change trend of result from the BCC α_{Fe} + FCC Cu model were more consistent with the results of the diffusion annealing experiment; this means that the α_{Fe} with BCC structure was the restrictive link of diffusion of Cu in Fe in the phase transition zone.

In order to further study the diffusion behavior of Cu in Fe, the RDF curves between Cu–Fe before and after diffusion under different temperature have been fitted in this research [36,37]. The results calculated by the BCC α_{Fe} + FCC Cu model have been chosen as the results of temperature lower than 900 °C, and the results calculated by FCC γ_{Fe} + FCC Cu model have been chosen as the results of temperature higher than 950 °C, all the results are shown in Figure 14.

Figure 14. The RDF curves of Cu–Fe before and after diffusion under different temperature.

In Figure 14, the RDF curves of Cu–Fe under different temperatures after the diffusion have been listed in the upper figure, and the RDF curves of Cu–Fe under different temperature before the diffusion have been listed in the lower figure. As shown in lower part of Figure 14, at the initial time, the main positional relationship between Cu–Fe was determined by the structure of Fe. When the temperature was less than or equal to 900 °C, it was a typical BCC α_{Fe} structure; and when the temperature was greater than or equal to 950 °C, it was a typical FCC γ_{Fe} structure. When diffusion occurred, the Cu–Fe positional relationship, corresponding to all temperatures, exhibited an FCC γ_{Fe} structure.

It can be seen from the RDF curves before and after the diffusion that, for the diffusion of Cu in α_{Fe} with BCC structure, in addition to the changes in the neighboring positions, the density of Cu atoms at the main neighboring positions of Fe atoms was significantly increased, and the amount of increase varies with the increase in temperature. As for the diffusion of Cu in γ_{Fe} with FCC structure, the main neighboring positions do not change significantly, but the density of Cu atoms at the main neighboring positions of Fe atoms was relatively reduced; the amount of decrease varied with the increased temperature, and only two main neighbor positions remained. This means that, as the r increases, the activity of the atom gradually increases too. The above RDF curves show that, when the temperature was in the phase transition zone, the main restrictive link for the diffusion of Cu in Fe was the phase transition process of Fe; and when the temperature was higher, the main restrictive link for the diffusion of Cu in Fe was the activity of the atom.

5. Conclusions

- (1) The diffusion of Cu in low-carbon steel can be realized by high-temperature annealing; as the temperature increases, the thickness of the Cu/low-carbon steel transition layer shows an increasing trend. When the annealing temperature is between 900 °C and 1000 °C, the thickness of the transition layer increases the fastest. When the temperature is between 750 °C and 900 °C, the concentration of Cu has little effect on the diffusion of Cu in low-carbon steel; when the temperature continues to rise, the higher the temperature, the greater the impact on the diffusion of Cu in low-carbon steel. The average value found of the diffusion activation energy was 159.5 kJ/mol in the phase transition zone and 172.1 kJ/mol in the austenite phase zone; this means that it was easier for Cu to diffuse in the phase transition zone than in the austenite phase zone.
- (2) For the calculation results of the MD models, we found the same changing trend of the diffusion coefficient of Cu in low-carbon steel, calculated for the annealing experiment. When the temperature was less than 850 °C, the diffusion coefficient calculated for the annealing experiment was closer to the value calculated by the MD model with BCC α_{Fe} and FCC Cu; when the temperature was higher than 980 °C, the diffusion coefficient calculated for annealing experiment was closer to the value calculated by the MD model with FCC γ_{Fe} and FCC Cu. The results of the RDF curves also show that when the temperature was in the phase transition zone, the main restrictive link for the diffusion of Cu in Fe was the phase transition process of Fe. When the temperature was higher, the main restrictive link for the diffusion of Cu in Fe was the activity of the atom.

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