

# FORMATION MECHANISM OF DIFFUSION-REACTION LAYER FOR A Cu/Ti DIFFUSION COUPLE UNDER DIFFERENT HEATING METHODS

## OBLIKOVANJE MEHANIZMA DIFUZIJSKO REAKCIJSKE PLASTI NA Cu/Ti POVRŠINI Z RAZLIČNIMI METODAMI SEGREVANJA

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Diffusion experiments with a Cu/Ti diffusion couple were conducted using the pulse-current-heating method and the conventional-heating method. The interfacial microstructure and the growth behavior of the diffusion-reaction layer were investigated with a scanning electron microscope (SEM), electron probe micro-analyzer (EPMA), energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). The results showed that the pulse-current heating could accelerate the diffusion of Ti atoms into a Cu matrix, significantly improve the growth rate of the diffusion-reaction layer, located at the side of the Cu matrix and make the growth of the interfacial reaction layer follow the parabolic rule. Meanwhile, under the pulse-current heating, the stratification of the diffusion-reaction layer was not obvious. Correspondingly, under the conventional heating method, the stratification of the diffusion-reaction layer was obvious and each reaction layer had a single microstructure, which was consistent with the reactant from the corresponding Cu-Ti binary-alloy phase diagram.

Keywords: Cu/Ti diffusion couple, pulse-current heating, diffusion, interfacial microstructure, interfacial-layer growth

Avtorji prispevka so izvedli difuzijske eksperimente na paru Cu/Ti. Pri tem so difuzijski par ogrevali na dva različna načina; z uporabo postopka impulznega tokovnega ogrevanja in konvencionalnega postopka ogrevanja. Medfazno mikrostrukturo in rast difuzijsko-reakcijske plasti so analizirali z vrstičnim elektronskim mikroskopom (SEM), mikroanalizatorjem z elektronsko sondo (EPMA), energijskim disperzijskim spektrometrom (EDS) in rentgensko difrakcijsko analizo (XRD). Rezultati analiz so pokazali, da impulzno tokovno ogrevanje lahko pospeši difuzijo atomov Ti v matriko Cu in očitno izboljša hitrost rasti difuzijske plasti, ki se nahaja na strani Cu matrike. Pri tem kinetika rasti difuzijsko-reakcijske plasti sledi paraboličnemu zakonu. Niso pa opazili izrazitega plastenja difuzijsko-reakcijske plasti, ki je bilo očitno pri konvencionalnem načinu ogrevanja difuzijskega para. V tem primeru je imela vsaka reakcijska plast enovito mikrostrukturo, skladno z reaktantoma v binarnem faznem diagramu Cu-Ti.

Ključne besede: difuzijski par Cu/Ti, impulzno tokovno ogrevanje, difuzija, medfazna mikrostruktura, rast medfazne plasti

## 1 INTRODUCTION

Titanium alloys have been widely used in aerospace, national defense, medical treatment, etc. since 1950s due to their high strength, good corrosion resistance and excellent heat resistance. However, their application is restricted due to the high price. Therefore, it is of great importance to study the joining technologies applicable for titanium alloys and other materials. Currently, the main joining technologies include brazing<sup>1,2</sup>, solid-phase diffusion welding,<sup>3,4</sup> superplastic forming and diffusion-bonding composite welding,<sup>5</sup> friction welding<sup>6</sup> and laser welding.<sup>7</sup> Diffusion welding has been widely used in the manufacture of titanium alloys that have a complex and thin-walled structure.<sup>8</sup>

A titanium alloy and copper alloy were joined with brazing and diffusion welding, respectively.<sup>9,10</sup> A comparative study showed that the microstructure and the strength of welded joints joined with two different methods show large differences. According to the Cu-Ti binary-alloy phase diagram,<sup>11</sup> titanium and copper gener-

ally cannot dissolve with each other. The solid solubility of titanium dissolved in copper is very small and the maximum solid solubility is ~5 % at 890 °C. Correspondingly, the solid solubility of copper dissolved in titanium is smaller and the maximum solid solubility is less than ~3 % at 798 °C. Several different kinds of interphases existed in a Cu-Ti binary-alloy system, and most of the interphases are intermetallic compounds.

The welding thermal process is a non-equilibrium thermodynamic process. It is difficult to simply judge the welding microstructure of titanium alloy and copper alloy joined by brazing and diffusion welding based on a Cu-Ti binary-alloy phase diagram. In this paper, diffusion experiments with a Cu/Ti diffusion couple were carried out using pulse-current heating and conventional heating at different heating temperatures and holding times. The effects of different heating methods and process parameters on the structure of an interfacial diffusion-reaction layer, together with the growth behavior of the diffusion-reaction layer under the condition of

pulse-current heating were carefully investigated. The related research is aimed to provide the necessary experimental data and theoretical analysis for predicting the structural type and growth characteristics of an interfacial reaction layer.

## 2 EXPERIMENTAL PART

### 2.1 Materials and methods

Cylindrical samples of pure copper and pure titanium (more than 99.99 %) with dimensions of  $\phi 20 \times 3$  mm were used as the diffusion matrix. The samples were first mechanically polished, then polished with sand papers and finally cleaned with ultrasonic vibration. The samples were assembled in the form of pure copper/pure titanium/pure copper, then diffused and joined in a heating furnace using different heating methods. When the pulse-current heating process was used, the vacuum was not less than 13 Pa, the axial pressure load was 1 MPa and the duty cycle of direct-current pulse was 16/2 (on/off). Meanwhile, the heating rate was set as 100 °C/min, the heating temperature was 700 °C and the holding time was chosen in a range of 3–10 min. The samples were cooled inside the furnace to room temperature after diffuse joining. For comparison, the diffusion experiment under conventional heating was conducted using the same diffusion couple and the related processing parameters were set as follows: the thermal vacuum degree was not less than  $1 \times 10^{-2}$  Pa, the axial pressure load was 1 MPa, the heating temperature was 800 °C with holding times of 10–60 min and a heating speed of 100 °C/min.

The analysis samples were cut by wire cutting along the centerline, and the surfaces of the analysis samples were polished with different-grade sand papers with Nos.1–5. The diffusion-reaction areas of the copper/tita-

nium samples were observed with a scanning electron microscope (SEM). The diffusion behavior between the Cu atoms and Ti atoms was analyzed with an electron-probe micro-analyzer (EPMA). The chemical compositions of feature points in the microstructure were detected with an energy dispersive spectrometer (EDS). The microstructure of the diffusion-reaction zone was characterized with X-ray diffraction (XRD).

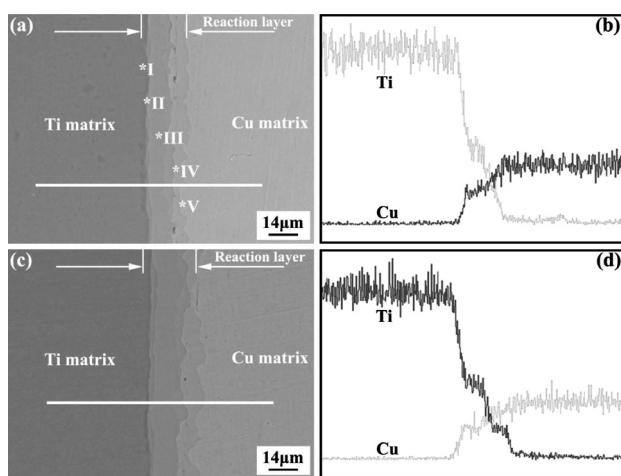
## 3 RESULTS AND ANALYSIS

### 3.1 Structure analysis of the diffusion-reaction layer under conventional heating

The diffusion-reaction experiments were carried on a Cu/Ti diffusion couple with a heating temperature of 800 °C, holding times of 10–60 min and axial pressure load of 1 MPa. **Figure 1** shows the morphology and elemental distribution of the diffusion-reaction layer at holding times of 30 min and 60 min.

**Figures 1a** and **1b** present SEM images and elemental-line scanning results for the sample with the holding time of 30 min. The results indicate that the inter-diffusion between the Cu atoms and Ti atoms occurred in the interface of the Cu/Ti diffusion couple. The deep-gray area on the left side is the Ti matrix, the gray region on the right side is the Cu matrix, and the middle region between them is the diffusion-reaction layer. The diffusion-reaction area is divided into five layers due to different contents of Ti atoms, namely, zones I–V. The width of zone I at the side of the Ti matrix is about 4–6  $\mu\text{m}$ , formed due to the reaction of the Cu atoms and Ti atoms when the Cu atoms diffused into the Ti matrix (**Figure 1b**). When the Ti atoms diffused into the Cu matrix, zone II was formed at the side of the Cu matrix. Its width is about 1–2  $\mu\text{m}$ . In addition, zone III, zone IV and zone V were formed along the depth direction of the Cu matrix. The widths of these three zones are (8–10, 2–3 and 5–7)  $\mu\text{m}$ , respectively. The total width of the diffusion-reaction layers is about 22–25  $\mu\text{m}$  after the holding time of 30 min.

**Figure 1c** shows a secondary electronic image of the diffusion-reaction layer after the holding time of 60 min. **Figure 1d** displays the elemental-line scanning result for the corresponding diffusion-reaction layer (**Figure 1c**). This diffusion-reaction layer also has five layers and the total width of the diffusion-reaction layer is increased to 30–34  $\mu\text{m}$  (**Figure 1c**), as compared with **Figure 1a**. The inter-diffusion behavior of the Cu atoms and Ti atoms in the Cu/Ti diffusion couple is more remarkable under the condition of conventional heating with the longer holding time of 60 min. Meanwhile, the rate of diffusion of the Ti atoms into the Cu matrix is higher than that of the Cu atoms into the Ti matrix. In order to determine the chemical composition of each reaction layer, EDS was employed to analyze the samples and the results are shown in **Table 1**. The compounds can be preliminary



**Figure 1:** Morphology and elemental distribution of diffusion-reaction layer in the case of conventional heating: a) morphology image for the holding time of 30 min; b) EPMA line-scanning result for the holding time of 30 min; c) morphology image for the holding time of 60 min; d) EPMA line-scanning result for the holding time of 60 min

determined based on the contents of the Ti atoms and Cu atoms for the feature points.

**Table 1:** EDS results for the interfacial reaction layer for conventional heating

Feature points	Ti	Cu	Compounds
I	95.78	4.22	( $\alpha$ -Ti)+Ti <sub>2</sub> Cu
II	72.06	27.94	Ti <sub>2</sub> Cu
III	51.46	48.54	TiCu
IV	23.23	76.77	TiCu <sub>4</sub>
V	9.26	90.74	(Cu)+TiCu <sub>4</sub>

In order to realize the diffusion of atoms, a driving force that can be either a concentration difference or a chemical potential difference is necessary. From the dynamic point of view, the inter-diffusion rate between the Cu atoms and Ti atoms was increased by increasing the temperature for the Cu/Ti diffusion couple. The driving force of diffusion was derived from the concentration difference for both sides of the interface. Meanwhile, as the diffusion rate of the Ti atoms was higher than that of the Cu atoms, the thickness of the diffusion-reaction layer at the side of the Cu matrix was increased significantly. From the view of thermodynamics, atoms always transferred spontaneously from the area of high chemical potential to the area of low chemical potential. As the chemical potential of Ti atoms was higher than that of Cu atoms, the gradient of chemical potential can also be deemed as a driving force that promoted the diffusion of the Ti atoms into the Cu matrix. According to the Cu-Ti binary-alloy phase diagram and reference<sup>12</sup>, there is a variety of intermediate phases between these two elements. Most of them are intermetallic compounds, including TiCu<sub>4</sub>, Ti<sub>2</sub>Cu<sub>3</sub>, Ti<sub>3</sub>Cu<sub>4</sub>, TiCu and Ti<sub>2</sub>Cu. Based on the experimental results and the existing related researches, we can say that when the heating temperature was set as 800 °C and

the holding time was 30 min, the reaction products of the Cu/Ti diffusion couple were ( $\alpha$ -Ti)+Ti<sub>2</sub>Cu in zone I, Ti<sub>2</sub>Cu in zone II, TiCu in zone III, TiCu<sub>4</sub> in zone IV and (Cu)+TiCu<sub>4</sub> in zone V. Under the conventional-heating conditions with sufficient holding time, practical structures of the diffusion-reaction layers were consistent with the compounds from the Cu-Ti binary-alloy phase diagram. However, it should be noted that it was hard to form a continuous and compact interfacial reaction layer in the Cu/Ti diffusion couple under the condition of the present conventional heating. In addition, microvoids can be found in the initial interface.

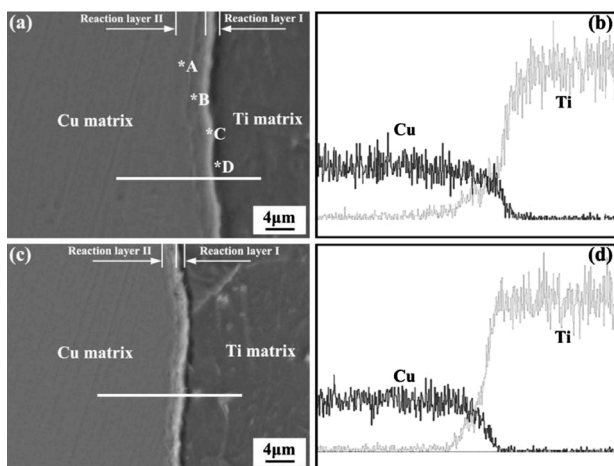
### 3.2 The structure of diffusion reaction layer under pulse current heating

For comparison, the diffusion experiment with the Cu/Ti diffusion couple was carried out under pulse-current heating at a temperature of 700 °C, holding times of 3–10 min and pulse-duty ratio of 16/2. **Figure 2** shows the morphology and elemental line-scanning results for the diffusion-reaction layer between the Cu matrix and the Ti matrix at holding times of 6 min and 3 min. **Table 2** lists EDS analysis results for feature points A, B, C and D.

**Table 2:** EDS results for the interfacial reaction layer for pulse-current heating

Feature points	Ti	Cu	Compounds
A	25.24	74.76	(Cu)+TiCu <sub>4</sub>
B	30.42	69.58	(Cu)+TiCu <sub>4</sub>
C	69.61	30.39	Ti <sub>2</sub> Cu
D	97.53	2.47	( $\alpha$ -Ti)+Ti <sub>2</sub> Cu

As shown in **Figure 2**, the Cu/Ti diffusion-reaction layer can be formed at different holding times. The width of the diffusion-reaction layer was 4–6  $\mu$ m at the holding time of 3 min (**Figure 2a**) while it grew up to 10–12  $\mu$ m at the holding time of 6 min (**Figure 2c**). When compared with the conventional heating method, a continuous and dense diffusion-reaction layer can be formed in a short holding time under the condition of pulse-current heating, proving that pulse-current heating can accelerate the process of interfacial reaction. **Figure 2b** shows the results of the elemental line-scanning analysis for the corresponding diffusion-reaction layer (**Figure 2a**). The diffusion of the Ti atoms into the Cu matrix can be clearly seen from **Figure 2b**. The depth of the titanium diffusion-reaction layer can be up to 10  $\mu$ m. However, the diffusion of the Cu atoms into the Ti matrix is invisible. These results confirmed that under the effects of pulse-current heating, the diffusion of the Ti atoms into the Cu matrix was promoted while the diffusion of the Cu atoms into the Ti matrix was suppressed. Although the heating temperature was relatively low and the holding time was very short, the diffusion-reaction layer between the Cu matrix and Ti matrix was formed.



**Figure 2:** Morphology and element distribution of diffusion-reaction layer in the case of pulse-current heating: a) morphology image for the holding time of 6 min, b) EPMA line-scanning result for the holding time of 6 min, c) morphology image for the holding time of 3 min, d) EPMA line-scanning result for the holding time of 3 min



When combining the line-scanning results with the EDS analysis, the interface reaction layer can be generally divided into two zones: the initial interface reaction layer I for the Cu/Ti diffusion couple (a width of about 1  $\mu\text{m}$ ) and the reaction layer II along the depth direction of the Cu matrix (a width of about 10  $\mu\text{m}$ ). According to the data in **Table 2**, the contents of Cu and Ti in points A and B were almost equal. When combining the Cu-Ti binary-alloy phase diagram with the related researches, it can be inferred that the compounds in points A and B were composed of a Cu solid solution and  $\text{TiCu}_4$  compound. Meanwhile, point C was composed of a  $\text{Ti}_2\text{Cu}$  compound and point D was composed of ( $\alpha$ -Ti) and  $\text{Ti}_2\text{Cu}$  compounds. That is to say, the  $\text{Ti}_2\text{Cu}$  phase was formed in the reaction layer I, while the  $\text{TiCu}_4$  phase was formed in the reaction layer II. Therefore, even though the heating temperature was only 700  $^\circ\text{C}$  and the holding time was only 6 min, the diffusion-reaction layer between the Cu matrix and the Ti matrix could still be formed under the condition of pulse current. When the holding time was prolonged, there was no obvious variation in the width of the reaction zone I, but the width of reaction zone II was increased remarkably.

**Figure 2d** shows the elemental line scanning of the diffusion-reaction layer between the Cu matrix and the Ti matrix at the holding time of 3 min. The elemental

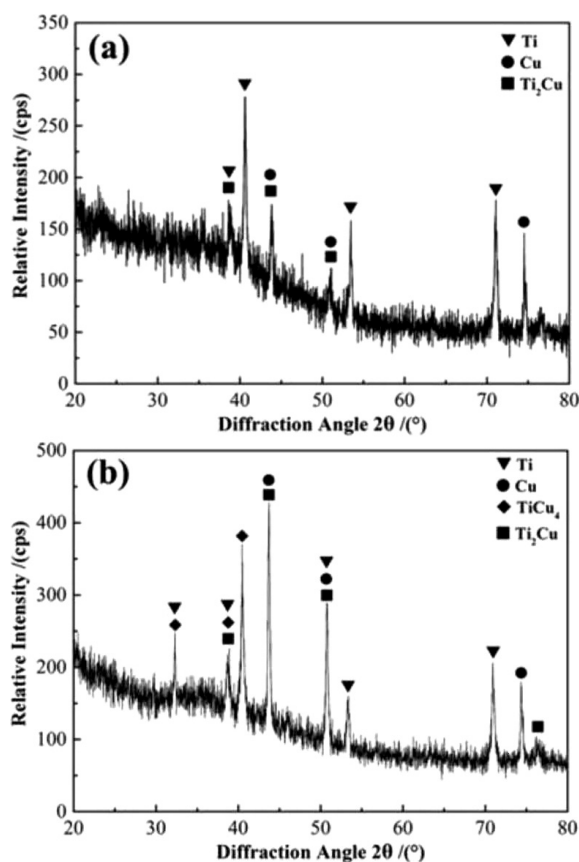
diffusion trends of the diffusion-reaction layer were approximately consistent with the results shown in **Figure 2b**. Namely, the diffusion rate of the Ti atoms into the Cu atoms was higher than that of the Cu atoms into the Ti atoms. The initial interfacial reaction layer I at the side of the Cu matrix was clearly visible, while the diffusion reaction layer II along the depth direction of the Cu matrix was invisible.

To further clarify the structural constitution of the interfacial reaction layer for the Cu/Ti diffusion couple under pulse current, the samples were grinded layer by layer, and then the interfacial reaction layer was tested with XRD. The XRD results are shown in **Figure 3**. It can be seen that the compounds were mainly composed of  $\text{TiCu}_4$  and  $\text{Ti}_2\text{Cu}$  at 700  $^\circ\text{C}$ , the holding time of 6 min and pulse-duty ratio of 16/2 (on/off).

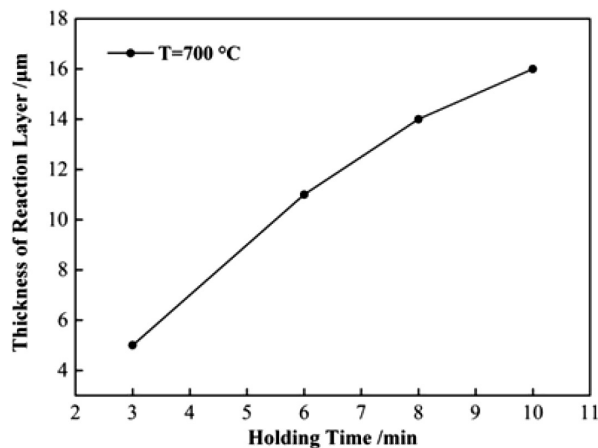
Based on the above analysis, it can be concluded that the width of the Cu/Ti diffusion-reaction layer increased with the increasing holding time for either conventional-heating diffusion or pulse-current-heating diffusion. By contrast, pulse current could accelerate the diffusion rate of the Ti atoms into the Cu matrix and also promote the formation of the interface reaction layer. Meanwhile, pulse current could also suppress the diffusion of the Cu atoms into the Ti matrix. In the case of conventional-heating diffusion, each reaction layer had only one single phase. The phase of each reaction layer was consistent with the phase from the Cu-Ti binary-alloy phase diagram. However, for pulse-current-heating diffusion, the stratification phenomenon of the whole reaction layer was not obvious. The  $\text{Ti}_2\text{Cu}$  compound was formed at the initial interface, while the  $\text{TiCu}_4$  compound was formed at the reaction layer along the depth direction of the Cu matrix. Although the diffusion of the Ti atoms into the Cu matrix was fast, no concentration gradient was formed in the whole reaction layer. It was inferred that pulse-current heating could change the structural constituent of the diffusion-reaction layer.

### 3.3 Growth of the interfacial reaction layer under pulse-current heating

According to the above analysis, the growth process of the interfacial reaction layer for the Cu/Ti diffusion couple under pulse-current heating could be divided into two stages, namely, (i) the nucleation and growth of a  $\text{Ti}_2\text{Cu}$  compound at the initial interface of the Cu/Ti diffusion couple, (ii) the nucleation and rapid growth of a  $\text{Ti}_4\text{Cu}$  compound at the side of the Cu matrix. During the first stage, a pure Cu/Ti diffusion couple was placed in a graphite heating body and pressure was pre-loaded with a pressure rod; the graphite heating body and the Cu/Ti diffusion couple were heated by pulsed direct current. The temperature at the initial interface was rapidly increased due to the heating of contact resistance. The inter-diffusion of the Ti atoms and Cu atoms was promoted; finally, the  $\text{Ti}_2\text{Cu}$  compound was formed.



**Figure 3:** XRD test results for diffusion-reaction layer at the holding time of 6 min: phases of initial interface reaction layer I, b) phases of reaction layer II



**Figure 4:** Relationship between the thickness of the interfacial reaction layer and the holding time under pulse-current heating

During the second stage, when the holding time was prolonged, free-state Ti atoms in the Ti matrix went across the  $\text{Ti}_2\text{Cu}$  compound layer, then they diffused into the Cu matrix and reacted with the Cu atoms; finally, the  $\text{TiCu}_4$  compound was formed. The  $\text{TiCu}_4$  reaction layer grew fast due to the higher diffusion rate of the Ti atoms. Meanwhile, the Cu matrix could provide enough free-state Cu atoms for the formation of a  $\text{TiCu}_4$  diffusion-reaction layer. However, the diffusion rate of the Cu atoms into the Ti matrix was slow, and it took more time for the Cu atoms to pass through the  $\text{Ti}_2\text{Cu}$  reaction layer, resulting in a relatively slow growth rate of the  $\text{Ti}_2\text{Cu}$  diffusion-reaction layer. The growth rate of the whole reaction layer depends on the growth rate of the  $\text{TiCu}_4$  compound.

According to **Figure 2** and the other experimental data, at the same heating temperature of 700 °C, axial pressure of 1MPa and pulse duty of 16/2, the average thickness values of the interfacial reaction layer of the Cu/Ti diffusion couple were (5, 11, 14 and 16)  $\mu\text{m}$ , corresponding with the holding times of 3, 6, 8 and 10 min. **Figure 4** shows the relationship between the holding time and the thickness of the diffusion reaction layer. The Y axis represents the thickness of the reaction layer and the X axis shows the square root of the holding time. It can be seen from Figure 4 that the growth of the interfacial reaction layer followed the parabolic law for the Cu/Ti diffusion couple under pulse-current heating.

#### 4 CONCLUSIONS

Under the condition of pulse-current heating, the diffusion rate of the Ti atoms into the Cu matrix was accelerated, the growth rate of the interfacial reaction layer was promoted, and the growth of the interfacial reaction layer followed the parabolic law.

For pulse-current-heating diffusion, the formation of the stratification of the whole reaction layer was not

obvious. A  $\text{Ti}_2\text{Cu}$  compound was formed at the initial interfacial layer while a single  $\text{Ti}_4\text{Cu}$  compound was formed in the depth direction of the Cu matrix.

For conventional-heating diffusion, a stratification of the whole reaction layer was obvious. If the holding time was long enough, the phase of each reaction layer was consistent with the phase from the Cu-Ti binary-alloy phase diagram.

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