Characteristic of temperature change in co-deposition of Al and Fe on copper by pack cementation

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ABSTRACT

An experimental apparatus was set up to simulate co-deposition of A1 and Fe on copper by pack cementation. The thermal history in the coating processes has been measured by K-type thermocouples. The effect of the pack mixture, holding temperature and heating rate on the temperature change on a copper surface were examined. The experimental results showed that a high A1 and Fe mass fraction in pack mixture causes an obvious temperature fluctuation while the NH_4C1 mass fraction and the $A1_2O_3$ mass fraction only slightly affect the temperature change. Two distinct jumps in the temperature of the sample occurred for all the experimental runs, which are strongly affected by the holding temperature. The heating rate of the pack mixture has a significant effect on the temperature change of the substrate surface. High heating rates cause an unsteady temperature change on the substrate surface.

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1. Introduction

The high electrical and thermal conductivity of copper makes it suitable for electronics and metallurgical industry. However, its strength and oxidation resistance are relatively low and cannot meet the requirements of fast developing industries. In order to improve these properties, many coating methods have been developed (such as internal oxidation, pack cementation, slurry fusion, hot dip, chemical vapor deposition, physical vapor deposition, electroplating, thermal spraying, and surface overlaying) [1–3]. Among all the coating processes which are used to improve the properties of copper surface, pack cementation has the advantages of economically producing coating on any substrate of complex geometry. The pack cementation process involves placing the substrates to be coated in a sealed or semi-sealed crucible together with a powder mixture that consists of metal elements to be deposited, halide activators and an inert alumina. The halide activators (stable halide or unstable halide salts such as AlF_3, NaCl, NH_4Cl and NH_4F) are added in small quantities (1–10 wt.%). When the sealed container is heated and held between 700 °C and 1150 °C for a certain duration, the activator reacts with metal element in the pack mixture to produce an atmosphere of source element halides which diffuse in the pack and transfer the source element to the substrate on which the coating is formed [4–6].

The deposition of aluminum by pack cementation is widely used as a coating method for high temperature materials because of its practical advantages over other coating method [7,8]. The deposition of aluminum by pack cementation is applied on steels to improve their corrosion resistance in oxidizing, sulfidizing and carburizing environments encountered in coal gasification plants, crude oil refineries and petrochemical industries. Another important application of the deposition of aluminum by pack cementation is on the inside surface of coolant channels in gas-turbine blades through which air is passed at high speed to keep the metal temperature low [4,9–11]. A frequent cause of turbine blade failure is the corrosion initiated from these channels. The high temperature resistance of aluminum is based on the formation of a continuous protective Al_2O_3 layer when exposed to oxidizing atmospheres. This layer provides a good diffusion barrier to withstand high temperature oxidation and therefore increases life time of substrate in aggressive atmospheres [12–15].

Although extensive researches have been conducted on the deposition of aluminum by pack cementation, most of these researches focused on understanding the structure and morphology of coating and investigating the oxidation and corrosion behaviors [16–20]. However, the temperature change on the substrate surface in pack cementation process is rarely mentioned in the literature. Knowledge of the temperature change on the substrate surface is very important to understand the coating process and to control the quality of the product by the co-deposition of aluminum and iron. Xiang and Datta [8,21] reported that the aluminising low alloy steels at temperatures below 700 °C by pack cementation shown the formation of complex Al–Fe intermetallic ($FeAl_3$, Fe_2Al_5, $Fe_{14}Al_{86}$) coating. This coating increases their high temperature durability in oxidative and corrosive environments without adversely affecting their mechanical strength and creep

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Table 1
Nominal composition of the T4 substrate (wt.%).

Element	Bi	Sb	As	Fe	Ni	Pb	Sn	S	O_2
Composition	0.003	0.05	0.05	0.05	0.2	0.05	0.05	0.01	0.1

resistance at elevated temperatures. So the co-deposition of aluminum and iron may expect to obtain complex Al–Fe intermetallic coating on copper due to the limited diffusion between copper substrate and co-deposited Al/Fe at low temperature. The aim of the present paper is to investigate characteristics of temperature change on the copper surface in co-deposition aluminum and iron on copper by pack cementation. Effects of pack mixture, holding temperature and heating rate on temperature change on copper surface were examined.

2. Experimental

The substrate used for this study is a commercial T4 grade copper. The nominal composition of this copper is given in Table 1, and its size is approximately 15 mm × 15 mm × 3 mm. The pack mixtures consist of aluminum and iron powder (−100 meshes) as diffusion metal, alumina powder (−100 meshes) as inert filler and NH$_4$Cl as activator. The aluminum and iron powder, alumina powder and NH$_4$Cl are commercially pure.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The cylindrical alumina crucible is 40 mm in the inner diameter, 50 mm in length and 3 mm in thickness. The inner layout of two crucibles (marked as crucible A and crucible B in Fig. 1) is completely symmetry, where the measuring point (marked C) of the furnace temperature is between crucible A and crucible B. The measuring points for the substrate temperature in the crucible A and crucible B are located at the center point of the rectangular surface of the substrate; K-type thermocouples are used in the experiments.

The surfaces of substrates were polished to a 1200 grit finish, washed in alkaline solution and ultrasonically cleaned with acetone for 20 min to remove surface rust and greasy dirt, and then rinsed with diluted sulfuric acid of 15% and air dried. Pack powder mixtures were prepared by weighing out and mixing appropriate amounts of Al$_2$O$_3$, Al, Fe and NH$_4$Cl. Packs were prepared by filling the pack powder mixtures around the substrates in the crucible. Thermocouples were inserted into the crucible (see Fig. 1). The crucible was sealed with an alumina lid and cement and then loaded into resistance furnace. Finally the experiment was carried on, and the data collected by a data collection device were recorded in the computer.

Table 2
Pack powder mixtures for the co-deposition of aluminum and iron.

No.	Composition (wt.%)				Al/Fe mass ratio	In crucible
	NH$_4$Cl	Al$_2$O$_3$	Al	Fe		
Group 1(A)	2	70	22.4	Balance	4:1	A
Group 1(B)	2	70	5.6	Balance	1:4	B
Group 2(A)	6	70	12	Balance	1:1	A
Group 2(B)	2	70	14	Balance	1:1	B
Group 3(A)	2	70	14	Balance	1:1	A
Group 3(B)	2	30	34	Balance	1:1	B

3. Results and discussion

Co-deposition of aluminum and iron on copper by pack cementation is a very complex dynamic system where pack mixture, holding temperature and heating rate have profound effects on the deposition rate and morphology. Upon heating, the NH$_4$Cl reacts with aluminum and iron to form NH$_3$ (g) and a series of volatile aluminum and iron halides; these halides then diffuse through the pack. These volatile halides react with copper substrate and generate aluminum and iron on substrate surface. Aluminum and iron continually diffuse into the copper substrate and then the film is formed.

3.1. Effect of pack mixture

Three groups of pack mixtures for the co-deposition of aluminum and iron listed in Table 2 were prepared by changing Al/Fe mass ratio, NH$_4$Cl mass fraction and Al$_2$O$_3$ mass fraction. The experiments were carried out according to the three groups; Fig. 2 shows the three groups of temperature curves.

As shown in Fig. 2, before reaching to 400 °C, the temperature change of the copper surface in the co-deposition of Al and Fe is similar for all three groups of pack mixtures. The temperature change has a certain delay relative to furnace temperature. At the same time, the slope of the temperature curve gradually increases; namely, temperature rising rate (dT/dt) increases slowly. Chemical reactions have not yet occurred among pack powders in this temperature range, so temperature change is due to heating from the furnace. The insulation of the crucible and pack powders in the heat transfer causes a certain delay in the substrate temperature change relative to the temperature of furnace.
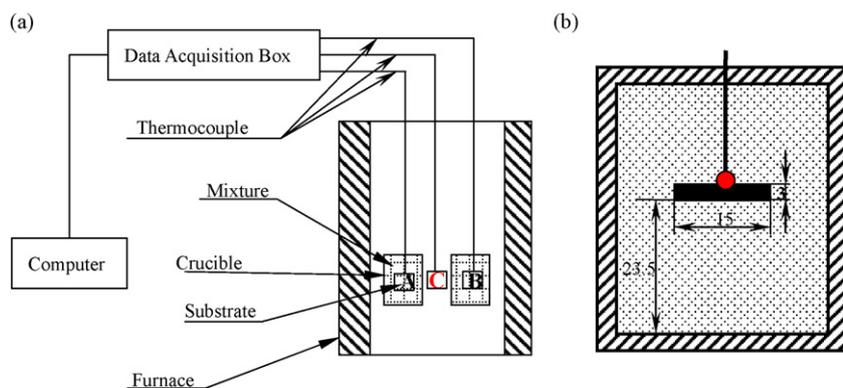
Fig. 1. Schematic diagram of the experimental apparatus.
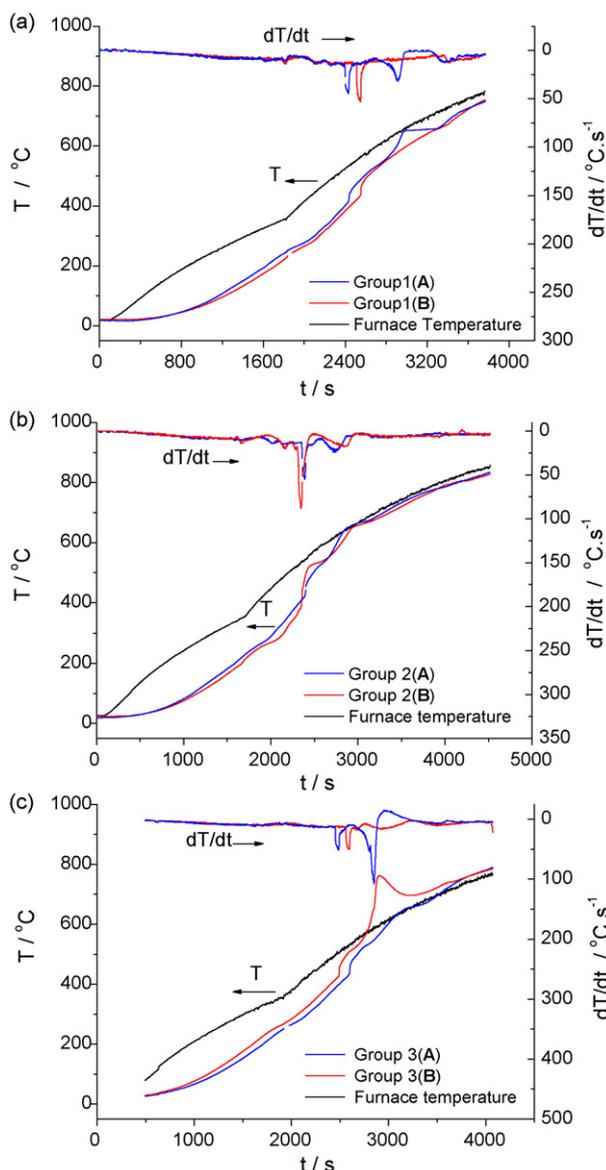
Fig. 2. Temperature curves at different pack mixtures (the curve represents copper surface temperature within different crucibles, for example: Group 3(A) represents the copper surface temperature for Group 3 of pack mixture within crucible A. Heating rate: 12 °C/min). (a) Effect of Al/Fe mass ratio on substrate surface temperature. (b) Effect of NH$_4$Cl mass fraction on substrate surface temperature. (c) Effect of Al$_2$O$_3$ mass fraction on substrate surface temperature.

The effect of the Al/Fe mass ratio on the substrate surface temperature is presented in Fig. 2(a). The first short-time temperature jump appears for both Group 1(A) and 1(B) at about 420 °C, and there is little difference between them. However, the second temperature jump for Group 1(A) (which has a longer duration and lower dT/dt than the first jump) appears between 550 °C and 630 °C; however, there is no obvious temperature jump for Group 1(B) at this temperature range. After a second temperature jump, the copper surface temperature for Group 1(A) approaches the furnace temperature and is maintained constant for a short time. As described previously, NH$_4$Cl reacts with aluminum and iron to form a series of metal halide vapor species. Among these vapor species, AlCl$_3$ and FeCl$_2$ are the main products and the thermochemical equations are as follows:

$$2HCl\ (g) + Fe\ (s) \rightarrow FeCl_2\ (g) + H_2\ (g) \quad \Delta_f H_m^\theta = -158\ kJ/mol \tag{1}$$

$$6HCl\ (g) + 2Al\ (s) \rightarrow 2AlCl_3\ (g) + 3H_2\ (g) \quad \Delta_f H_m^\theta = -615\ kJ/mol \tag{2}$$
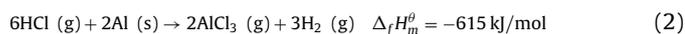
The above-mentioned exothermic reactions may cause two temperature jumps in Fig. 2(a). The activity of aluminum is higher than that of iron, and the specific surface area of aluminum powder is higher than that of iron powder, so aluminum reacting with NH$_4$Cl for Group 1(A) with a Al-to-Fe mass ratio of 4:1 is higher than Group 1(B) with a Al-to-Fe mass ratio of 1:4. The standard molar enthalpy of the formation of AlCl$_3$ is much higher than FeCl$_2$, so more heat is generated for Group 1(A), resulting in a higher temperature jump of its substrate than for Group 1(B) (between 550 °C and 630 °C). Furthermore, an inward aluminum diffusion would be induced in the coating process for a high Al-to-Fe mass ratio but an outward copper diffusion for a low Al-to-Fe mass ratio because the coating for high activity packs is formed predominantly by an inward diffusion of the deposition element while the coating for low activity packs grows predominantly by an outward diffusion of the substrate element [4,8,21,22].

The effect of the NH$_4$Cl mass fraction on the substrate surface temperature is given in Fig. 2(b). As shown in Fig. 2(b), two temperature jumps appear in the temperature curves for both of Group 2(A) and 2(B) at about 420 °C and 600 °C, respectively. After the second jump, both copper surface temperatures approach furnace temperatures, and the rising rate of the temperature is almost the same as the furnace temperature. These jumps may be due to exothermic reactions in the pack mixture and heat transfer from the furnace to the crucible. The rising rate of the first temperature jump for Group 2(B) is higher than that for Group 2(A) while the rising rate of the second temperature in two curves is almost the same. Chaliampalias et al. [23] reported that the activator mass fraction affects the coating quality and integrity. Coatings formed with a moderate mass fraction of NH$_4$Cl activator (about 3%) are compact, homogeneous with elevated thickness and have the best qualities to offer the maximum protection to the substrate. A lower NH$_4$Cl activator mass fraction (about 1%) leads to porous coatings with many voids and cavities which are likely to offer a diffusion path for corrosive elements to reach and react with the protected substrate. Comparing the results in Fig. 2(b), the curve with a lower mass fraction of NH$_4$Cl activator (about 2% for Group 2(B)) has a higher rising rate for its first temperature jump, causing a higher mass transfer of the deposition metal and consequently leading to the occurrence of the Kirkendall effect [24]. The jump for a moderate mass fraction of the NH$_4$Cl activator is smaller than for a lower mass fraction of the NH$_4$Cl activator because the generated gases for a lower mass fraction of NH$_4$Cl caused a small amount of heat transfer from the substrate. This is in agreement with the effect of the activator mass fraction reported by Chaliampalias et al. [23].

Fig. 2(c) shows the effect of the Al$_2$O$_3$ mass fraction on the substrate surface temperature. There is a short-time temperature jump in the temperature curves for both Group 3(A) and 3(B) near 420 °C, and the difference in temperature rising ranges between Group 3(A) and 3(B) is not obvious. However, the difference between them near 600 °C is distinct. The second temperature jump for Group 3(A) is slight, while the jump for Group 3(B) is much higher, and the substrate surface temperature for Group 3(B) greatly exceeds the furnace temperature. After reaching 750 °C, the temperature for Group 3(B) begins to drop rapidly until it reaches to the furnace temperature and remains consistent with it. Although the Al-to-Fe mass ratio remains constant in this group, the mass fraction of aluminum and iron increases with the decrease in the alumina mass fraction. Inert alumina do not react with other pack mixtures while the higher mass fraction of aluminum and iron make the reactions (1) and (2) more rapid, leading to an obvious temperature fluctuation for Group 3(B) curve. Three different disadvantages are caused by rapid reactions (1) and (2). Firstly, products generated by rapid reactions are not completely trans-

ferred from reaction site to the substrate in time, leading to the accumulation of products in the reaction site. This accumulation may cause the occurrence of side reactions which have a deleterious effect on the deposition of diffusion metal. Secondly, rapid reactions make the concentration gradient of products high from the reaction site to the substrate, causing an increase in the mass transfer and consequently making the replacement reaction incomplete on the substrate surface. Finally, the rapid occurrence of replacement reactions can cause defects on the surface (such as voids and cavities). In consideration of disadvantages of the high mass fraction of aluminum and iron, this situation should be avoided. In summary, the reactions (1) and (2) for the three groups of pack mixtures cause the jumps in temperature curves between 400 °C and 650 °C and no jump at temperature over 650 °C means no reaction happened. The characteristic of temperature jumps represents the reaction processes, which is helpful to understand the coating process and to control the quality of the coating by pack cementation.

3.2. Effect of holding temperature

In order to prevent oxidation on the surface of pure copper, the furnace temperature should be hold for a sufficiently long period to facilitate the decomposition of NH_4Cl and drive off the air in the packs by the decomposed gas. The effect of the holding temperature on the substrate surface temperature was examined.

As shown in Fig. 3(a), there is no obvious sudden temperature change on the substrate surface in crucible B when holding temperature is 350 °C. Then two temperature jumps appear at about 410 °C and 620 °C, respectively, in the following heating process. The temperature rising range of the second jump is quite large. The substrate surface temperature greatly exceeds the furnace temperature after jump, but it quickly drops to the furnace temperature and keeps consistent with it.

As shown in Fig. 3(b), a slight temperature jump on the substrate surface appears for crucible B when holding temperature is 430 °C. When the substrate surface temperature reaches 450 °C, it begins to drop until it is almost the same as the furnace temperature. Then the second jump occurring at 590 °C also slightly exceeds the furnace temperature and has a small rising range. The first temperature jump occurs during the holding process and the second temperature jump occurs in the following heating process.

As shown in Fig. 3(c), there is a slight temperature jump on the substrate surface in crucible B when the holding temperature is 510 °C, and the second temperature jump occurs in the holding process subsequently. When the temperature reaches 600 °C it begins to drop and gradually approaches the furnace temperature. Both temperature jumps occur in the holding period.

There are obvious differences in the position of temperature jumps for holding temperatures of 350 °C, 430 °C and 510 °C; these results indicate that the occurrence of the two temperature jumps is strongly affected by the holding temperature. In addition, there are some differences in the range of temperature jumps and the temperatures when the jumps occur. The temperatures when the first jumps occur for the holding temperatures of 350 °C, 430 °C and 510 °C are almost the same (about 410 °C) while the temperatures when the second jumps occur decrease with an increase in the holding temperatures (about 620 °C, 590 °C and 550 °C, respectively). Similarly, the range of the first jump for holding temperatures of 350 °C, 430 °C and 510 °C has no obvious difference, while the range of the second jump is reduced with the increase in the holding temperature. A wide range of temperature jumps and high temperatures when the jumps occur has a deleterious effect on the quality of the deposition layer, so in order to obtain a high
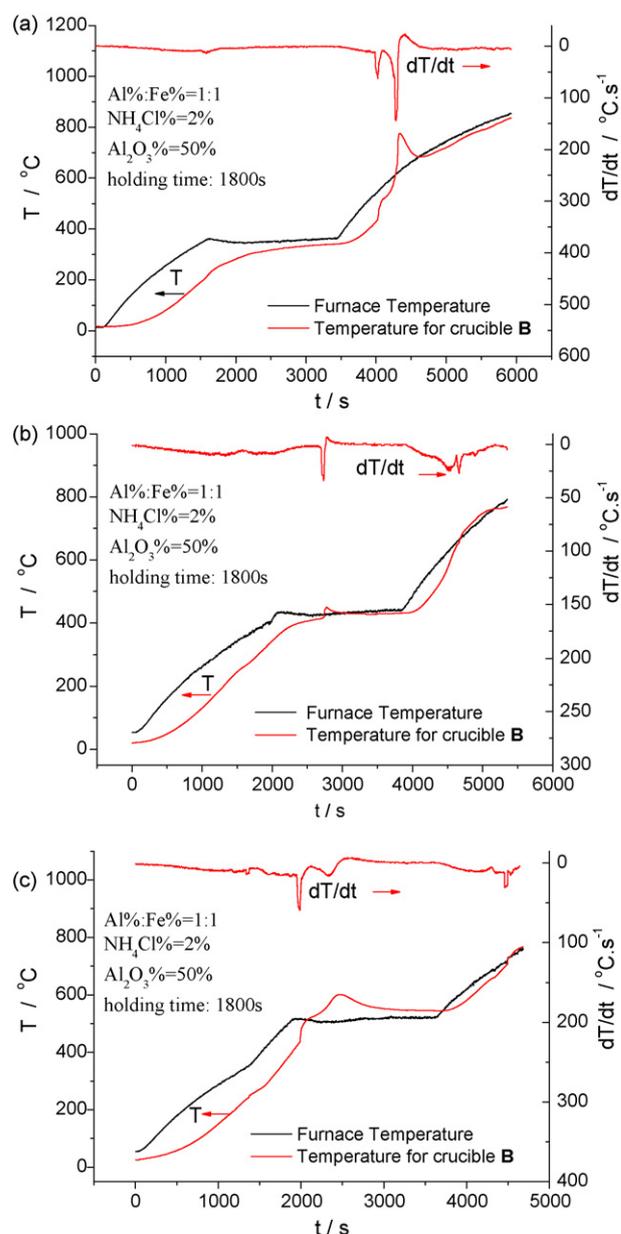
Fig. 3. Temperature curves at different holding temperatures (heating rate: 12 °C/min). Holding temperature of 350 °C (a), 430 °C (b) and 510 °C (c).

quality deposition, the holding temperature should be increased. However, energy consumption rises with the increasing of holding temperature. Furthermore, the effect of holding temperature on the range of temperature jump and temperature when the jumps occur is weakened with the increased holding temperature. In order to balance the coating quality and economic benefits, it is appropriate to choose a holding temperature of 430 °C for the co-deposition of aluminum and iron on copper in this experiment.

3.3. Effect of heating rate

Another factor that effects temperature change is the heating rate during the process of co-deposition of Al/Fe on copper by pack cementation. It is possible to improve the working efficiency with the higher heating rate, but it needs to control the heating rate in many situations. Too high a heating rate adversely affects the coating quality.
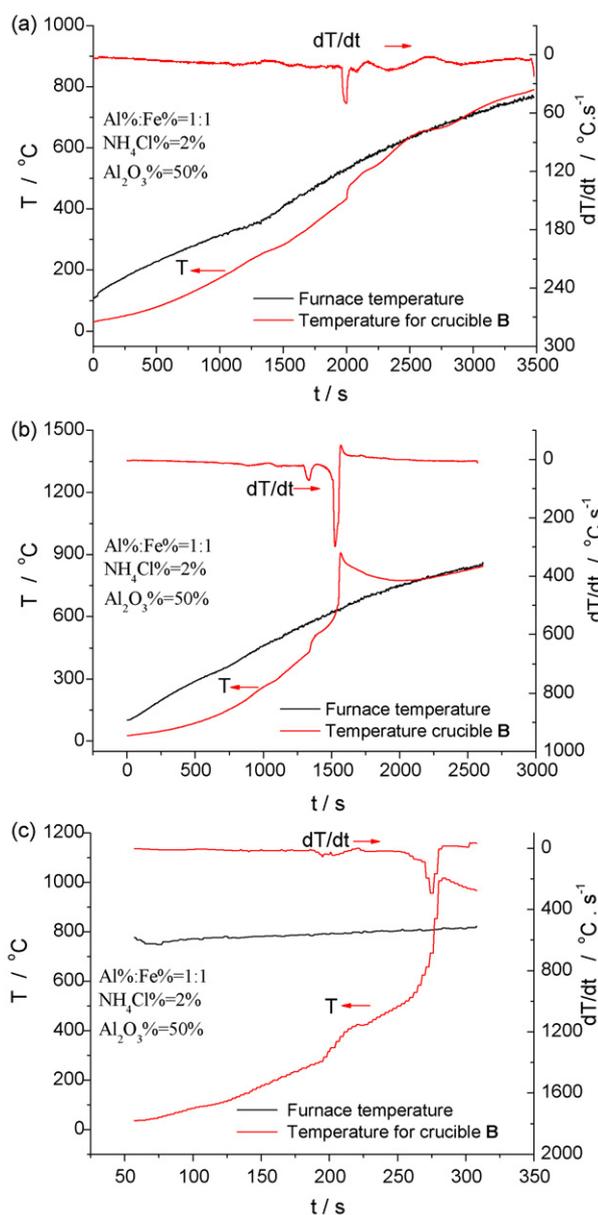
Fig. 4. Temperature curves at different heating rates. Heating rate at $0.2\,°C\,s^{-1}$ (a), $0.35\,°C\,s^{-1}$ (b) and holding temperature at $800\,°C$ (c).

As shown in Fig. 4(a), two temperature jumps for the substrate in crucible B are not obvious for the heating rate of $0.2\,°C/s$. The range of the first jump is $40\,°C$ within $80\,s$, while the range of the second jump is $100\,°C$ within $300\,s$. The temperature difference between the furnace and the substrate in crucible B is small during the entire heating process. As shown in Fig. 4(b), the range of the first jump is quite small (only $70\,°C$ within $60\,s$) while the range of the second jump is much higher, reaching above $400\,°C$ within less than $130\,s$ for the heating rate of $0.35\,°C/s$. The temperature change is unsteady with such a heating rate. As shown in Fig. 4(c), both temperature jumps for the substrate in crucible B are obvious when the furnace temperature is continuously maintaining at $800\,°C$. The range of the first jump is about $150\,°C$ within $25\,s$, and the range of the second jump is over $500\,°C$ within $50\,s$. The temperature approaches $1000\,°C$ after the second jump. The whole heating process merely lasts $300\,s$.

The stability of the temperature change for the substrate in crucible B strongly depends on the heating rate. The temperature change is steady with a heating rate of $0.2\,°C/s$. However, the temperature fluctuation for the heating rate of $0.35\,°C/s$ shows an unsteady temperature change. For the run of the holding furnace temperature for $800\,°C$ the temperature change on the substrate surface is rapid because its heating rate can be regarded as infinite. In order to control the diffusion rate of the coating metal on the substrate, the heating rate should be controlled at a low level, and a heating rate less than or equal to $0.2\,°C/s$ is suitable for strict temperature control in the coating process.

4. Conclusion

In the present paper, the thermal history of the substrate surface in the co-deposition of iron and aluminum on copper by pack cementation was researched. The effect of the pack mixture, holding temperature and heating rate on the temperature change of a copper surface was examined. The results obtained are summarized as follows:

(1) The Al-to-Fe mass ratio, A1/Fe mass fraction has important effects on the temperature change of the substrate surface. A high A1/Fe mass fraction causes an obvious temperature fluctuation and should be avoided while the NH_4Cl and Al_2O_3 mass fraction only slightly affect the temperature change. The high temperature fluctuation for high mass fraction of Al/Fe affects its heat transfer as well as the diffusion of the coating metal on the substrate, so a high mass fraction of Al/Fe in packs should be avoided.
(2) In the experimental conditions used in this work, the occurrence of two distinct temperature jumps at the substrate surface was observed for all the runs, which is strongly affected by the holding temperature. For the holding temperature of $350\,°C$, both jumps occur after the holding period; for the holding temperature of $430\,°C$, one jump occurs during the holding period while the other jump occurs later; for the holding temperature of $510\,°C$, the two jumps occur only in the holding process.
(3) The heating rate has a significant effect on the temperature change on the substrate surface. A high heating rate causes an unsteady temperature change on the substrate surface, so it is beneficial to keep the heating rate less than or equal to $0.2\,°C/s$ for strict temperature control in the coating process.

Acknowledgement

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