Effect of substrate annealing on wetting behavior and interfacial reaction between Sn-0.7Cu and amorphous Fe84.3Si10.3B5.4 alloy

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Abstract: Wetting behaviors of Sn-0.7Cu on amorphous Fe84.3Si10.3B5.4 substrate and substrates annealed at various temperatures (i.e., 400 °C, 500 °C and 650 °C) were investigated at 250 °C, 300 °C, 350 °C and 400 °C by the sessile drop method, and the interfacial reaction of Sn-0.7Cu on different Fe84.3Si10.3B5.4 substrates with different annealing treatments were studied by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). Obtained results show that at the same soldering temperature, the final equilibrium wetting angle of Sn-0.7Cu on Fe84.3Si10.3B5.4 substrates gradually increases with the increase of annealing temperature. That means the wettability becomes worse and the interfacial reaction becomes weaker. With the increase of soldering temperature from 250 °C to 400 °C, the final equilibrium wetting angle of Sn-0.7Cu on Fe84.3Si10.3B5.4 substrates decreases gradually, suggesting a better wettability.

1. Introduction

Amorphous alloys have been extensively used in aerospace, chemical engineering, biomedicine and other fields due to the unique physical properties, such as electromagnetic properties and mechanical properties, which are significantly different from the corresponding crystalline alloys, induced by the different atomic configurations compared with that in the crystalline alloys [1, 2]. However, the application of this materials is severely limited by sizes attainable with the material. In order to prepare bulk amorphous alloys or realize the assembly of amorphous alloys with other materials, it is necessary to develop effective and reliable joining technique. As a low-temperature joining method, soldering is very suitable for the joining of amorphous alloys.

Fe-based amorphous alloy, one of the most successful amorphous alloy, has attracted great attention because of their superior soft magnetic and mechanical properties. Fe-based amorphous alloys are thermodynamic metastable and sensitive to heat treatment. Complicated transformation including structural relaxation and crystallization may occur when the temperature of heat treatment increases to a certain value [3]. After different annealing treatments, the microstructures, energy state of amorphous substrate can be significantly influenced. Thus, the wettability and interfacial characteristic of the molten solder on these substrates subjected to different heat treatments can show prominent diversity. Some works investigated the wettability and interfacial characteristic of molten solders on the Fe-base amorphous alloy substrate [4-6]. Accordingly, the wettability and interfacial characteristic of molten
solder on the substrates play very important role in acquiring a high-quality joint. Unfortunately, few works were focused on the effect of annealing treatment on the wettability and interfacial characteristic of molten solders on Fe-based amorphous alloy substrates. It still lacks of a thorough understanding on the relationships among the wettability, interfacial reaction and microstructure of the soldering process of Fe-base amorphous alloy. In this work, the influence of soldering and annealing temperature on the wettability and interfacial characteristic of molten Sn-0.7Cu on Fe₈₄₅Si₁₀₃B₅₄ amorphous substrates are investigated. It would be helpful for high reliability joining of Fe-based amorphous alloys, further enrich and develop the process theory for soldering advanced metallic materials by the study.

2. Experimental procedure

Sn-0.7Cu solder with nominal composition of 0.7 wt.% Cu with residual Sn was fabricated at 450 °C for 120 min under the protection of KCl and LiCl. Amorphous Fe₈₄₅Si₁₀₃B₅₄ strip (25 mm × 25 mm × 30 μm) was prepared as substrates. The onset of the crystallization temperature (Tₓ), the glass transition temperature (Tₘ) and two peak temperatures (Tₚ₁, Tₚ₂) of the amorphous Fe₈₄₅Si₁₀₃B₅₄ alloy were determined at the heating rate of 20 °C/min by differential scanning calorimetry (DSC, NETZSCH STA 449C). Ribbon shaped amorphous samples were isothermally annealed at 400 °C (T₁), 500 °C (T₂) and 650 °C (T₃) for 30 min using the high temperature tube furnace under Argon gas. The structures of original amorphous and annealed samples were determined by using X-ray diffraction (XRD, D8 ADVANCE). Wetting experiment was performed by the sessile drop method using Dataphysics OCA-20 in an N₂ atmosphere. The amorphous and annealed substrates were polished using 1μm diamond past and cleaned ultrasonically 10 minutes in acetone, and then the substrates were prefixed on a Cupper supporter. The solders surrounded by an activated flux were located at the center of the substrates. Then, those samples were put into stainless-steel chamber and adjusted to a suitable position through the vertical and horizontal adjustment button, and then the chamber was heated to different soldering temperatures ranged from 250 °C to 400 °C with an interval of 50 °C. The high resolution charge-coupled- device camera was used to record the drop profiles. The cross-section of the solidified samples was ground and then polished. Interfacial microstructure was observed by using a scanning electron microscope (SEM, SUPRA 55V Zeiss). Using an attached energy diffraction spectrum (EDS) to determine the chemical composition of interface compounds.

3. Results and discussion

3.1. Influence of Anneal treatment on substrate microstructure

Figure 1(a) shows the DSC curves of the employed Fe₈₄₅Si₁₀₃B₅₄ amorphous alloy. Clearly, the glass transition temperature (Tₘ) was 488 °C, and the onset of the crystallization temperature (Tₓ) was 511 °C. There are two successive exothermic events in the crystallization process, with peak temperature about 515 °C (Tₚ₁), 555 °C (Tₚ₂). Figure 1(b) presents the XRD pattern of Fe₈₄₅Si₁₀₃B₅₄ substrates subjected different annealing treatments. For the original sample, no crystalline peak can be detected, indicating a fully amorphous state. When the annealed temperature is 400 °C (T₁) which is lower than (488 °C) Tₓ, the substrates are still no crystalline peak which are in structural relaxation state [7]. Although XRD pattern of structural relaxation substrate presents similarly to that of amorphous substrate, its microstructures, electron configuration and atoms distribution have been changed by diffusion of atoms, transforming into metastable state having lower internal energy [8]. After annealed at 500 °C which is between Tₓ and Tₘ for 30 min, α-Fe(Si) and Fe₂B phases appeared. The onset crystallization occurs in the amorphous alloy annealed at 500 °C in the supercooled liquid region [9], and it also contains some amount of amorphous phase. When the annealed temperature is 650 °C much higher than Tₚ₂, it is determined that the structure contains only α-Fe(Si) and Fe₂B phases. It results in complete crystallization of the amorphous phase [10].
3.2. Effects of annealing temperature on wetting behavior

Figure 2(a) shows the evolution of contact angle with the increasing soldering time, and Figure 2(b) presents the equilibrium contact angle (ECA) of Sn-0.7Cu on Fe$_{84.3}$Si$_{10.3}$B$_{5.4}$ substrates subjected to different annealing treatments. It is noteworthy that the soldering temperature is 350 °C. Normally, the contact angle of solder decreases gradually and finally tends to be wetting equilibrium state as soldering time increases. It can be seen from Figure 2(a) that all cases show normal decrease tendency of contact angle of solder with increasing soldering time. The ECA of Sn-0.7Cu on original Fe$_{84.3}$Si$_{10.3}$B$_{5.4}$ amorphous substrate is 36.8 °, which is smaller than that of other annealed cases. With the increase of annealing temperature from 400 °C to 650 °C, the ECA of Sn-0.7Cu on Fe$_{84.3}$Si$_{10.3}$B$_{5.4}$ substrates increases from 48.8 ° to 78.1 °. Clearly, annealing treatment induces an increase in the ECA of Sn-0.7Cu on Fe$_{84.3}$Si$_{10.3}$B$_{5.4}$ substrates, suggesting a poorer wettability. Moreover, with the increasing annealing temperature, wettability of Sn-0.7Cu on Fe$_{84.3}$Si$_{10.3}$B$_{5.4}$ substrates becomes worse.

According to Young’s equation, the ECA $\theta$ for nonreactive wetting is defined as:

$$\cos \theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}} \quad (1)$$

Where $\sigma_{sg}$, $\sigma_{sl}$ and $\sigma_{lg}$ are the solid-gas, solid-liquid and liquid-gas interfacial tension, respectively. $\sigma_{lg}$ is mainly determined by inherent bonding of the atoms in the liquid metal, which can be assumed as a constant value for a predetermined material. $\sigma_{sl}$ is an excess energy due to broken bonds usually defined as the difference in the interfacial tension between surface atoms and inner ones. $\sigma_{sg}$ is mainly affected by the affinity between the liquid and solid atoms.

There may be two causes resulting in the rules of wetting behavior. Firstly, as the annealing temperature increases, complicated transformations including structural relaxation and crystallization
may occur, respectively, and the solid-gas surface energy \( \sigma_{SG} \) is smaller. Thus, the ECA is larger and the wettability is worse. Secondly, as the annealing temperature increases, atomic activity and diffusion ability of substrate alloy decreases, the atomic bonding at the interface between solder and substrate gradually decreases and lead to a larger solid-liquid surface energy \( \sigma_{SL} \), thus makes the wettability become worse.

Figure 2 (c) presents the comparison curve of ECA with time of Sn-Cu on different microstructural Fe\(_{84.3}\)Si\(_{10.3}\)B\(_{5.4}\) substrate. Clearly, along with the increasing soldering temperature, the ECA of Sn-0.7Cu on the same microstructural substrate gradually decrease, which indicates a better wettability. That is because the wetting surface tension of Sn-0.7Cu solder decreases as increasing the soldering temperature. Meanwhile, the activity and diffusion capacity of atoms gradually increases. Thus, wetting process was promoted and the wettability become better.

3.3. Effects of annealing temperature on interfacial reaction

Figure 3 presents the SEM micrographs showing the interface between Sn-0.7Cu and Fe\(_{84.3}\)Si\(_{10.3}\)B\(_{5.4}\) substrate subjected to different annealing treatments. The soldering test was conducted at 350 °C for a dwelling time of 30 min. Obviously, the intermetallic compounds at the interface of Sn-0.7Cu/Fe\(_{84.3}\)Si\(_{10.3}\)B\(_{5.4}\) amorphous are continuously distributed, as shown in Figure 3(a). It also can be found that the density of interfacial intermetallic compounds gradually decreases as the annealing temperature increases, which implies the interfacial reaction is gradually weaker.

![Figure 3. SEM micrographs showing the interface between Sn-Cu and Fe\(_{84.3}\)Si\(_{10.3}\)B\(_{5.4}\) substrate: (a) primary amorphous substrate; (b) 400°C annealed; (c) 500°C annealed; (d) 650°C annealed for 30 min.](image)

The EDS point analysis of the intermetallic compounds formed at the interface of Sn-0.7Cu/Fe\(_{84.3}\)Si\(_{10.3}\)B\(_{5.4}\) amorphous is shown in Figure 3 (a). The intermetallic compound is Sn-38.6 at.% Fe. According to the phase diagram of Sn-Fe alloy system [11], although there are two stable intermetallic compounds, FeSn and FeSn\(_2\) in the binary Sn-Fe system at 250 °C, FeSn\(_2\) is formed readily at the interface for the soldering performed at 350 °C due to the small solubility of Fe in liquid Sn at T ≤ 513 °C. Previous studies have reported that FeSn\(_2\) phase is the dominant reaction product in the Sn/Fe and Sn-based solder/Fe couples reacted at temperatures below 513 °C [12, 13].

According to the theory of chemical thermodynamics, whether a chemical reaction can occur is determined whether the Gibbs free-energy of the system can be reduced, namely, the Gibbs free-energy
change ΔG is less than 0. The fundamental chemical reactive process includes the following chemical reaction:

$$\text{Fe} + 2\text{Sn} \rightarrow \text{FeSn}_2$$

(2)

The Gibbs free-energy change ΔG° for this reaction when generating per Moore’s FeSn₂ can be calculated definitely by using a simple relation shown in Equation (3) [14]:

$$\Delta G°(\text{FeSn}_2) = (-6672 + 6.78T) \times 4.1816$$

(3)

Where T is the thermodynamic temperature. When the temperature is 250°C, namely T= 523 k, the values of ΔG°(FeSn₂)= 13.072 KJ/mol< 0 calculated by using Equation (3); Similarly, when the temperature is 300 °C, i.e., T= 573 k, the values of ΔG°(FeSn₂)= -11.654 KJ/mol<0; when the temperature is 350 °C, namely T= 623 k, the values of ΔG°(FeSn₂)= -10.236 KJ/mol<0; when the temperature is 400 °C, namely T= 673 k, the values of ΔG°(FeSn₂)= -8.819 KJ/mol<0. This is main reason why the FeSn₂ phase can be found at or near the interface of Sn-0.7Cu/Fe₄.₃Si₁₀.₃B₅.₄ amorphous.

According to the thermodynamics, amorphous alloys are metastable and their atoms are arranged in the long-range disorder [15]. Thus they might possess high energy to react and interdiffuse with the counterpart. Through the above annealing experiment, amorphous Fe₄.₃Si₁₀.₃B₅.₄ annealed at 400 °C, 500 °C and 650 °C, the transformation is corresponding to structural relaxation, onset crystallization and complete crystallization. With the increase of annealing temperature, internal atoms of the amorphous Fe₄.₃Si₁₀.₃B₅.₄ are preferential combination, even forming a stable α-Fe(Si) and Fe₅B phases in a completely crystalline state when amorphous Fe₄.₃Si₁₀.₃B₅.₄ annealed at 650 °C, indicating the activity and ability of dissolution and diffusion of Fe atoms decrease gradually, thus, it is more difficult for Sn atoms in the Sn-0.7Cu solder to capture Fe atoms. Therefore, the boundary layer of the Sn-0.7Cu is more difficult to become saturated or reach local equilibrium solubility, so the interfacial reaction is increasingly weaker.

4. Conclusions

(1) Annealing treatment results in a worse wettability of Sn-0.7Cu on Fe₄.₃Si₁₀.₃B₅.₄ substrates. Relatively higher surface energy of amorphous alloy caused the better wettability. As the annealing temperature increases, equilibrium wetting angle (ECA) of Sn-0.7Cu on Fe₄.₃Si₁₀.₃B₅.₄ substrate gradually increases from 36.8 ° to 78.1 °.

(2) With the increase of soldering temperature from 250 °C to 400 °C, the ECA of Sn-0.7Cu on Fe₄.₃Si₁₀.₃B₅.₄ substrates decreases gradually.

(3) Annealing treatment brings to a weaker interfacial reaction between Sn-0.7Cu and Fe₄.₃Si₁₀.₃B₅.₄ substrates. With the increase of annealing temperature, formation of FeSn₂ at the interface of Sn-0.7Cu/Fe₄.₃Si₁₀.₃B₅.₄ substrate is more difficult.

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