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Growth kinetics for intermetallic compound layer between molten In−Sn alloy and CuZr-based bulk metallic glass

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Abstract: The growth kinetics of intermetallic compound layer between molten In−Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ bulk metallic glass substrate was examined by solid state isothermal aging at the temperature range between 333 and 393 K. The aged samples were characterized by scanning electron microscopy and energy dispersive spectrometry. It is found that the intermetallic compound layer is composed of Zr, Cu and Sn. The layer growth of the intermetallic compound is mainly controlled by a diffusion mechanism over the temperature range and the value of the time exponent is approximately 0.5. The apparent activation energy for the growth of total intermetallic compound layers is 98.35 kJ /mol calculated by the Arrhenius equation.

Key words: bulk metallic glass; compound layer; kinetics; diffusion mechanism

1 Introduction

Among many bonding techniques, soldering has become an important joining technology in the electronic industry and has been used widely in packaging processes [1,2]. The liquid alloy melt can react with substrates resulting in the formation of intermetallic compounds at the interface during soldering [3,4]. It is desirable to achieve a good metallurgical bond while forming a thin intermetallic compound layer. However, excessive intermetallic compounds growth may have a deleterious effect since the intermetallic compounds are brittle and hard in nature [5,6].

Bulk metallic glasses (BMGs) usually possess high strength, soft magnetic properties and good corrosion resistance, which are considered to have many potential applications as advanced engineering materials [7,8]. In order to adopt BMGs in a broader range of engineering applications, it is very important to establish appropriate joint processes for BMG/BMG and BMG/crystalline metal [9]. Until now, several joint processes have been attempted to join a BMG to a BMG and a BMG to a crystalline metal, and successful joints are obtained by some processes, such as electron-beam welding, friction welding and laser welding [10−13]. However, in the BMG joint, the most important issue is the reformation of glassy phase at high temperature area. Hence, the soldering process is studied to join BMGs in order to avoid the crystallization of the glassy phase. The soldering process between molten In−Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG was investigated in previous study [14]. It is found that the intermetallic compound exists at the interface between the molten In−Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG. It is well known that intermetallic compounds at the interface have significant effect on the performance of joints. Therefore, the information of the interfacial growth kinetics between molten alloys and BMGs is fundamentally important for the reliability evaluation of BMG joints.

In this work, the growth of intermetallic compound layer between molten In−Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG was studied during solid state isothermal aging. The constants of the growth rate for intermetallic compounds were measured as a function of time and temperature, and the activation energy for intermetallic

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growth was calculated by the Arrhenius equation.

2 Experimental

The eutectic alloy with composition of 49.1Sn−50.9In (mass fraction, %) was prepared by induction melting in high purity argon atmosphere (purity>99.99%). Then the alloy was cut into pieces of about 50 mg. $Cu_{40}Zr_{44}Al_8Ag_8$ alloy was produced by arc melting under a Ti-gettered Ar atmosphere. The purity of all the elements was above 99.5%. $Cu_{40}Zr_{44}Al_8Ag_8$ alloys were remelted in a quartz tube by induction melting, followed by casting into copper moulds with plate cavity of 2 mm in thickness. $Cu_{40}Zr_{44}Al_8Ag_8$ BMG plates were cut into small substrates with dimensions of 20 mm× 20 mm and then polished. Before being subjected to the measurements, both substrates and pieces of In−Sn alloy were cleaned in acetone.

Soldering experiments were performed by sessile drop method in a high vacuum furnace at 473 K for 5 min. For the molten In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG system, the isothermal aging was performed in a high vacuum furnace. The aging temperatures were 333, 353, 373 and 393 K and the time periods were 1−10 h in order to avoid crystallization. The solidified drops were sectioned and polished to examine the possible interfacial reactions using high resolution scanning electron microscopy (HRSEM). The intermetallic phase was analyzed by energy dispersive X-ray spectra (EDS). Thickness measurement of the intermetallic layer was performed by using image analysis software.

3 Results and discussion

Figure 1 shows the HRSEM micrographs of the molten In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG reaction couples after aging for 6 h at various temperatures (333−393 K). It is found that the intermetallic compound exists at the interface between In−Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG, as marked by the arrows. The thickness of the intermetallic compound increases with the increase of aging temperature. The cross-section HRSEM image and EDS analysis after aging at 373 K for 10 h are shown in Fig. 2. It is seen that the reaction layer consists of Sn, Zr and Cu by the EDS analysis. Previous XRD results showed that the reactive products were Zr_3Sn, CuZr and InSn compounds, respectively [14].

Figure 3 shows the HRSEM micrographs of the molten In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG reaction couples aged at 393 K for different aging time. The thickness of the intermetallic compound layer increases with the increase of aging time. The intermetallic thickness is approximately 3.5 μm when aged at 393 K for 10 h.

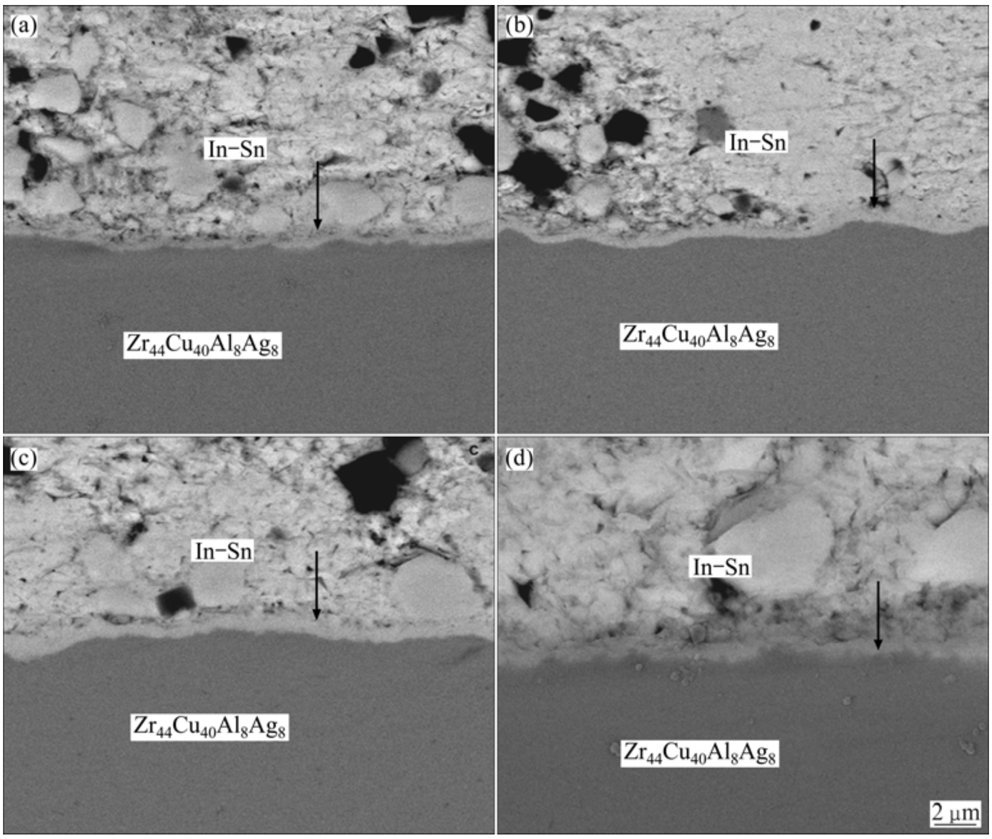

Fig. 1 HRSEM micrographs of In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG interface after aging for 6 h at different temperatures: (a) 333 K; (b) 353 K; (c) 373 K; (d) 393 K

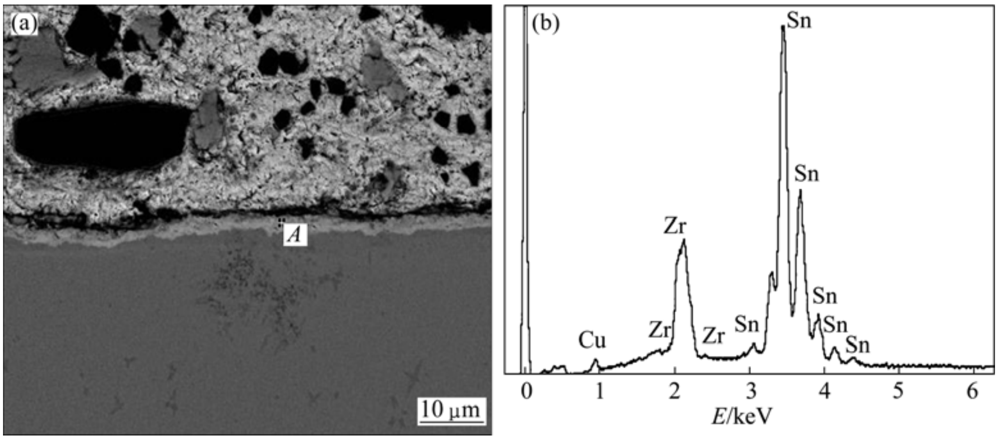

Fig. 2 Cross-section HRSEM image (a) and EDS analysis (b) of In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG interface after aging at 373 K for 10 h

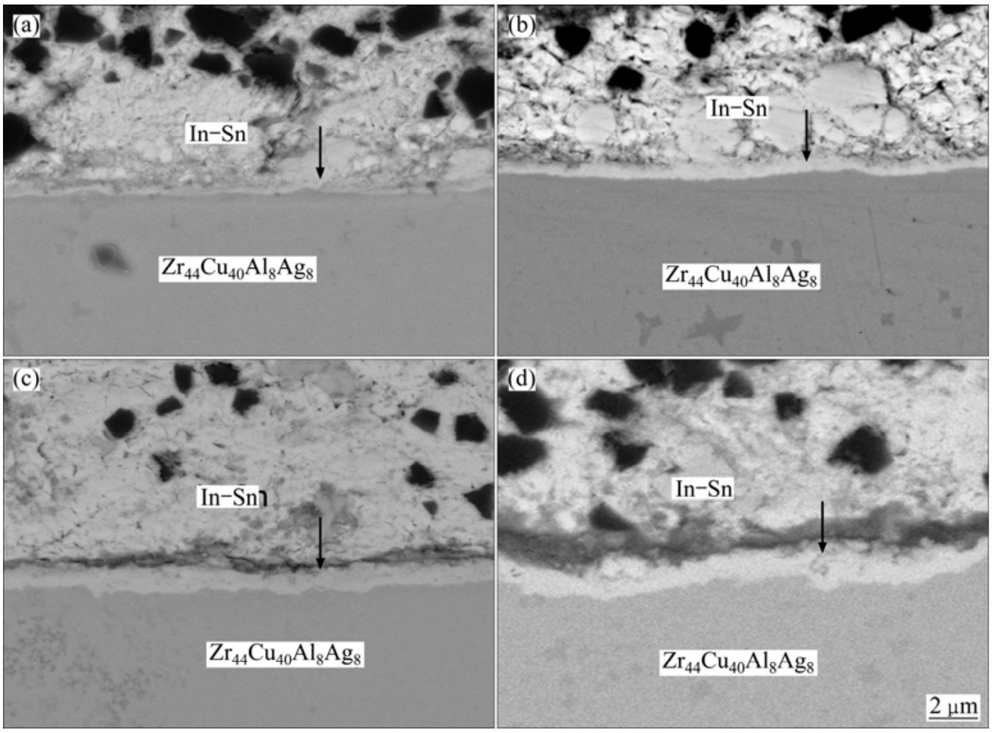

Fig. 3 HRSEM micrographs of In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG interface aged at 373 K for different aging time: (a) 1 h; (b) 4 h; (c) 8 h; (d) 10 h

Generally, the thickness of a reaction layer in the diffusion couples is expressed by the simple parabolic equation [15]:

$$d=kt^n \quad (1)$$

where d is the thickness of the reaction layer; k is the growth rate constant; n is the time exponent; t is the reaction time.

The thickness of the intermetallic compound layer as a function of the square root of time for each aging temperature is shown in Fig. 4. These intermetallic thicknesses were measured at every interval of time. The mean thickness of the intermetallic compound is found to increase linearly with the square root of aging time and the growth is faster at higher aging temperature.

The atomic diffusion of Cu, Zr and Sn through the intermetallic compound layer is the controlling process for the intermetallic compound growth during aging. If the growth process is controlled by diffusion mechanism, the thickness increase of the intermetallic compound layer after aging should follow the square root time law, $d=kt^{0.5}$. It is empirically found that n takes the value of 0.5 when the reaction is mainly controlled by diffusion mechanism. From Fig. 4, it can be seen that the growth of intermetallic compounds follows a parabolic law, implying that the growth of the intermetallic layer is

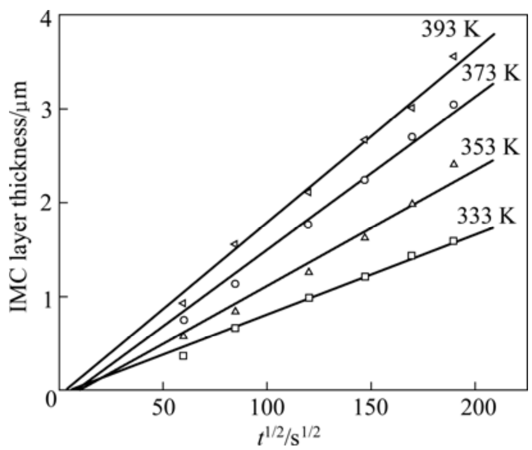

Fig. 4 Thickness of IMC layer vs square root of reaction time at different temperature

diffusion-controlled.

The growth rate constant is calculated from a linear 0.5 regression analysis of d versus t, where the slope is k. The calculated growth rate constant k ranges from 2.3×10^{-19} to 1.47×10^{-18} $m/s^{1/2}$. Most of the linear correlation coefficient values R for these plots are greater than 0.98. This confirms that the growth of the intermetallic compound layers is diffusion-controlled over the temperature range studied.

To evaluate the time exponent, the growth kinetics at each temperature can be represented as [15]:

$$Y=At^n+B \tag{2}$$

where Y is the layer thickness; t is reaction time; n is the time exponent; B is the layer thickness at t=0; A is a constant. This equation is converted into a logarithmic expression as:

$$\ln (Y–B)=n\ln t+\ln A \tag{3}$$

The time exponent n can be obtained from the slope of the ln(Y−B) versus ln t. The time exponent is determined by the linear regression analysis of each aging temperature using Eq. (3). The values of the exponents are around 0.53, 0.437, 0.51 and 0.56 at 333, 353, 373 and 393 K, respectively. The diffusion processes appear to be largely responsible for the growth of the intermetallic compound layer.

It could be deduced that the following interfacial reactions between the In−Sn alloy and $Cu_{40}Zr_{44}Al_8Ag_8$ BMG probably occur as [14]:

$$3Zr+Sn\longrightarrow Zr_3Sn \tag{4}$$

$$10Cu+7Zr\longrightarrow Cu_{10}Zr_7 \tag{5}$$

Here, the liquid/solid interfacial reaction is only analyzed by using the standpoint of atomic diffusivity. Usually, the atomic diffusivity is made up of two parts in the growth process of the intermetallic compound layer. For the molten In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG system, firstly Sn diffusion in $Cu_{40}Zr_{44}Al_8Ag_8$ BMG is restrained because of no grain-boundaries nor interfaces in the amorphous alloy. Secondly, Zr and Cu diffusion in molten In−Sn alloy is also affected because of the interfacial crystallization reaction of the molten In−Sn alloy/$Cu_{40}Zr_{44}Al_8Ag_8$ BMG, as shown in Eq. (5). Hence, the layer growth of the intermetallic compound is mainly controlled by atomic (Sn, Zr and Cu) diffusion.

The following simple Arrhenius relationship is used to determine the activation energy for the total intermetallic compound as:

$$k=k_0\exp(-Q/RT) \tag{6}$$

where k is the square of growth rate constant; k_0 is the frequency factor; Q is the activation energy; R is the gas constant; T is the aging temperature. The activation energy is calculated from the slope of the Arrhenius plot using a linear regression model. Figure 5 shows the Arrhenius plots for the growth of the total intermetallic compound Cu−Zr−Sn. The apparent activation energy calculated for the growth of the intermetallic compound is 98.35 kJ/mol. The thickness of a reaction layer in the diffusion couples can be expressed as:

$$d = 4.18\times10^{-16}\exp[-98.35/(RT)]t^{0.5} \tag{7}$$

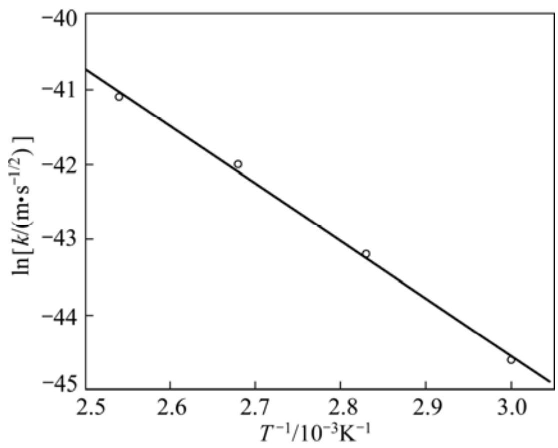

Fig. 5 Arrhenius plot of Cu−Zr−Sn intermetallic compound growth

4 Conclusions

1) In the solder joints between the molten In−Sn alloy and the $Cu_{40}Zr_{44}Al_8Ag_8$ BMG, the intermetallic compound layer is composed of Zr, Cu and Sn.

2) The growth of the intermetallic layer is controlled by a diffusion mechanism over the temperature range because the value of the time exponent n is approximately 0.5.

3) The thickness of intermetallic compound layer reaches 3.5 μm after solid state isothermal aging at 393 K for 10 h.

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In−Sn 熔体合金与 CuZr 基块状非晶合金界面生长动力学

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摘　要：研究 In−Sn 熔体合金与 $Cu_{40}Zr_{44}Al_8Ag_8$ 块状非晶合金的界面生长动力学。通过扫描电镜和能谱对时效的样品进行分析，发现界面层由 Zr、Cu 和 Sn 组成。在时效温度区间，扩散机制是反应速度的控制步骤，且时间指数值近似为 0.5。计算得到的反应激活能为 98.35 kJ/mol。

关键词：块状非晶；界面层；动力学；扩散机制

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