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Enhancement of solderability of Cu₆₀Zr₃₀Ti₁₀ bulk metallic glass by dealloying in hydrofluoric acid solution[†]

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KEY WORDS: (Bulk metallic glass) (Dealloying) (Laser soldering) (Lead-free solder)

1. Introduction

Despite the good mechanical, chemical [1] and magnetic [2] properties of bulk metallic glasses (BMGs), the serious issue during the joint of BMG is the recrystallization of the glassy phase at high temperatures. In order to extend the engineering application of BMG it is necessary to establish appropriate joint processes of BMG/BMG and BMG/crystalline metal [3-4]. The lead-free soldering process is a low temperature joining process and therefore it can be performed below the crystallization temperature of BMGs. However, many kinds of BMGs such as $Zr_{55}Cu_{30}Ni_5Al_{10}$ and $Cu_{60}Zr_{30}Ti_{10}$ exhibit no wetting of lead-free solder on the surface of BMGs because of Zr- and Ti-oxide on their surface [5]. In previous research, we found that selective leaching of Zr and Ti occurred upon immersing Cu₆₀Zr₃₀Ti₁₀ into HF solution, which resulted in the formation of a Cu rich layer [6].

The objective of this study is to evaluate wettability of solder on the surface of HF treated $Cu_{60}Zr_{30}Ti_{10}$ in order to make better joints between $Cu_{60}Zr_{30}Ti_{10}$ and lead-free solder.

2. Experimental

 ${\rm Cu_{60}Zr_{30}Ti_{10}}$ BMG ribbon was cut into 20 mm \times 20 mm \times 70 µm strips and polished by SiC paper with 2000-grit. The surface treatment was performed by immersing in 0.5 mol/L HF solution for 13 s at room temperature. The formation of Cu phase was confirmed with the amorphous pattern by X-ray diffraction (XRD) as in the previous study [6]. The porous layer with the thickness of about 500 mm was observed from scanning electron microscopy (SEM) image as shown in **Fig. 1**.

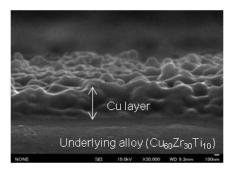


Fig. 1 Cross section of sample after HF treatment

In the reflow process, a Sn-3.0 mass%Ag-0.5 mass%Cu (SAC) solder ball with a diameter of 1 mm was set on the HF treated $Cu_{60}Zr_{30}Ti_{10}$ sample with RMA flux. Then, the sample was put into a radiation furnace in a N_2 atmosphere and heated according to the temperature rise profile shown in **Fig. 2.**

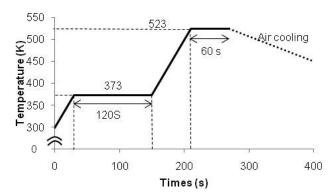


Fig. 2 Thermal profile of the reflow process.

Table 1 Some characteristics and preheating process of solder pastes used for laser soldering.

Solderpaste	Composition (mass%)	Solidus/Eutectic temperature (K)	Viscosity(298K) (Pa•s)	Flux content (mass%)	Preheating process	
SAC	Sn-3.0Ag-0.5Cu	490 (Solidus)	218	14.0	423 K 300 s	
SB	Sn-57Bi	412 (Eutectic)	221	11.7	398 K 300 s	

[†] Received on 30 September 2010

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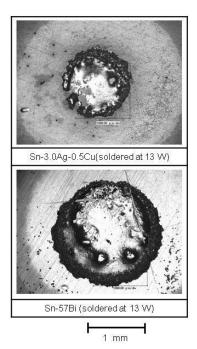


Fig. 3 The top surface of the soldered sample.

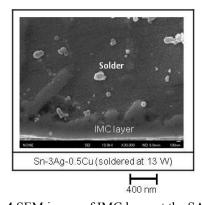


Fig. 4 SEM image of IMC layer at the SAC/Cu layer interface after laser process

In the laser process, two kinds of solder pastes were prepared as shown in **Table 1**. Solder pastes were applied with 50 μm thickness on the HF treated Cu $_{60}Zr_{30}Ti_{10}$. After preheating, the laser irradiation was performed. The laser irradiation time was 0.01 s and the laser power range from 8 to 20 W at 1 W interval. The top surface of the soldered sample was observed by optical microscope (OM) and the cross sections of joint interfaces were observed by SEM.

3. Results & Discussion

The wetting behavior of lead-free solder on the HF treated sample was evaluated by the spread area of the solder on the sample. In the reflow process, during the early stage of the process, the molten solder seemed to spread on the sample surface, and then the sample showed complete dewetting during the heating due to dissolution of the thin Cu-rich layer into the molten solder.

Table 2 Wetting behavior of solder pastes.

LaserPower (W)	8	9	10	11	12	13	14	15	16	17	18	19	20
SAC	Unm	elted	×	×	0	0	×	×	Dewetting				
SB	×	×	×	0	0	0	0	0	0	0	0	×	×

○···Solder was remained after scratching ×···Solder was removed after scratching

In the laser soldering process, the wetting behavior of lead-free solder on the sample was summarized in **Table 2**. In the case of SAC there is a serious effect of laser power on the wetting behavior of the solder. A good wetting behavior of solder paste at only 12 W and 13 W was observed. On the other hand, SB solder paste showed good wetting at higher and lower laser power than SAC. This is due to the differences in melting temperature of solder paste and dissolution rate of Cu into molten solder. As shown in Table 1, the melting temperature of SAC is 490 K and SB is 412 K. So, at 11 W, SAC showed insufficient wetting behavior because of inadequate melting time, although SB showed good wetting at the same laser power. Additionally, SB exhibited no dewetting from 16 W to 18 W, which showed dewetting in the case of SAC because of too long reaction time with Cu surface. This is because it could be estimated from Sn-Bi-Cu and Sn-Ag-Cu ternary alloy phase diagrams that dissolution rate of Cu into SB is slower than that into SAC. Therefore SB showed no dewetting at high laser power.

Figure 3 is the top view of solder pastes after the laser heating at 13 W. The spread area of SB is larger than that of SAC despite the same laser power. In the case of SAC, the diameter of spread area is about 1.2 mm equal to the diameter of laser irradiation area, and SB spread with the diameter of about 2 mm, which is larger than the laser irradiation area. This would appear that SB solder melted not only in the laser irradiated area but also in the heat affected zone because of the low eutectic temperature of SB. In fact, the wetting behavior of SB solder is better than SAC.

Figure 4 shows the SEM image of a cross section at the joint interface between HF treated $Cu_{60}Zr_{30}Ti_{10}$ / SAC solder paste. The intermetallic compound layer with the thickness of about 400 nm was formed at the interface. This means that the porous Cu layer properly reacted with SAC solder by the laser heating.

4. Conclusion

HF treatment and laser soldering was carried out to react with $Cu_{60}Zr_{30}Ti_{10}$ BMG and lead-free solder. The main results were summarized as follows

- (1) In the reflow process, the HF treated $Cu_{60}Zr_{30}Ti_{10}$ sample showed complete dewetting due to the dissolution of the thin Cu-rich layer into the molten solder.
- (2) The laser process with 0.01 s irradiation time offered good wettability of SAC and SB solder pastes. At the interface, an IMC layer was observed. The wetting behavior of SB is better than SAC because SB solder

paste showed good wetting at broader laser power ranges than SAC paste. The spread area of SB is larger than that of SAC. This is attributed to the lower melting temperature and slower Cu dissolution rate of SB.

In this study, the possibility to enhance the solderability of $Cu_{60}Zr_{30}Ti_{10}$ by selective leaching in HF solution and laser soldering was found.

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