Solderability of Bulk Metallic Glasses Using Lead-Free Solders

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A feasibility study has been conducted to determine whether the low temperature joining process such as soldering process and wire bonding process can be applied to join a bulk metallic glass (BMG) to a BMG and a BMG to a crystalline metal. Therefore, in order to evaluate the solderability of BMGs, the spread test of the solder was basically performed for three kind of BMGs in this study. As a result, Pd-based BMG exhibited a good wetting behavior of the solder at 503 K and 523 K. On the other hand, concerning Cu-based and Zr-based BMGs, there was no wetting of the solder on the surface of BMGs regardless of the peak temperature. Then the ultrasonic soldering process was tested to establish the joint process for BMGs. It was clear that the application of ultrasonic is effective to the soldering process.

Keywords: bulk metallic glass, lead-free solder, solderability, wetting behavior, ultrasonic soldering, intermetallic compound

1. Introduction

Bulk metallic glasses (BMGs) exhibit remarkable combination of mechanical, chemical and physical properties as compared to the conventional crystalline materials.¹⁻⁵) Hence, BMGs have been considered as the promising structural and functional materials. The formation of BMGs has been achieved by avoiding nucleation and growth of crystalline phases when the alloy is cooled from the molten liquid. Much effort has been devoted to develop new BMGs exhibiting high thermal stability and useful engineering properties. As a result, many kinds of BMGs such as Zr-, Ni-, Pd-, Cu-, Fe-, Pt-based BMGs and so on have been prepared. And the statistic valence electron contribution to the thermal stability of all glassy alloys has been discussed.⁶) The stabilization has enabled the production of large and thick BMGs. Then, in order to adopt many kinds of BMGs in a broader range of engineering applications, it is indispensable to establish and master appropriate joint processes of BMG/BMG and BMG/crystalline metal. During the joint of BMG, the most serious issue is the reformation of glassy phase at the high temperature area. Namely, in the case of the melting process such as electron beam welding and laser welding, it is very significant to control the heating and cooling rates.

Until now, several joint processes were attempted to join a BMG to a BMG and a BMG to a crystalline metal, and successful joints were obtained by some processes such as electron beam welding, friction welding, explosion, laser welding and ultrasonic bonding.⁷⁻¹³) For example, Kawamura⁷) reported that a Zr₅₅Al₁₀Ni₅Cu₃₀ BMG plate could be welded to crystalline Ti alloy plate by the parallel-plate explosive welding. There was no defect or pore in the interface. And electron-beam welding was investigated for two kinds of BMGs.⁸) No crystallization was observed and no defect or pore was observed in the bead and the heat-affected zone by electron-beam welding. Then, Swiston et al.⁹) have successfully demonstrated the ability to weld Zr-based BMG in air using reactive multilayer foils.

In our group, in order to avoid the recrystallization of glassy phase, the low temperature joining process such as soldering process and wire bonding process has been studied to appropriately join BMGs. For the soldering process, the wetting behavior of lead-free solders for base metal is very important,¹⁴) and information on the relationship between wetting characteristic on amorphous metals and the composition of lead-free solders is scarce.¹⁵,¹⁶) Therefore, the objective of this study is mainly to determine the solderability of BMGs using lead-free solders by measuring the spread area of the solder on BMGs and to characterize the interface between the solder and BMG.

2. Experiment

In this study three kinds of bulk metallic glasses (BMSs) were used. Cu₆₂Zr₃₀Ti₃0 BMG (Cu-based BMG), Zr₅₅Cu₃₀Ni₅Al₁₀ BMG (Zr-based BMG), and Pd₄₂Cu₃₀Ni₇₅P₂₀ BMG (Pd-based BMG) were employed as the test sample. These BMGs were selected in order to examine whether differences in alloy composition affected the wetting behavior. The glasstransition temperature and crystallization temperature of these BMGs are listed in Table 1.¹⁷⁻¹⁹) Then, the most common Sn-3.0 mass%Ag-0.5 mass%Cu (SAC305) was used as lead-free solder. The solidus temperature and the liquidus temperature of this solder are 490 K and 492 K respectively.

The spread test of the solder was basically performed for all BMGs to evaluate the wetting behavior of the solder on BMG. And an ultrasonic soldering was tried for some BMG samples. The procedure of the spread test is as follows. The BMG sample was first immersed in a 4%HCl solution for 120 s and rinsed with ethanol solution, and then the solder (6.8 mm²) with an activated flux (0.01 ml) was placed on the center of the BMG sample as shown
in Fig. 1(a). The test sample was placed in a radiation furnace and heated in a nitrogen atmosphere. In this heating process, the peak temperature ranged from 503 to 653 K depending on the BMG composition, and the peak time was 60 s. After the heating process, the sample was cooled in air. For the aging process, some samples were heat-treated in an oil bath at 403 K for 168 h and 504 h. For all samples, the spread area of the solder on the BMG was observed by using the optical microscope. Then, some samples were cut and the cross-section of the sample was polished to observe the interface between the solder and BMG. A scanning electron microscope (SEM) was used to observe the interface and the optical microscope was used to measure the thickness of the intermetallic compound (IMC) at the interface.

For the ultrasonic soldering, the schematic diagram of the experimental setup (KURODA TECHNO Co., Ltd: KDB-100A) was shown in Fig. 1(b). A commercial Sn-Zn-Sb system solder (KURODA TECHNO Co., Ltd: Cerasolzer) was employed. The ultrasonic oscillator was set at the bottom of the solder bath. The frequency of the oscillator was 20 kHz and the output power was 40 W. The BMG sample was immersed into the molten solder at 533 K for 60 s without a flux. The dipping test was carried out in air. After the dipping test, in order to confirm the inter-reaction between the solder and BMG, the reheating test was performed. After dropping the flux on the test sample, the sample was heated at 573 K for 60 s. The optical microscope was used to observe the surface of the sample.

### 3. Results and Discussion

The wetting behavior of lead-free solder on bulk metallic glasses (BMGs) was evaluated by measurements of the spread area of SAC305 solder on BMGs. Each of the three BMGs was tested as a function of the peak temperature. The results are summarized in Table 2. Pd-based BMG exhibited a good wetting behavior of the solder at 503 K and 523 K. The spread area at 523 K was clearly larger than that at 503 K. On the other hand, concerning Cu-based and Zr-based BMGs, there was no wetting of the solder on the surface of BMGs regardless of the peak temperature. The molten solder was never attached to the BMG surface during the heating process. So in order to clarify the reason why there was no wetting on Cu-based BMG, X-ray photoelectron spectrometry (XPS) analysis was performed on the surface of Cu-based BMG. As a result of XPS analysis, Zr oxide and Ti oxide were detected on the surface except Cu oxide. Due to the stability of Zr oxide and Ti oxide, these oxide layers may prevent the wetting of the solder on Cu-based BMG even if common activated flux is used. In other words, when a BMG contains Zr and/or Ti as a component, it is difficult to get a good wettability of a usual solder on the BMG.

Figure 2 shows an optical microscope image of the appearance of typical test sample and a SEM image of the interface between the solder and Pd-based BMG after spread test at 523 K for 60 s. From the optical microscope image, the solder spread on Pd-based BMG roundly. It was clear that the wettability of SAC305 solder on the BMG was extremely
good. From the SEM image of the interface, the formation of the intermetallic compound (IMC) layer could be confirmed at the interface. This means that Pd-based BMG reacted with SAC305 solder. The influence of the solder composition on the wetting behavior on Pd-based BMG and the detailed analysis of the interface were discussed in other paper.\textsuperscript{16}

Figure 3 shows the measured IMC thickness just after the heating process at 523 K for 60 s and the effect of aging time at 403 K on the IMC thickness. During the aging process at 403 K, the IMC thickness increased with the increase of aging time. This means that the reaction between the SAC305 solder and Pd-based BMG continues to be induced in the solid-state. The thickness is proportional to the square root of aging time. Accordingly, the growth of the IMC layer between the SAC305 solder and Pd-based BMG during the aging process can be considered a diffusion control process.

Concerning Cu-based and Zr-based BMG which had poor wettability for the SAC305 solder, the ultrasonic soldering process was tested to establish the joint process for BMGs containing Zr and/or Ti. Figure 4 shows the appearance of test samples after immersing into the molten solder at 523 K for 60 s with ultrasonic. For both Cu-based BMG and Zr-based BMG, BMGs are seemingly covered with the solder. Therefore, the application of ultrasonic is very effective to the soldering process. In order to confirm the inter-reaction between the solder and BMGs, the heating test of the sample covered with the solder was performed using a common activated flux. Figure 5 shows the appearance of test samples after heating at 573 K for 60 s with flux. As can be seen in this figure, the sample covered with the solder showed complete dewetting during the heating process. The solders were remained like an island on the surface after reheating test. The remained solder could be removed from the surface after ultrasonic cleaning. This means the solder was only attached to the surface of the BMG by the mechanical adhesion such as an anchor effect. So, the effect of the ultrasonic on the
soldering process would be to remove the harmful factors such as oxide layer, air layer and organic substance from the BMG surface. As a result, the wettability on Cu-based and Zr-based BMGs was improved and the mechanical adhesion was expected to be formed between the BNG and the solder.

4. Conclusion

In this study, the spread test of the solder was basically performed for three kinds of BMGs, which were Cu-based, Zr-based and Pd-based IMC, in order to clarify the wetting behavior of the solder on BMG. Then, the ultrasonic soldering process was tested for Cu-based and Zr-based BMG. The main results were summarized as follows:

(1) Pd-based BMG exhibited a good wetting behavior of the solder at 503 K and 523 K. The spread area at 523 K was clearly larger than that at 503 K. On the other hand, concerning Cu-based and Zr-based BMGs, there was no wetting of the solder on the surface of BMGs regardless of the peak temperature.

(2) Due to the stability of Zr oxide and Ti oxide, these oxide layers may prevent the wetting of the solder on Cu-based BMG even if common activated flux is used.

(3) For both Cu-based BMG and Zr-based BMG, BMGs are seemingly covered with the solder using ultrasonic. However, it was found that the solder was only attached to the surface of the BMG by the mechanical adhesion such as an anchor effect.

Acknowledgements

This work was supported by Grant-in-Aid for Cooperative Research Project of Nationwide Joint-Use Research Institute on Development Base of Joining Technology for New Metallic Glasses and Inorganic Materials from The Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES


Fig. 5 Appearance of BMG samples after the reheating test with flux at 573 K for 30 s. (a) Cu-based BMG, (b) Zr-based BMG.