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BONDING OF ALUMINA AND METAL
USING BULK METALLIC GLASS FORMING ALLOY

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Metal-alumina joints have found various practical applications in electronic devices and high technology industry. However, making of sound metal ceramic brazed couple is still a challenge in terms of its direct application in the industry. In this work we successfully braze copper with Al_2O_3 ceramic using $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ bulk metallic glass forming alloy as filler alloy. The shear strength of the joints can reach 140 MPa, and the microstructrural analysis confirms a reliable chemical boning of the interface. The results show that the bulk metallic glass forming alloys with high concentration of active elements are prospective for using as filler alloy in metal-ceramic bonding.

Keywords: Bulk metallic glass forming alloy; brazing; ceramic-metal bonding.

1. Introduction

With high strength, high temperature resistance and high erosion resistance, Al_2O_3 ceramics have a very excellent potential to be used as special materials in aerospace and biomaterials[1-5]. However, ceramics has low toughness and is hard to manufacture into complex shapes. Therefore, it is very reasonable and important to focus on welding ceramics to metals[6-8]. Till now, making of sound metal ceramic brazed couple is still a challenge in terms of its direct application in the industry[9,10]. In liquid phase bonding process, the quality of bond is often limited by wetting phenomena of ceramics by liquid metal and formation of interfacial phases due to chemical reactions between both components. Therefore, it is necessary to develop a reaction layer at the ceramic surfaces to increase their wetting behavior with the liquid filler alloy. One such method is active metal brazing, which is extensively used in the recent past. Addition of chemically active elements such as Ti or Zr to the filler alloy improves its wettability to ceramic substrate[11-13]. Many conventional brazing alloys containing Ti and Zr are brittle and difficult to fabricate into thin shapes conducive to brazing. A conventional form of brazing alloys is paste or plastic bonded tape, in which a powdered form of the alloys is carried by an organic binder. The drawback, however, lies in the residue and porosity. In contract, amorphous filler metals have many advantages, such as ductility, thin gauge,

homogeneity of microstructure, low melting temperature, narrow temperature interval of the solidus and liquidus temperature, short brazing time, and high atom diffusion activity[14-16].

In this work, we have successfully brazed copper with alumina using $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ amorphous alloy ribbons. This filler alloy has high ductibility and toughness. And the active components, Zr and Ti, are in favor of the reaction and diffusion between the amorphous alloys and the bonding materials. Besides, the components of the filler alloy do not contain Ag, which has a high saturated vapor pressure. The mechanical properties of the joints were characterized by shear and tensile tests. The microstructure of the joints was investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

2. Experiment Procedure

The starting materials used for the preparation of amorphous alloy ribbons were Zr, Cu, Ni, Al and Ti with as least 99.9 % purities. The master alloy, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ ingot (all in at. %) was prepared by arc melting the pure elements in a titanium-gettered argon atmosphere. The amorphous $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ ribbons were fabricated by a conventional single roller melt-spinning facility in an high purity argon atmosphere. The obtained ribbons are about 8 mm in width and 50 μm in thickness. The purity of the copper material was more than 99.99 % (in wt. %). The size of the copper rods was 6.0 mm in diameter and 30.0mm in length. Commercial Al_2O_3 panels with the purity of 95.71 wt. % are used in this work. They were cut into 20 mm×20 mm×4 mm pieces before brazing.

Thermal analysis of the $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ amorphous alloy ribbons was performed using a Netzsch 404C differential scanning calorimeter (DSC) at a heating rate of 20°C/min in an argon atmosphere. Dynamic wetting angle measurements were carried out using a traditional resistance vacuum furnace at the temperature 900°C, 920°C and 940°C, respectively, for 0-1800 seconds[12,13]. A piece of filler alloy with the weight 0.2 g was put on the ceramic disk in a vacuum resistance furnace for wetting angle experiment. The heating rate of the furnace was set at 20°C/min from room temperature till it reached 700°C and kept for 20 minutes at that temperature. Then it was heated again to the brazing temperature at the heating rate 10°C/min.

The brazing surface of the copper pole was dry polished using sand papers. The roughness of the ceramic (Al_2O_3) surface is 0.8 μm. All the samples were cleaned ultrasonically using ethanol. The joining procedure consisted of placing the amorphous alloy ribbon between the copper pole and the ceramic panel, and heating the assembly under a vacuum (~10^{-3} Pa) to the brazing temperature in the vacuum resistance furnace. The self weight of the copper pole was kept over the assembly as a normal load during brazing. The furnace was heated at a rate of 20°C/min from room temperature till it reached 700°C and kept for 20 minutes at that temperature. Then it was heated again at a rate of 10°C/min to the brazing temperature (900°C, 920°C and 940°C) and kept for 5, 30

and 60 minutes, respectively. The cooling rate was maintained at 10°C/min till it reached 200°C, and thereafter the assembles cooled naturally within the furnace.

Shear and tensile tests were carried out through a Material Test System (MTS-810). A loading speed of 0.1 mm/min was applied during the tests. Strength was determined by dividing the maximum load applied at which fracture took place by the cross section area of the joint. To explore the relationship between the mechanical properties and the brazing conditions, the welded samples were tested in tension and shear mode (with the weld line perpendicular and parallel to the loading axis respectively).

For morphological and structural examinations, the brazed samples were cut in order to get a fresh surface for characterization observation. The cut samples were mechanically polished, chemically etched, and cleaned ultrasonically using ethanol. The microstructure of the joint was examined by Polyvar MET optical microscopy and LEO-1530-FESEM scanning electron microscopy (SEM) coupled with Oxford energy dispersive spectroscopy (EDS).

3.   Results and Discussions

Thermodynamic parameters and thermal stability of the $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ ribbons were studied using DSC at a continuous heating rate of 20°C/min. The results are shown in Fig. 1. The alloy exhibits an endothermic reaction caused by glass transition, followed
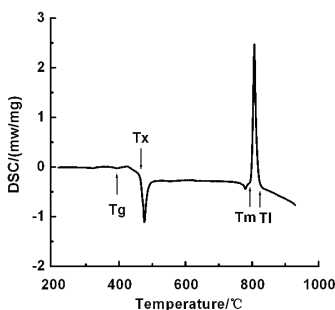

Fig. 1. The DSC result of the $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ amorphous alloy ribbons.

by a sharp exothermic reaction caused by crystallization, indicating the amorphous nature of the ribbons. The onset temperature of glass transition (T_g) and the onset temperature of crystallization (T_x) are 413.2°C and 459.3°C respectively. These values agree well with the reported results of the $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ bulk metallic glasses with similar composition[17]. The melting temperature (T_m) is 793.6°C, and the liquidus temperature (T_l) is 835.8°C. The melting region span (the difference between T_l and T_m) of the alloy is 42.2°C. T_l of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ is much lower than that of pure copper (about 1083°C), and is closer to that of the conventional TiAgCu filler alloy used in Cu-Al_2O_3 joints. This is one reason of choosing the Zr-based amorphous as filler alloy. Besides, the components, Zr and Ti, have good activity to react with copper and Al_2O_3. Furthermore

the alloy does not contain the high saturated vapor pressure element, Ag. This can greatly reduce the cost of the filler alloy and more importantly suitable for the high vacuum sealing applications.
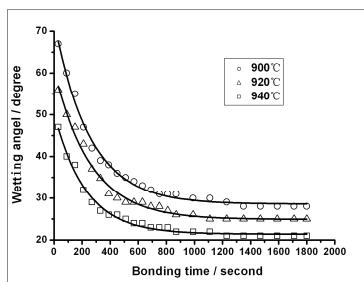

Fig. 2. The dynamic wetting angel measurements of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ at various holding temperatures.

Figure 2 shows the dynamic wetting angle measurements of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ filler alloy holding at 900°C, 920°C and 940°C, respectively for up to 1800 seconds. The wetting angle of filler alloy decreases rapidly with holding time during the first 300 seconds, and becomes stable after that. It is also seen that the wetting angle decreases with increasing the holding temperature. The final wetting angle of filler alloy at 900°C, 920°C and 940°C is 28, 25 and 21 degree, respectively. According to the results, $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ demonstrates good ability to wet Al_2O_3 ceramics[18-20]. The wetting alloy has shown a strong tendency to interact at the solid-liquid interface to form solid solutions and a certain degree of active metal intergranular penetration.
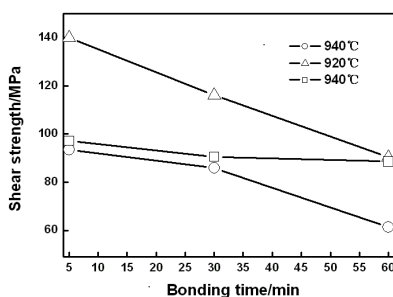

Fig. 3.   Effects of brazing time and temperature on shear strength of joints.

Depending on the wetting measurement results, we choose the brazing temperature from 900°C to 940°C, as further higher brazing temperature will induce higher thermo stress into the final joints. Shear and tensile tests were carried out for the joints at a constant displacement rate of 0.1 mm/min. The dependence of shear strength on the brazing temperature and time are shown in Fig. 3. It can be seen that the shear strength of the sample decreases with the increase of the bonding time at all three applied brazing temperatures. The samples brazed for 5 min exhibit the highest shear strength. This

means that a great extension of reaction time does not contribute to a higher joint mechanical performance. It can also be found in Fig. 3 that brazing at 920°C provides a higher strength than those at 900 and 940°C. The highest shear strength is obtained at 920°C for a bonding time of 5 min, which is 140MPa. The tensile strength of the joints is much smaller than the shear strength. That is because the tensile strength of ceramic is much smaller than that of shear strength.

It should be mentioned that all the samples for mechanical property measurements fail on the ceramic part of the joints. This means that the strength of the interfaces is stronger than the ceramic itself, indicating an effective bonding between copper and Al_2O_3 ceramics. The change of the joint strength may also be caused by the embrittlement upon high temperature exposure. It can be expected that the strength of the joints could be improved greatly when high purity ceramic are used.
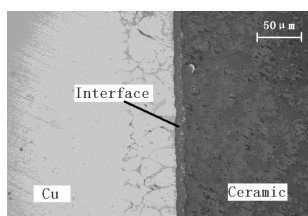

Fig. 4. The interface between copper and ceramics using the optical microscopy.

Figure 4 shows the interface between copper and ceramic brazed at 920°C for 5 minutes using an optical microscopy. A clean and smooth interface with the thickness of about 10 μm can be seen clearly. No impurities and porosities can be found. The SEM morphology and EDS analysis of the interface are shown in Fig. 5. It can be seen that the microstrcture of interface is fine and homogeneous, and no coarse intermetallic phase can be found. EDS analysis results show that Zr element in the filler alloy effectively diffuse into ceramic and copper layer, proving a strong chemical bonding. The uniform distribution of Zr element around the interface further proves that the interface microstructure is fine and homogeneous without the precipitation of coarse crystalline phase. These all contribute to the high bonding strength of the joints. The achievement of the dense and fine interface microstructure and the strong bonding is related to the inherent nature of the present filler alloy with bulk amorphous forming ability. Although the quite slow cooling rate upon liquid phase reaction is insufficient for forming an amorphous interfacial layer, the sluggish crystallization kinetics of the bulk glass forming alloy leads to much better microstructure compared with that of conventional alloys at the same cooling rate. In addition, the present Zr-based glassy ribbons with high ductility are easy to be cut and shaped, which are important for the welding of parts with a complicated profile. Furthermore, the novel filler alloy without high saturated vapor pressure element is especially suitable for the high vacuum sealing applications.
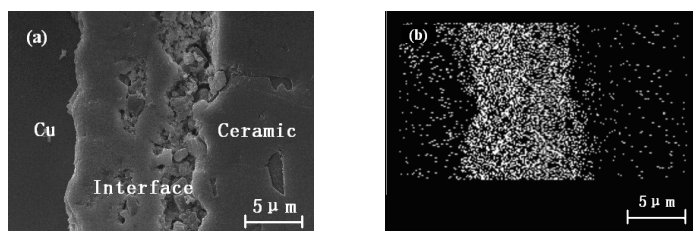
Fig. 5. EDS analysis of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ brazed at 920°C for 5 minutes: (a) SEM image; (b) Zr mapping.

4. Conclusions

Al_2O_3 Ceramic has been successfully brazed to copper using $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ amorphous alloy ribbons. The glass forming filler alloy shows a good wettability with the Al_2O_3 ceramics. Microstructural examinations confirm a strong chemical bonding of the two parts. All the mechanical tests show that the Al_2O_3-filler alloy-copper assembly failed at the ceramic part, indicating an effective bonding. Shear strength of 140 MPa is obtained after brazing at 920°C for 5 minutes. Higher joint strength could be expected when high purity ceramic are used.

Acknowledgments

References

1. A. Urena, J.M.G. DeSalazar, J. Quinones, *J. Mater. Sci.* **27**, 599 (1992).
2. K.S. Weil, J.S. Hardy, *Electrochem. Solid-State Lett.* **8**, 136 (2005).
3. J.W. Park, P.F. Mendez, T.W. Eagar, *Scr. Mater.* **53**, 857 (2005).
4. C.H. Bates, M.R. Foley, G.A. Rossi, G.J. Sundberg, F.J. Wu, *Am. Ceram. Soc. Bull.,* **69**, 350 (1990).
5. B.R. Zhao, G.B. Li, P. Gao, T.Q. Lei, S.C. Song, X.J. Cao, *Nucl. Instrum. Methods Phys. Res.* **239**, 147 (2005).
6. A.K. Jadoon, B. Ralph, P.R. Hornsby, *J. Mater. Process. Technol.* **152**, 257 (2004).
7. V.G. Novikov, *Welding International,* **65**, 477 (1995).
8. A. Kar, S. Mandal, K. Venkateswarlu, A.K. Ray, *Mater. Characterization,* **58**, 555 (2007).
9. J.Q. Li, G.M. Zhu, P. Xiao, *J. Mater. Sci. Lett.,* **22**, 759 (2003).
10. A.E. Martinelli, R.A.L. Drew, *Mater. Sci. & Eng.,* **191**, 239 (1995).
11. A. Passerone, M.L. Muolo, D. Passerone, *J. Mater. Sci.* **41**, 5088 (2006).
12. C.C. Lin, R.B. Chen, R.K. Shiue, *J. Mate. Sci.,* **36**, 2145 (2001)
13. M.L. Muolo, E. Ferrera, A. Passeronen, *J. Mater. Sci.,* **40**, 2295 (2005).
14. Y. Sato, T. Ozawa, T. Sato, *J. Japan Institute of Metals,* **56**, 553 (1992).
15. C. Schuh, T. Hufnagel, U. Ramamurty, *Acta Mater.,* **55**, 4067 (2007).

16. A. S. Sidhu, R. A. Varin, *Polymer Composites,* **14**, 64 (1993).
17. X. Gu, L.Q. Xing, T.C. Hufnagel, *J. Non-Crystalline Solids,* **311**, 77 (2002).
18. Y. Duan, Z.D. Zou, S.Y. Qu, *Welding & Joining,* **3**, 37 (2002).
19. D. Xu, D.N. Wang, G.Q. Liu, D.L. Lin, *Acta Materiae Compositae Sinica,* **12**, 41 (1995).
20. C.G. Wan, P. Kritsalis, N. Eustathopoulos, *Trans. China Welding Institution,* **15**, 209 (1994).