Direct brazing of Al₂O₃ without reaction layer by self-removing oxide film Aluminum foil solder

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This paper proposed a kind of Aluminum (Al) foil filler with sputtering Ni/Al double layers on surface and a brazing method of elevating temperature. Results showed that this coated foil filler could make Al₂O₃ film on aluminum surface broken and sweep them into brazing seam because it was buried by Ni/Al double layer. The direct brazing of Al alloy to Al₂O₃ could be realized without interface reaction transition layer. Rising brazing temperature could enhance the interface between seam and ceramic, making joint fracture transfer from the interface into seam gradually. The shear strength of joint was improved to the maximum of 158 MPa at above 840 °C from 49 MPa at 680 °C.

Key-words : Al₂O₃, Al foil solder, Joining, Interface, Strength

1. Introduction

Brazing is the most important method to bond ceramics, where melting metal needs to wet ceramics. Unfortunately, most metals cannot effectively wet ceramics including Al₂O₃. Typical brazing techniques include the premetalized method where an active metal (e.g., Ti, V and Cr) layer is applied to ceramics surface¹⁻³ or the active filler method where active metal is added to fillers.⁴⁻⁷ Both methods create a reaction layer of active metal and ceramics to improve the wettability of liquid metal on ceramics. However, reaction transition layers are detrimental to joint properties: strength, thermal conductivity and thermal fatigue, etc.

Aluminum shares many desirable properties with common filler metals (e.g., Cu, Ni and Ag), such as low elastic modulus and good plasticity, conducive to joint stress mitigation and fatigue performance improvement. The excellent corrosion resistance of aluminum helps expand service environment of the joint and the melting temperature below 660 °C helps potentially reduce the brazing temperature. Unlike common filler metals, liquid Aluminum (Al) can directly wet Al₂O₃ at high temperature without interface reaction.³⁻¹⁰

Up to now, however, Al and its alloys have seldom been used as brazing fillers even though they can wet ceramics, due to two significant challenges. First, the temperature required to achieve wetting of liquid Al on Al₂O₃ is very high (only at 850 °C or above would contact angle reduce below 90°).¹⁻³ High temperature complicates the brazing process. Second and more importantly, liquid Al, like its solid form, is covered by a layer of dense oxide film of Al₂O₃. The Al₂O₃ film prevents the direct contact of Al with ceramics and is very difficult to remove. Although only 5–10 nm of nanometers thick,¹¹ Al₂O₃ film has a very high melting point of 2050 °C, decomposed only under high temperature of 1000 °C and oxygen pressure of 10⁻³² Pa,¹² conditions not easily achieved using existing technologies. As the result, this oxide film will crack and be going to back to form still covered on the surface of Al liquid. The presence of the oxide film also makes the study of the wettability of Al on ceramics very difficult and study results highly inconsistent.

This paper realized Al₂O₃ brazing without interface reaction transition layer, using Ni coated Al filler. The joint shear strength was improved by elevating brazing temperature.

2. Material and methods

A 30μm pure Al foil was ultrasonically cleaned in alcohol and dried before mounted on the substrate holder in the vacuum chamber of the ANELVASPC-350 multi-target magnetron sputtering system. When the background pressure reached below 4.0 × 10⁻⁴ Pa prior to the deposition, high purity Ar gas (99.999%) with a pressure of 0.6 Pa was aerated into the vacuum chamber.

A 2 μm Al layer was deposited on each side of the Al foil, followed by a 0.1 μm Ni layer, forming bi-layered film. When melted, the coated foil would form Al alloy
liquid with 0.9 at.% Ni.

High purity polycrystalline Al2O3 ceramic plate (12 × 12 × 1 mm) was selected as the substrate. Holding the coated Al foil between two Al2O3 substrates, a stainless steel weight was placed on top of the sample to exert pressure at approximately 1 kPa. The brazing was carried out in vacuum of 10⁻¹² Pa at various temperatures between 680 and 880 °C for 30 min.

The composition profile of coated Al foil filler surface was analyzed by Glow Discharge Optical Emission Spectroscopy (GD-OES). The sheer strength of brazed joints was evaluated using an electron-tensile tester, based on the average of 10 tests. Hitachi S3400N scanning electron microscope (SEM) and optical microscope were used to observe the joint tissue and appearance of fracture.

3. Results

The depth distribution of Ni, Al and O is analyzed by GD-OES to demonstrate the surface structure of coated foil filler. To save time, only 60 nm thick Ni and Al layers are deposited on the Al foil surface respectively. As shown in Fig. 1, the outside layer is a Ni layer and its oxide. With the increasing of depth, sputtered Al film with low O content appears after the Ni/Al interface. Further down, there is a 20 nm oxygen-rich area between sputtered Al film and Al foil, showing that Al2O3 film on Al foil surface is buried by Ni/Al bi-layer film.

Figure 2 illustrates the mechanism of removing Al2O3 film from this Al foil filler surface through Ni/Al bi-layer film. In Fig. 2(a), the uncoated Al foil adheres to the ceramic under external pressure, and the Al2O3 film on the surface directly contacts the ceramic. During the heating process, this brittle Al2O3 film will crack due to the large thermal expansion coefficient difference between Al (26 × 10⁻⁶ °C⁻¹) and Al2O3 (8.8 × 10⁻⁶ °C⁻¹). However, after the Al foil is melted, the molten Al cannot push these broken solid Al2O3 films completely away from the interface. Most of them are still blocked between the Al melt and the ceramic.

Unlike the uncoated Al foil, in Fig. 2(b), the Al2O3 film is buried by the Ni/Al double layers outside the coated Al foil and will crack during heating process. After the Al foil and the Ni/Al double layers are melted, the broken Al2O3 film will be swallowed by molten Al on both sides and highly dispersed in the brazing seam. The outermost layer of NiO film will be decomposed by the reaction of Al + NiO → Al2O3 + Ni with the Al melt. Therefore, the direct contact of the molten Al–Ni alloy to the Al2O3 ceramic is achieved.

The SEM observation found that the joints brazed at different temperature present the same seam structure, as Fig. 3, brazed at 680 °C. The seam exhibits high density without pronounced brazing defects such as incomplete penetrations and pores. With 0.9 at.% Ni, the seam mainly forms Al solid solution structure. It should be noted that there is no reaction layer in the interface between the Al seam and Al2O3.

In order to further demonstrate the effect of removing Al2O3 film by the coated Al foil, the surface scan of Al, Ni,
and O elements was performed on the brazed joint using energy dispersive X-ray spectroscopy (EDS), and the results are shown in Fig. 4. In this figure, there is no element enrichments and reaction transition layer in the interface between the Al seam and Al₂O₃ ceramics. It is shown that the Al₂O₃ film on the surface of the Al foil was successfully removed, and the direct contact of the Al liquid to the Al₂O₃ ceramic was achieved. In addition, no significant enrichment of Ni and O elements was found in brazing seam, indicating that the broken Al₂O₃ and Ni were evenly dispersed in the seam.

Shown in Fig. 5, the shear strength of the joint brazed at 680 °C is 49 MPa. As the brazing temperature rose, the joint strength gradually increased till plateauing at the maximum value of 158 MPa at 840 °C.

Observation of the fracture surfaces of the joints by optical microscope is shown in Fig. 6. The fracture morphology of joints changes significantly as the brazing temperature increases. It exhibits a clear Al₂O₃ surface dispersed tiny Al fracture spots at 680 °C, indicating the fracture essentially occurred at the interfaces between the seam and ceramics. At 760 °C [Fig. 6(b)], in addition to interface fracture morphology, furrow like scratch marks emerged, caused by shear fracture of the high plastic Al. The furrow area expanded in the joint as brazing temperature rose and at 840 °C, fracture morphology consisted of entirely furrow scratch marks, indicating the fracture transferred from the interface to the inside of the seam [Fig. 6(d)]. The transfer of fracture location demonstrated that as temperature rose, the enhancement of joint strength was driven by the increase of interface strength between seam and ceramic.

As shown in Fig. 7, the surface scan of Al, Ni, and O elements is performed on the fracture surface using EDS. A large amount of O elements and few Al-rich little regions are distributed on the fracture surface at 680 °C [Fig. 7(a)]. This result indicates that the fracture essen-

Fig. 3. SEM image of 680 °C brazing joint.

Fig. 5. The relationship between joint shear strength and brazing temperature.

Fig. 4. (a) SEM secondary electron images of joint brazed at 680 °C and corresponding area-scan images of (b) Al, (c) Ni and (d) O elements.
tially occurred at the interfaces between the seam and ceramics. As the temperature rose, the Al-enriched area gradually increases, while the O element decreases accordingly, indicating that the fracture transferred from the interface to the inside of the seam. At 840 °C, the fracture surface is basically covered by the Al element, and the fracture mainly occurs inside the brazing joint [Fig. 7(d)]. During the whole process, the distribution of Ni element hardly changes with temperature.

4. Discussion

The removal of oxide film and improvement of joint strength were two critical procedures in the brazing ceramic by Al filler. In this paper, they were cleverly resolved by using coated Al foil filler and rising brazing temperature respectively.

Al and its alloys, although not used for ceramic brazing, are common filler metals for Al and other metals. The removal of oxide film is a critical procedure in the brazing process. To remove Al2O3 film, Mg steam is used for vacuum brazing, while chloride flux for non-vacuum brazing. However, these chemical methods are not suitable for ceramic brazing because the reaction products are difficult to dispose. In this paper, the removal of Al2O3 film was accomplished by burying it with Ni/Al bi-layer films. This method is a physical approach, much easier to operate and could avoid the pollution of reaction products on work pieces and heating chamber.

It should be noted that although Ni was used as outside layer of the bi-layer film in this paper, Cu, Ag, Si etc., can also be used and will have the same effect. They were alloy elements of Al and have much higher free energy of oxide formation than Al.

Previous researches showed that the liquid Al cannot wet Al2O3 directly near the melting point. With the tem-

![Fig. 6. Optical microscope images of the fracture morphologies of joints brazed at different temperatures (a) 680 °C; (b) 760 °C; (c) 800 °C; (d) 840 °C.](image)

![Fig. 7. SEM images and corresponding area-scan images of Al, Ni and O elements of joints brazed at different temperatures (a) 680 °C; (b) 760 °C; (c) 800 °C; (d) 840 °C.](image)
perature increasing, the contact angle gradually decreases from about 130° to below 90° at 850 °C or above.11) The wetting improvement comes from reduction of the solid/liquid interfacial tension, which is attributed to the formation of the chemical bond between Al atom in liquid and the O atom on the ceramic surface.16) The higher temperature provides enough kinetic energy for Al atoms, so they could overcome the energy barrier to form Al–O bonds.

Unlike common brazing methods at 20–50 °C above filler melting temperature, this paper introduced an approach with significantly higher brazing temperature. The aforementioned results showed that the joint strength significantly increased from 49 MPa at 680 °C to 158 MPa at 840 °C, although no observable changes in the structure of seam and interface. Meanwhile, the fracture transferred from the interface to the inside of the seam.

5. Conclusions

This paper proposed a kind of Al foil filler coated Ni/Al bi-layer films and a brazing method of elevating temperature. The Al2O3 on the Al foil surface could be broken and swallowed into brazing seam through burying it with Ni/Al bi-layer films. Direct brazing of Al2O3 without interfacial reaction layers was achieved and the joint was enhanced through elevating brazing temperature. The shear strength increased from 49 MPa at 680 °C gradually to the maximum of 158 MPa at 840 °C.

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References

1) W. Cui, J. C. Yan, Y. Dai and D. D. Li, Ultrason. Sonochem., 22, 108–112 (2015).
2) M. Ali, K. M. Knowles, P. M. Mallinson and J. A. Fernie, Acta. Mater., 96, 143–158 (2015).
3) D. P. Yadav, R. Kaul, P. Ganesh, R. Shiroman, R. Sridhar and L. M. Kukreja, Mater. Design, 64, 415–422 (2014).
4) K. M. Jasim, F. A. Hashim, R. H. Yousif, R. D. Rawlings and A. R. Boccaccini, Ceram. Int., 36, 2287–2295 (2010).
5) A. Laik, P. Mishra, K. Bhanumurthy, G. B. Kale and B. P. Kashyap, Acta. Mater., 61, 126–138 (2013).
6) H. Y. Xia, A. P. Wu, Y. L. Fan, G. S. Zou and J. L. Ren, Surf. Coat. Tech., 206, 2098–2104 (2012).
7) S. Ghosh, R. Chakroborty, N. Dandapat, K. S. Pal, S. Datta and D. Basu, Ceram. Int., 38, 663–670 (2012).
8) A. Sangghaleh and M. Halali, J. Mater. Process. Tech., 197, 156–160 (2008).
9) S. B. Lee and Y. M. Kim, Acta. Mater., 59, 1383–1388 (2011).
10) Z. Q. Yu, G. H. Wu, D. L. Sun and L. T. Jiang, Mater. Lett., 57, 3111–3116 (2003).
11) P. Shen, H. Fujii, T. Matsumoto and K. Nogi, J. Am. Ceram. Soc., 87, 2151–2159 (2004).
12) A. Sangghaleh and M. Halali, Appl. Surf. Sci., 255, 8202–8206 (2009).
13) G. Pilania, B. J. Thijssse, R. G. Hoagland, I. Lazić, S. M. Valone and X. Y. Liu, Sci. Rep., 4, 1–9 (2014).
14) B. R. Strohmeier, Surf. Interface Anal., 15, 51–56 (1990).
15) H. Fujii, H. Nakae and K. Okada, Acta Metall. Mater., 41, 2963–2971 (1993).
16) Q. Zhang, T. Çağın, A. V. Duin and W. A. Goddard, Phys. Rev. B, 69, 45423 (2004).