

Explosive Coating of Ag–Cu Filler Alloy on Metal Substrates and Its Effect on Subsequent Brazing Process

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(Received on March 23, 2010; accepted on May 10, 2010)

An austenitic stainless steel plate was coated with a sheet of Ag–Cu filler alloy by using explosive energy to simplify the subsequent brazing operation. The coated specimen had a typically wavy interface, and there were no defects like void. The adhesion at the interface was retained even after heating at a temperature of more than eutectic point of the Ag–Cu binary system (1 052 K), although the molten Ag–Cu alloy did not show a good wettability on the stainless steel without coating. To investigate the effect of the coating on the interfacial microstructure and the bonding strength of finally obtainable joints, two coated specimens were overlapped and then heated at 1 173 K for 0.3 ks in a low vacuum. The obtained joint had a shear strength of about 200 MPa, and broke mainly within the Ag–Cu alloy after a shear test. The joint brazed with the Ag–Cu alloy was also fabricated under the same heating conditions. Its shear strength was about 90 MPa, and the fracture position was at the Ag–Cu alloy/stainless steel interface. This indicates that the substantial bond between the Ag–Cu alloy and the stainless steel, which is achieved by explosive energy, contributes to the subsequent brazing process. Additionally, a commercially pure Ti plate was used as a substrate. In this case, the advantages of the coating process could not be recognized in the finally obtained joint. It is found that the substantial bond provided by explosive energy is canceled by the formation of a reaction layer on the brazing operation.

KEY WORDS: austenitic stainless steel; titanium; Ag–Cu filler alloy; explosive coating; brazing.

1. Introduction

Various metal substrates, which are coated with a brazing filler metal, are produced to simplify the manufacturing process of industrial products. For example, composite materials consisting of aluminum alloy substrate and aluminum filler alloy are normalized as a brazing sheet in Japanese Industrial Standards (JIS Z 3263) and applied in the practical use such as heat exchanger. Since the bonding of the substrate to the brazing filler metal is preliminarily completed, the following advantages are provided: (1) the bonding surface of the substrate is prevented from oxidation on heating in the fabrication process; (2) the influence of ambient atmosphere on wetting of the brazing filler metal on the substrate is negligible; (3) when two coated substrates are overlapped and then heated at brazing temperatures, this is regarded as fusion welding of similar material and it becomes easy to join. Such a coating of the brazing filler metal is generally performed by rolling, spraying and ion plating.^{1–3)} In these methods, however, the adhesion strength between the substrate and the brazing filler metal may be low due to the influence of coating factors such as the atmosphere in the pre-bonding process.

In the present study, explosive welding process was applied to the coating of the brazing filler metal on the sub-

strate. We refer to this process as “explosive coating”. One of its positive aspects is the capability for the formation of substantial bond between two materials, which cannot be joined by conventional methods like diffusion bonding. Furthermore, the bonding strength is higher than that of the joint fabricated by any other bonding methods. Stainless steel and Ti plates, which are a typical structural material, were coated with a Ag–Cu filler alloy sheet by explosive coating technique. Subsequently, the bonding operation for these specimens was carried out by the intermediary of the coating layer. The effectiveness of the coating by explosive energy was discussed on the basis of the interfacial microstructure and the bonding strength of the finally obtained joints.

2. Experimental Procedures

Commercially produced austenitic stainless steel (SUS304; 18.28 mass% Cr, 8.13 mass% Ni) and commercially pure Ti (TP340H) were used as a substrate. These were machined into plates with dimensions of 90 mm×40 mm×5 mm and then annealed at 973 K for 3.6 ks in a vacuum of less than 3 mPa. Ag–Cu filler alloy (BAG-8) with eutectic composition was also prepared. This sheet with a thickness of 0.3 mm was heat-treated at 1 023 K for 3.6 ks

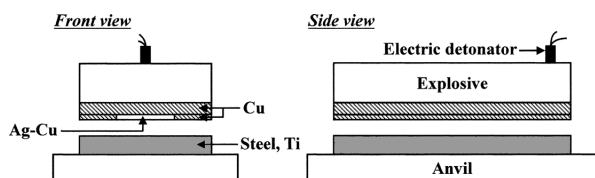


Fig. 1. Schematic illustration of experimental assembly for coating.

in an evacuated silica tube to soften before shock coating. These bonding surfaces were finished with #1200 emery paper. These were degreased in acetone using an ultrasonic cleaner and dried with hot air.

The coating operation was carried out using experimental apparatus shown in Fig. 1. The Ag–Cu filler alloy was combined with Cu plates to play a role as a flyer plate and fixed parallel to the steel and Ti substrates. The distance between the Ag–Cu filler alloy and the substrate was 5 mm. The powdery explosive consisting mainly of ammonium nitrate was set on the flyer plate. Its detonation velocity is about $2400 \text{ m} \cdot \text{s}^{-1}$, and the explosive with a weight of 64.8 g was used. The flyer plate velocity on the coating was estimated to be approximately $320 \text{ m} \cdot \text{s}^{-1}$.⁴⁾

The substrate coated with the Ag–Cu filler alloy was cut into a rectangular block with dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 5 \text{ mm}$. The surface of the Ag–Cu filler alloy was finished with #1200 emery paper. In some cases, the thickness of the Ag–Cu filler alloy on the substrate was adjusted from 0.3 to 0.15 mm by grinding. After degreasing, two pieces were overlapped by the intermediary of the Ag–Cu filler alloy. This couple was fixed in a jig consisting of two Mo rods and two stainless steel blocks. The assembly was heated in the range from 1023 to 1173 K for 0.3 and 3.6 ks in a vacuum of less than 3 mPa. After a holding step, this was allowed to cool in the furnace to room temperature. To demonstrate the effectiveness of the coating, the bonding treatment was also carried out in a low vacuum of approximately 1 Pa, which was provided only by an oil rotary vacuum pump.

For comparison, the Ag–Cu filler alloy with a thickness of 0.3 mm was inserted between two stainless steel blocks and between two Ti blocks, respectively, and then heat-treated under the same conditions. This corresponds to conventional vacuum brazing.

The specimens were cut perpendicular to the interface to reveal the microstructures. The cross sections were ground with emery papers and then finished with alumina powder. They were examined by using an optical microscope and a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX). The specimens for transmission electron microscopic (TEM) observations were also prepared. The bonding strength was evaluated at room temperature by a shear test, which was performed at a crosshead speed of $8.3 \mu\text{m} \cdot \text{s}^{-1}$ by using an Instron-type tensile machine equipped with a special gripping device. After the shear test, optical microscopic observations and SEM-EDX analysis were conducted to clarify the fracture position.

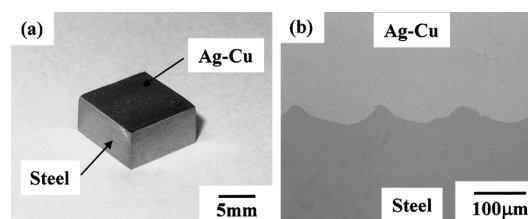


Fig. 2. (a) External view of as-coated specimen. (b) Optical micrograph of the interface between Ag–Cu filler alloy and stainless steel.

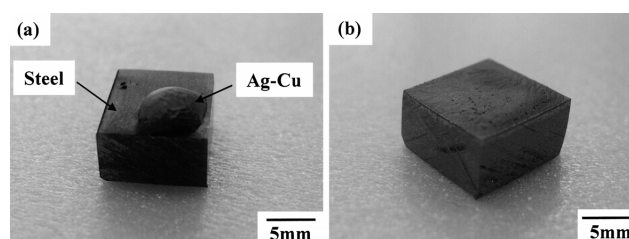


Fig. 3. External views of Ag–Cu filler alloy on stainless steel heated at 1173 K for 3.6 ks in a vacuum. (a) Non-coated specimen. (b) Coated specimen.

3. Results and Discussion

3.1. Stainless Steel Coated with Ag–Cu Filler Alloy Sheet

Figure 2(a) shows an external view of stainless steel coated with Ag–Cu filler alloy sheet by using explosive energy. The thicknesses of the steel and the alloy sheet were 5 mm and 0.3 mm, respectively. An optical micrograph of its interface is shown in Fig. 2(b). The specimen had a typically wavy interface and there were no defects like void. An eutectic structure in the Ag–Cu alloy could not be seen in an optical microscopic scale because of its fineness. TEM observations were carried out at the interface between the steel and the alloy sheet. There was a fine grain region in the vicinity of the collision interface. It was difficult to index Debye ring patterns taken from this region, since austenitic stainless steel, Ag and Cu have a FCC structure and these lattice parameters are pretty close. There is also a possibility that a supersaturated solid solution of Ag and Cu is formed by melting and subsequently rapid solidification at the contact surface.⁵⁾ It is presumed, however, that the formation of the fine grains in the vicinity of the collision interface occurred in the Ag–Cu alloy side with relatively lower melting point. Such a microstructure appears to be helpful for substantial bond at the interface, as reported on the explosively welded Cu–Be alloy/stainless steel joint.⁶⁾

Figure 3 shows external views of the specimen heated at 1173 K for 3.6 ks in a vacuum. In Fig. 3(a), the Ag–Cu alloy sheet with dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 0.3 \text{ mm}$ was fixed on the stainless steel by using a steel wire before the heat treatment. The alloy became agglomerated on the steel. This indicates that the wetting of the molten Ag–Cu alloy is essentially poor on the stainless steel. On the other hand, the bonding state was retained in the coated specimen even after heating, as shown in Fig. 3(b). The adhesion achieved by explosive energy is found to be unaffected by the melting of the Ag–Cu alloy. Therefore, we do not need attention to the wetting in the subsequent brazing operation.

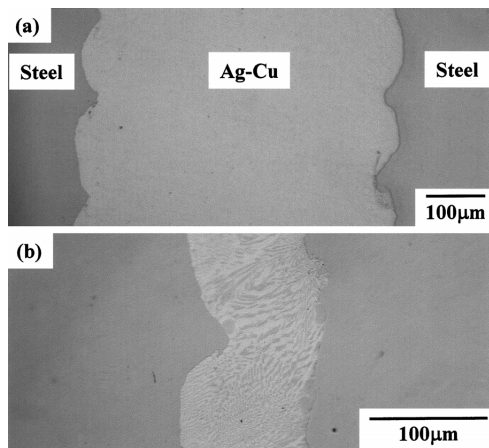


Fig. 4. Optical micrographs of the interface in stainless steel/stainless steel joints fabricated via coating process. Bonding temperature and holding time: (a) 1023 K, 3.6 ks; (b) 1173 K, 3.6 ks.

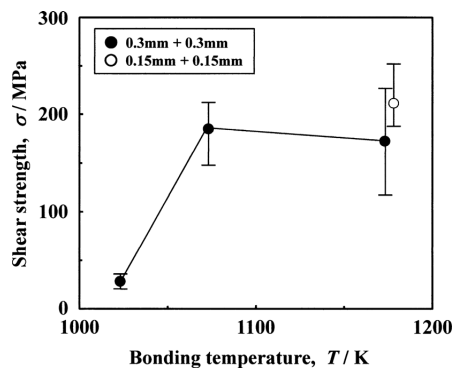


Fig. 5. Relationship between bonding temperature and shear strength of stainless steel/stainless steel joints fabricated via coating process. Bonding time was 3.6 ks. “0.3 mm” and “0.15 mm” mean the thickness of Ag–Cu filler alloy on the steel before bonding treatment.

3.2. Joining of Stainless Steel Coated with Ag–Cu Filler Alloy Sheet

To utilize the advantage of explosive coating, two stainless steels, which were coated with the Ag–Cu filler alloy sheet with a thickness of 0.3 mm, were overlapped and bonded at 1023, 1073 and 1173 K for 3.6 ks in a vacuum. Figures 4(a) and 4(b) show optical micrographs of the interface in the joints fabricated at 1023 K and 1173 K, respectively. Figure 4(a) corresponds to solid state bonding, and the Ag–Cu alloy remained thickly at the interface. In the joints bonded at 1073 and 1173 K, a large amount of the molten Ag–Cu alloy overflowed out of the interface. Consequently, the thickness of the Ag–Cu region decreased from 0.6 mm in total to about 0.1 mm, as shown in Fig. 4(b). The excluded alloy formed spherical blocks in touch with the joint. No reaction layers could be seen between the filler alloy and the steel in all cases.

The bonding strength of these joints is shown in Fig. 5. The joint bonded at 1023 K showed the lowest strength of less than 50 MPa. Figure 6(a) shows a SEM micrograph of its fracture surface. The fracture surface was relatively flat and smooth, and had a fine eutectic structure of the Ag–Cu

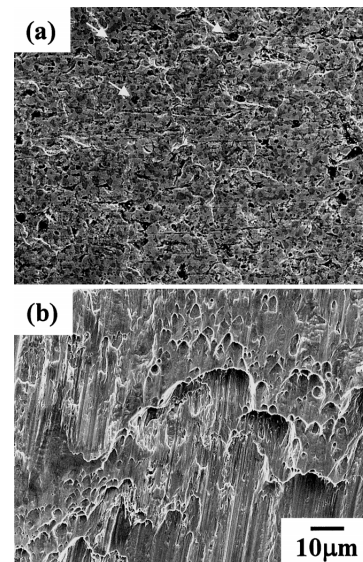


Fig. 6. SEM micrographs of fracture surface of stainless steel/stainless steel joints after shear test. The joints were fabricated at (a) 1023 and (b) 1173 K for 3.6 ks after coating.

alloy. The opposite surface also showed the same microstructure. Therefore, the fracture position is thought to be located in the contact surface of the Ag–Cu alloy sheet. It is noteworthy that there were many voids indicated by white arrows. This indicates that the shrinkage and disappearance of such defects was not promoted by deformation and diffusion at interface during the bonding process.⁷⁾ On the other hand, the joints bonded at 1073 and 1173 K had a high bonding strength of about 200 MPa, as shown in Fig. 5. These joints broke within the Ag–Cu alloy after the shear test. A micrograph of its fracture surface is presented in Fig. 6(b). The aspect differed markedly from that in Fig. 6(a). This results from fusion welding between the alloy sheets. In Fig. 5, the bonding strength of the joint using the alloy sheet whose thickness was mechanically adjusted to 0.15 mm before bonding is also plotted. The total thickness of the alloy sheet was 0.3 mm before bonding. After bonding, the interfacial microstructure was similar to that in Fig. 4(b). It seems that the bonding strength and its dispersion are slightly affected by the initial thickness of the alloy sheet.

Since the bonding of the steel to the filler alloy is already completed by the coating process, the subsequent brazing operation is equivalent to fusion welding of the filler alloy. This has a possibility to be practicable under an extreme condition such as lower vacuum level and shorter holding time. To conduct this verification, the joint using the coated steels was fabricated at 1173 K for 0.3 ks in a rough vacuum, which was provided only by an oil rotary vacuum pump. Its bonding strength is shown in Fig. 7. Before bonding, the alloy sheet on the steel was mechanically ground from 0.3 to 0.15 mm thick, and its total thickness in a couple was 0.3 mm. For comparison, “non-coated” joint brazed with the Ag–Cu alloy sheet with a thickness of 0.3 mm was also prepared under the same heating condition. The bonding strength of the coated joint was almost equal to that in Fig. 5, and approximately 2 times higher than that of the

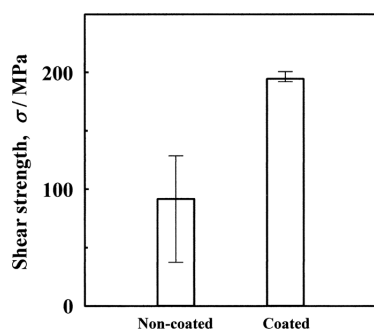


Fig. 7. Shear strength of stainless steel/stainless steel joints bonded at 1173 K for 0.3 ks in a low vacuum. Ag–Cu filler alloy with a thickness of 0.3 mm was used in non-coated specimen. In coated specimen, two steels coated with the filler alloy of 0.15 mm thick were overlapped.

non-coated joint. In this case, the fracture position was within the Ag–Cu alloy, while the non-coated joint broke at the Ag–Cu alloy/stainless steel interface. This indicates that the substantial bond between the Ag–Cu alloy and the stainless steel due to explosive coating is retained through solid–liquid state in the bonding treatment. As a result, the pre-bonding by explosive energy serves to make a high-strength joint under the simplified brazing condition. In other words, the combination of explosive coating and brazing is a beneficial bonding process for the Ag–Cu alloy/stainless steel system.

3.3. Joining of Ti Coated with Ag–Cu Filler Alloy Sheet

As shown in Fig. 4, no reaction layer could be observed at the Ag–Cu alloy/stainless steel interface. To investigate the influence of the reaction layer on the bonding process proposed in the present study, a commercially pure Ti was selected as a substrate with reference to the Ag–Ti⁽⁸⁾ and Cu–Ti⁽⁹⁾ binary phase diagrams.

The bonding of the Ti substrate to the Ag–Cu filler alloy sheet was well achieved by using explosive energy, as well as the combination of the Ag–Cu alloy and the stainless steel. When this coated specimen was heated at 1173 K in a vacuum, the molten Ag–Cu alloy spread on the Ti surface. Such a behavior was also confirmed in the specimen without coating. This means that the alloy reacts readily with Ti. Therefore, the bonding of the coated Ti substrate was carried out at 1073 K for 0.3 ks in a vacuum. **Figure 8(a)** shows an optical micrograph of the interface in the obtained joint. A wavy interface introduced by the coating process could be clearly seen between the Ag–Cu alloy and the Ti substrate. There was a continuous reaction layer, which is indicated by arrows, along the interface. Its thickness was about 10 μm . This was identified as TiCu by composition analysis. It has been known that TiCu is a major reaction phase at the interface in Cu/Ti diffusion couple.⁽¹⁰⁾

This joint had a shear strength of more than 150 MPa. However, the obvious difference with the non-coated joint, which was brazed with the Ag–Cu filler alloy sheet, could not be recognized. **Figure 8(b)** shows a cross-sectional view of the coated joint after the shear test. The propagation of cracks was observed not only within the Ag–Cu alloy but also in the TiCu layer, as indicated by the arrows in the fig-

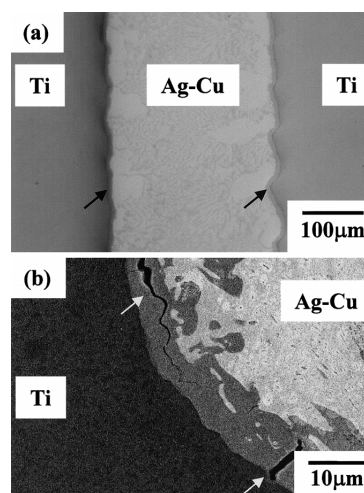


Fig. 8. (a) Optical micrograph of the interface in Ti/Ti joint fabricated *via* coating process. Two Ti substrates coated with Ag–Cu filler alloy of 0.3 mm thick were overlapped and then heated at 1073 K for 0.3 ks. (b) SEM micrograph of the interface in (a) after shear test.

ure. The non-coated joint also broke at the Ag–Cu alloy/Ti interface by the shear test, and the aspect similar to Fig. 8(b) was frequently confirmed by SEM observations. These results show that the bonding strength of the Ti/Ti joint brazed with the Ag–Cu filler alloy is greatly influenced by the reaction layer formed at the interface.

The substantial bond between the Ag–Cu alloy and the substrate, which is provided by explosive energy, is canceled by the formation of the reaction layer at the interface. In conclusion, the combination of explosive coating and brazing leads to the greatest benefit in non-reactive system such as Ag–Cu alloy/stainless steel system.

4. Conclusions

Austenitic stainless steel and Ti plates were coated with a sheet of Ag–Cu filler alloy by using explosive energy to simplify the subsequent brazing operation. Its effectiveness was discussed on the basis of the interfacial microstructure and the bonding strength of finally obtainable joints. The main conclusions are summarized as follows.

(1) Although the stainless steel coated with the Ag–Cu alloy was heated at a temperature of more than eutectic point of the Ag–Cu binary system, their adhesion at the interface was retained. This indicates that the influence of wetting between both materials is negligible in the subsequent brazing operation.

(2) In the stainless steel, two coated specimens were overlapped and then heated at 1173 K for 0.3 ks in a rough vacuum. The obtained joint had a bonding strength of about 200 MPa. This was approximately 2 times higher than that of the non-coated joint, which was brazed with the Ag–Cu alloy under the same heating condition. The brazing operation *via* the coating process is equivalent to fusion welding of the alloy. Therefore, the pre-bonding by explosive energy is of help to the fabrication of a high-strength joint through the simplified brazing operation.

(3) In the Ti/Ti joint bonded by the intermediary of the Ag–Cu alloy, the pre-bonding by explosive energy did not

have an advantage on the shear test. This is attributed to the formation of a reaction layer at the interface. In other words, the combination of explosive coating and brazing leads to the greatest benefit in non-reactive system such as Ag–Cu alloy/stainless steel system.

Acknowledgements

The authors would like to express their appreciation to Dr. M. Matsuda and Dr. T. Yamamuro of Kumamoto University for their kind assistance in the experiment. The present study was partially supported by the Ministry of Education, Culture, Sports, Science and Technology through Grant-in-Aid for Scientific Research (C) No. 21560749 (2009–2011), and we greatly appreciate their support.

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