Brazed Bonding between SiAlON and Heat-Resistant Alloys with Application of Filler Materials

Toko Tokunaga1, Masayuki Koshiyama2, Kazuya Kurokawa1, Munekazu Ohno1 and Kiyotaka Matsuura1

1Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
2Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

It has been required to improve the heat efficiency of thermal power generation system for the sake of mitigation of the global warming and resource depletion problems. For improving the heat efficiency, it is effective to increase the steam temperature, and as a result, appropriate heat-resistant alloys are needed. Although SUS304 stainless steel and Ni-based superalloys have been proposed as promising heat-resistant alloys until now, there still remain some concerns such as high-temperature corrosion by flaming gas and erosion by combustion ash. Thus, the present authors propose SiAlON ceramic coating on SUS304 and INCONEL X-750 because SiAlON has excellent heat, wear and corrosion resistances.

In the present study, brazed bonding between SiAlON and these heat-resistant alloys was attempted with the applications of Cu and Ag as a soft filler material to reduce the residual stress generated due to the difference in thermal expansion coefficient between SiAlON and the heat-resistant alloys. As for the bonding with the Cu filler, the SiAlON/Cu/SUS joint was successful when the brazing time was short. However, when the brazing time was long (for example, 60 minutes), Fe-based grains were formed in the Cu filler layer, and the cracks were formed in the SiAlON near the joint interface during cooling in the brazing process. It was considered that the Cu filler was hardened by the formation of the Fe-based grains and could not reduce the residual stress. As for the bonding with the Ag filler, on the other hand, the SiAlON/Ag/SUS joint was successful even for a long brazing time. The SiAlON/Ag/INCONEL joint was also successful. The bending strengths of these SiAlON/Cu/SUS, SiAlON/Ag/SUS and SiAlON/Ag/INCONEL joints were evaluated by a three point bending test, and the results were approximately 200, 270 and 350 MPa, respectively. In all cases fracture occurred in the SiAlON, which means that the SiAlON and the alloys were strongly bonded. [doi:10.2320/matertrans.M2018038]

Keywords: ceramic coating, SiAlON, bonding, filler, stainless steel, Ni-based alloy, brazing

1. Introduction

The currently used ultra-supercritical thermal power generation system is known for its high thermal effectivity owing to the high steam temperature of approximately 630°C. However, higher thermal efficiency is required to reduce global warming and for the efficient use of fuel resources. To achieve such a high thermal efficiency, a higher steam temperature is necessary.1) Thus, an advanced ultra-supercritical (A-USC) system is being developed, whose steam temperature is over 700°C. To realize the A-USC system, heat-resistant alloys with excellent high-temperature endurance above 700°C are necessary. These alloys must have high strength and excellent oxidation resistance at elevated temperatures, high anticorrosion characteristics for flaming gas and high wear resistance for combustion ash.1) Furthermore, in actual applications, they must be safely utilized in the cooling/heating cycle.13)

In the present study, to meet the above requirements, a SiAlON ceramic coating on conventional heat-resistant alloys is proposed and the feasibility of the coating is investigated. SiAlON has a low density, high oxidation and corrosion resistances, a low thermal expansion coefficient and superior mechanical properties, such as high heat resistance, hardness, ductility, wear resistance, creep resistance and high-temperature strength. Therefore, it can be expected that a SiAlON coating on a heat-resistant alloy can enable the long-term application of the alloy even under a severe high-temperature environment in a coal thermal power generation plant. However, one must pay attention to the difference in the thermal expansion coefficients between SiAlON and a conventional heat-resistant alloy when considering the practical application of a SiAlON-coated heat-resistant alloy composite. For example, the thermal expansion coefficients of SUS304 stainless steel and INCONEL X-750 Ni-based alloy which are conventional heat-resistant alloys are 16.4 × 10⁻⁶ K⁻¹ 2) and 12.6 × 10⁻⁶ K⁻¹,3) respectively. On the other hand, the coefficient of SiAlON is only 2.45 × 10⁻⁶ K⁻¹.4) Thus, there is a significant difference in the thermal expansion coefficient between heat-resistant alloys and SiAlON. This difference generates stress during the cooling process after bonding or during a heat cycle in actual operation, and subsequently cracks may form at the bonding interface or inside SiAlON. Therefore, in the present study, a soft filler material of pure Cu or pure Ag is used to mitigate stress generation.5) The brazing bonding of SiAlON/SUS304 and SiAlON/INCONEL X-750 have been attempted, and the optimum bonding conditions and bending strengths of the bonded samples are investigated.

2. Experimental

Combustion-synthesized Y₀.₄Si₁₀₂Al₁₅O₆N₁₅.₄ powder having an average particle diameter of 0.5 μm was sintered by spark plasma sintering6) to fabricate a SiAlON ceramic green compact. The powder was sintered into a disc shape with a diameter of about 10 mm under a vacuum condition at
a pressure of 50 MPa and a temperature of 1500°C with a heating rate of about 50°C/min and a holding time of 10 min. The thickness of the SiAlON disc was about 0.8 mm for the investigation of the bending strength.

The thickness of the SiAlON disc was about 0.8 mm for the investigation of the bonding feasibility, the conditions resulting in strong bonding without the formation of cracks and voids were clarified, and such conditions were used to produce bonding specimens with a 5-mm-thick SiAlON disc, as shown in Fig. 1(c). The length, thickness and width of the bending specimens were set to 10, 1 and 2 mm, respectively, as shown in Fig. 2. The longitudinal edges and the lower basal surface of the bending specimens were polished in the longitudinal direction with emery papers of #1000 and #600, respectively. A schematic drawing of the equipment used in the three-point bending test is shown in Fig. 2. Two rods having a diameter of 1.5 mm were placed at a distance of 8 mm from each other, which served as supporting points. As the loading point, a rod with a diameter of 2 mm was placed at the midpoint between the supporting points. The specimen was bent when the loading point moved lower, guided by the columns at the sides. The bending tests were conducted at room temperature in air. The cross-head speed was set to 0.001 mm/s. The bending strength, \( \sigma \) (MPa), was calculated in accordance with JIS R 1601 “Testing method for flexural strength (modulus of rupture) of fine ceramics at room temperature” using the following equation:

\[
\sigma = \frac{3PL}{2wt^2},
\]

where \( P \) is the maximum load (N), \( L \) is the distance between the supporting points (mm), \( w \) is the width of the specimen (mm) and \( t \) is the thickness of the specimen (mm).

3. Results and Discussion

3.1 SiAlON/Cu/SUS304 bonding

Figure 3 illustrates the bonding interface of SiAlON/Cu/SUS304. No cracks were observed at the interface in the sample bonded with a holding time of 30 min (Fig. 3(a)) or 10 min. On the other hand, as shown in Fig. 3(b), cracks were observed inside the SiAlON bonded with a holding time of 60 min. To clarify the reason for the crack formation,
the interfaces in the samples bonded with holding times of 10, 30 and 60 min were observed in detail under higher magnification, as shown in Fig. 4. It was observed that columnar grains formed in the Cu filler from the SiAlON side toward the SUS side. The length and thickness of the grains increased as the holding time increased. Figure 5 illustrates the results of element analysis for the grains performed using the FE-EPMA. It was found that the grains were SUS-based, containing 70 mass%Fe, 15 mass%Cr, 7 mass%C and 6 mass%Ni. The formation mechanism of the SUS grains is discussed below. When the SiAlON/Cu/SUS sample was set as shown in Fig. 1 and held at 1150°C, which is slightly above the melting point of Cu, the SUS part was melted at the Cu/SUS interface and the constituent elements of the SUS such as Fe dissolved into the liquid Cu. Subsequently, when the concentrations of the constituent elements including Fe reached the solubility limit (about 4 mass% for Fe in Cu at the bonding temperature of 1150°C), the SUS grains were crystallized, as shown in Figs. 4 and 5, and additional dissolution of the SUS part occurred to compensate for the crystallization of the SUS constituent elements in the liquid Cu filler. The continuation of such crystallization and dissolution can be considered to lead the continuous growth of the SUS grains. On the other hand, the reason why the growth of the SUS grains did not end even after the concentration of the SUS elements in the liquid Cu reached the solubility limit is as follows. It is considered that at the interface of the liquid Cu and solid SUS, Cu and the constituent elements of the SUS diffused each into other in opposite directions. This is supported by the microstructure observed in the lower part of Fig. 4(c), which shows Cu diffusion into the SUS grain boundaries and implies subsequent SUS dissolution. Owing to the large difference in thickness between the Cu filler and the SUS part, the SUS elements in the liquid Cu filler become saturated in a short time, while the diffusion of Cu into the SUS part can continue for a significantly long time. This continuous diffusion of Cu into the SUS part can be considered to be the reason for the continuous dissolution of the SUS into the liquid Cu filler without equilibrium. The reason why the SUS grains did not form on the SUS side but formed on the SiAlON side is considered to be due to the continuous dissolution of SUS on the SUS side. The continuous dissolution of SUS prevented the crystallization of SUS on the SUS side, while on the SiAlON side, the solid SiAlON provided nucleation sites for the crystallization of SUS grains. It is not yet clear why the solid/liquid interface of the SUS grains was not planar but cellular and why the SUS grains did not always grow continuously from the SiAlON/Cu interface. As discussed above in this section, the use of Cu filler for the bonding of the SiAlON and SUS cannot compensate the thermal stress due to the hardening of the Cu filler caused by the formation of SUS grains in the filler. This is considered to be a reason for the formation of the cracks in the bonding sample with a holding time of 60 min, where the coarse SUS grains formed as shown in Fig. 3(b). On the other hand, in the samples with a shorter holding time of 30 or 10 min, the growth of SUS grains was suppressed and thermal stress was compensated by the soft Cu filler, which resulted in the sound bonding without cracks.

3.2 SiAlON/Ag/SUS304 bonding

For the bonding with the Ag filler, the bonding temperature and holding time were set to 1050°C and 60 min, respectively. Figure 6 shows a cross-sectional image of the SiAlON/Ag/SUS304. In contrast to the bonding with the Cu filler (Fig. 3(b)), no cracks were observed in the SiAlON. Figure 7 illustrates the results of element analysis performed using the FE-EPMA at the bonding interface in the SiAlON/Ag/SUS sample. In this figure, no cracks or voids can be seen at both the SiAlON/Ag and Ag/SUS interfaces. Although there were a small number of Fe-based grains at the SiAlON/Ag interface, their amount and size were much smaller than those in the Cu filler. This can be considered to be due to the very low solubility of Fe in Ag and also the low bonding temperature. Therefore, the grains did not have an adverse effect on the bonding in this case, in contrast to the case with the Cu filler.

In summary, regarding the bonding between the SiAlON and SUS, the Cu filler was hardened by the precipitation of SUS grains in the filler when the holding time was as long as 60 min, therefore plastic deformation did not occur to compensate the thermal stress generated during cooling and subsequently cracks formed inside the SiAlON, while bonding with the shorter holding time of 30 min was successful. Using the Ag filler, on the other hand, sound bonding was obtained regardless of the holding time.

3.3 SiAlON/Cu/INCONEL X-750 bonding

Figure 8 shows the bonding interface of SiAlON/Cu/INCONEL X-750. The samples shown in Figs. 8(a) and (b) were prepared with holding times of 10 and 60 min, respectively. For both samples, cracks can be seen in the SiAlON near the bonding interface. Since the cracks were observed only in the SiAlON near the interface, it is considered that the Cu filler could not compensate the thermal stress by undergoing plastic deformation. In the case
Fig. 5 (a) SEM image and (b) Cu and (c) Fe mappings of bonding interface in SiAlON/SUS joint with Cu filler held at 1150°C for 60 min.

Fig. 6 Cross section of SiAlON/SUS joint sample with Ag filler held at 1050°C for 60 min.

Fig. 7 (a) SEM image and (b) Ag and (c) Fe mappings of bonding interface in SiAlON/SUS joint with Ag filler held at 1050°C for 60 min.

Fig. 8 Micrographs of interfaces in SiAlON/INCONEL joint with Cu filler held at 1150°C for (a) 10 min and (b) 60 min.
of SiAlON/Cu/SUS304 bonding, no cracks were observed with a holding time of 10 min, while in the case of SiAlON/Cu/INCONEL bonding, cracks formed for the same holding time. To investigate the reason for the crack formation, element analysis was performed on the interface. The results are shown in Fig. 9. Ni was detected in the Cu filler in the SiAlON/Cu/INCONEL samples prepared with holding times of 10 and 60 min. The amount of detected Ni was almost the same in these samples regardless of the holding time. Since the Ni–Cu binary alloy has a fully isomorphous solution system, the Cu filler was hardened by alloying with Ni from the INCONEL during the bonding. Thus, the expected compensation of thermal stress by a soft filler of pure Cu was not achieved and cracks formed in the SiAlON. In addition, since the hardening occurred even in the bonding sample prepared with the short holding time of 10 min, reducing the holding time is not effective for preventing the diffusion of Ni from the INCONEL.

### 3.4 SiAlON/Ag/INCONEL X-750 bonding

Figure 10(a) shows an SEM image obtained at the interface of the SiAlION/Ag/INCONEL X-750 sample. No cracks or voids were observed in both the SiAlON/Ag and Ag/INCONEL interfaces. Figure 10 shows the element analysis results for both the interfaces. The diffusion of the constituent elements into the opposite bonding parts only
occurred for a very short distance at both the interfaces, and almost no diffusion of the elements into the Ag filler was observed. Thus, in contrast to the case of the Cu filler, hardening of the Ag filler by alloying did not occur and thermal stress was compensated as expected. Consequently, it was found that the Ag filler is useful for the bonding between SiAlON and INCONEL X-750.

3.5 Bending tests

The bending tests were conducted on the bonding samples prepared under the three bonding conditions for which sound bonding was obtained, i.e., SiAlON/Ag/SUS304 and SiAlON/Ag/INCONEL X-750 with a holding time of 60 min and SiAlON/Cu/SUS with a holding time of 10 min. The fractured part of the bent SiAlON/Ag/SUS sample is shown in Fig. 11. The fracture appears to have occurred near the interface. To investigate the point where the fracture originated in detail, the fractured surfaces were observed on both the SUS and SiAlON sides, as shown in Fig. 12. Gray SiAlON without a metallic luster covered both fractured surfaces. This indicates that the fracture occurred not at the bonding interface but inside the SiAlON, and therefore there was strong bonding between the SiAlON and the filler material. Similarly, fracture occurred inside the SiAlON in the bending tests on the other bonding samples, i.e., SiAlON/Cu/SUS and SiAlON/Ag/INCONEL. Therefore, it is expected that the samples with sound bonding obtained in this study should exhibit high bonding strength.

The bending strength was evaluated from the maximum load obtained in the bending test. The results are shown in Fig. 13. All the bonding samples had bending strengths higher than 200 MPa, and hence the actual bonding strength in these samples should be higher than this value. The reasons for the differences in the bending strength among the bonding samples are discussed below.

Since all the bonding samples fractured inside the SiAlON, the differences in the bending strength shown in Fig. 13 can be considered to be related to the difference in the thermal stress in the SiAlON generated during cooling after bonding. Thus, from the standpoint of the thermal stress remaining inside the SiAlON, the differences in the bending strength are discussed as follows. The bending strengths of the SiAlON/Cu/SUS and SiAlON/Ag/SUS samples were approximately 200 and 270 MPa, respectively, and hence the bonding with the Ag filler exhibited 35% higher bending strength. At the SiAlON/Cu/SUS bonding interface shown in Fig. 4, SUS grains formed in the Cu filler, which resulted in the hardening of the filler and hence the cracking of the SiAlON due to thermal stress. On the other hand, in the case of SiAlON/Ag/SUS bonding, the formation of a solid solution or the precipitation of a second phase was not observed. Therefore, it is considered that the Ag filler remained soft and compensated the thermal stress by undergoing plastic deformation. To confirm the validity of this discussion, Vickers hardness tests were conducted on the Cu and Ag fillers. The hardness of the Cu filler in the SiAlON/Cu/SUS sample and the Ag filler in the SiAlON/Ag/SUS sample were about 120 and 55, respectively. There is a significant difference in hardness between the filler materials. It can be considered that the thermal stress generated in the SiAlON was small in the bonding sample with the Ag filler and thus, higher bending strength was obtained. However, the use of the Ag filler with different alloys resulted in a difference in the bending strength; the bending strengths of the SiAlON/Ag/SUS and SiAlON/Ag/INCONEL samples were approximately 270 and 350 MPa, respectively, which means that the bonding with INCONEL exhibited 30% higher bending strength than the bonding with SUS. This can be due to the difference in the thermal expansion coefficients between the two heat-resistant alloys; the thermal expansion coefficients of SUS304 and INCONEL X-750 are 16.4 × 10⁻⁶ K⁻¹ 2¹ and 12.6 × 10⁻⁶ K⁻¹ 3² respectively. This indicates that the heat shrinkage during cooling in INCONEL is less than that in SUS. It has been reported that this magnitude of difference
in the thermal expansion coefficient can generate a large difference in thermal stress. Therefore, it can be considered that the heat shrinkage was less in the bonding sample with INCONEL than in the sample with SUS and, consequently, smaller thermal stress was generated in the SiAlON in the bonding sample with INCONEL, which resulted in the higher bending strength.

4. Conclusions

The feasibility of a SiAlON coating on a heat-resistant alloy was investigated with the aim of developing a new material for coal thermal energy plants employing the advanced ultra-supercritical technique. SUS304 stainless steel and INCONEL X-750 Ni-based alloy were selected as the heat-resistant alloys, pure Cu or pure Ag was used as the filler material and brazing was conducted. Consequently, the following conclusions were obtained.

(1) The sound bonding of SiAlON and SUS304 was obtained using the Cu filler with a bonding temperature of 1150°C and a holding time of 10 or 30 min. Bonding failed for a holding time of 60 min because of crack formation in the SiAlON. Sound bonding was also obtained using the Ag filler with a bonding temperature of 1050°C and a holding time of 60 min.

(2) The bonding between SiAlON and INCONEL X-750 failed when using the Cu filler with a bonding temperature of 1150°C and a holding time of 10 or 60 min since cracks formed in the SiAlON. On the other hand, sound bonding was obtained when using the Ag filler with a bonding temperature of 1050°C and a holding time of 60 min.

(3) The SiAlON/Cu/SUS304, SiAlON/Ag/SUS304 and SiAlON/Ag/INCONEL X-750 samples exhibited strong bonding between the filler material and the SiAlON since the fracture occurred in the SiAlON in the bending tests. The bending strengths of these samples were approximately 200, 270 and 350 MPa, respectively.

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