

論文 / 著書情報
Article / Book Information

Title(English)	Brazing of C/C composites and Ni Base Alloys with Fe-base Brazing Filler Alloys
Authors(English)	Toshi-Taka Ikeshoji, Tetsutaro Amanuma, Akio Suzumura, Takahisa Yamazaki
Citation(English)	5th International Brazing and Soldering Conference (IBSC2012), , , pp. 465-469
Pub. date	2012, 4
Copyright	(c)2012 ASM International(R) All Rights Reserved. www.asminternational.org
Note	Proceedings of 5th International Brazing and Soldering Conference (IBSC2012), 4. 22, 2012,- 4. 25, 2012, Las Vegas, USA, R. Gourley and C. Walker, editors

Brazing of C/C Composites and Ni Base Alloys With Ag-Cu-Ti and Fe-Based Braze Filler Alloys

Toshi-Taka Ikeshoji, Tetsutaro Amanuma, Akio Suzumura, Takahisa Yamazaki

Tokyo Institute of Technology, Tokyo, Japan

2-12-1 O-okayama, Merugo-ku, Tokyo, 152-8552, Japan, E-mail: Ikeshoji.t.aa@m.titech.ac.jp

Abstract

Carbon/carbon composites have high specific strength and high heat resistance. To utilize its high heat resistance, it has been brazed to the heat resistance alloys using Ni-base brazing alloys. In this research, the feasibility of using Ag-Cu-Ti and Fe-based brazing filler alloys to braze C/C composites and Ni-base heat resistance alloys, Inconel 600 and Hastelloy C-276, and the austenitic stainless steel, SUS304, is investigated. The Ag-Cu-Ti brazing filler was 63.63Ag-34.65Cu-1.72Ti (Cusil-ABA®, Morgan Ceramics), and the Fe-based brazing filler alloy was Fe-20Cr-42-Ni-12(Si+P) (TB-2720, Tokyo Braze). To relieve the residual stress induced by the mismatch in the coefficient of thermal expansion (CTE), an interlayer was added to some of the brazing specimens that consisted of inserting either a piece of Ni foil or a piece of Cu foil at the brazing interface. The samples were brazed in a vacuum furnace at a brazing temperature of 830°C for the Ag-Cu-Ti brazing filler alloy and 1070°C for the Fe-based brazing filler. The microstructure of the brazed interface was observed using an optical microscope and SEM. It was found that brazed joints were obtained for the combinations of C/C composites / Cu foil / Inconel 600 and C/C composites / Cu foil / Hastelloy C-276, both of which were brazed with Ag-Cu-Ti brazing filler alloy. The brazed joints of the other combinations could form a bond between the C/C composites and the brazing filler layer, but later cracked upon cooling.

Introduction

Carbon fiber reinforced carbon composites (C/C composites) have high heat resistance, which is derived from the properties of graphite. If the C/C composites could be joined with the conventional heat resistance alloys, their application will be expanded[1]. Brazing is an expected method to join C/C composites and heat resistance alloys. The Ni-based brazing fillers were attempted to braze C/C composites and Hastelloy® and Inconel® but most of the Ni-based brazing fillers do not include the carbide formers[2,3]. The carbide formers, e.g. Ti, Cr or Si, are called active elements and are considered to be necessary in the brazing of C/C composites because the C/C composites are hard to wet as well as the graphite[4,5].

Besides, the problem of wettability of C/C composites, the residual stress induced by the mismatch in the coefficient of

thermal expansion is expected to initiate the crack in the brazing joint. For example, the 2D cross-ply laminates C/C composites has CTE of $\pm 0.1 \mu\text{m}/(\text{m}\cdot\text{K})$ in the laminate plane but its cross sectional direction's CTE is almost $10 \mu\text{m}/(\text{m}\cdot\text{K})$ [6]. On the other hand, the CTE value of Hastelloy® C-276 is $10 - 12 \mu\text{m}/(\text{m}\cdot\text{K})$, and that of Inconel® 600 is $11.5 \mu\text{m}/(\text{m}\cdot\text{K})$. If the laminate plane is brazed to Ni base alloys like Hastelloy and Inconel, the mismatch in their CTE values are too large and joint will not be obtained. The metals should be brazed to the C/C composites' cross sectional plane to obtain the strong joint[7].

In this research, Ag-Cu-Ti brazing filler and the Fe-based brazing filler containing Cr was attempted in the brazing of C/C composites and Hastelloy® C-276, Inconel® 600 and the austenitic stainless steel, SUS304. The Ti and Cr are expected to perform as the active element. The mismatch in the coefficient of thermal expansion (CTE) between C/C composites and the metals mentioned above could cause cracking at the brazing interface. So Cu and Ni interlayer foils were inserted to overcome the problem of cracking due to the residual thermal stress. The CTE of Cu is $16.5 \mu\text{m}/(\text{m}\cdot\text{K})$, and Ni's CTE is $13.4 - 16.5 \mu\text{m}/(\text{m}\cdot\text{K})$. The cross sections of the brazed joints are observed and analyzed using SEM, EDX, and optical microscopy.

Experimental Details

Brazing of Nickel Base Alloys and C/C Composites

In this work but joints were made between three high temperature metal alloys by brazing each to a carbon/carbon composite using two braze alloys. The high temperature alloys that were used were Inconel 600, Hastelloy C-276, and austenitic stainless steel SUS304 plates. These plates were cut into the dimensions of $10\text{mm} \times 10\text{mm} \times 3 \text{mm}$.

The carbon/carbon composites (AC200, Across Corp., Saitama, Japan) had a density of $1.8 \text{ kg}/\text{m}^3$. The original C/C composites plate had the thickness of 10 mm. From the plate, a carbon/carbon composites plate was cut out into the dimensions of $10\text{mm} \times 10\text{mm} \times 3\text{mm}$. The laminates of the C/C composites plate were $[0^\circ/90^\circ]_s$. The two sides of the specimen with dimensions $10\text{mm} \times 3\text{mm}$ were laminate's

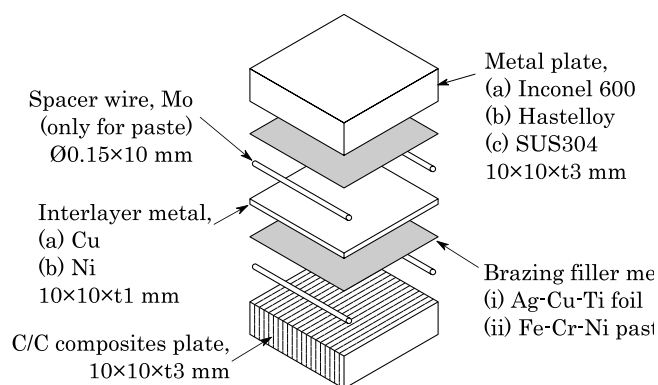


Figure 1 Schematic of brazed specimens.

Table 1 Properties of brazing filler metals

	Compositions, mass%	T _S	T _L
Fe-Cr-Ni	Fe-20Cr-42Ni-(10-12)(Si+P)	990	1050
Ag-Cu-Ti	63.63Ag-34.65Cu-1.72Ti	780	815

T_S : Solidus, °C, T_L : Liquidus, °C

surface. So the top and bottom surface with dimensions of 10mm×10mm were the cross section of the laminates. .

Two braze filler metals were used in the brazing tests (Table 1). The Fe-based brazing filler (TB-2720 of Tokyo Braze) was in paste form. It had a composition of Fe-20%Cr-42%Ni-(10-12%)(Si+P), where the percentage is a mass fraction (wt%). In the following the Fe-based brazing filler is called Fe-Cr-Ni brazing filler. Its solidus temperature was 990°C and liquidus temperature was 1,050°C. Ag-Cu-Ti (Cusil-ABA® of Morgan Ceramics) was applied as foil. The compositions of Ag-Cu-Ti brazing filler metal were Ag-38.8%Cu-1.72%Ti and foil's thickness was 0.05 mm.

For some of the specimens, interlayer metal sheets were inserted between the metal and C/C composite plates (Fig. 1). For the case of Ag-Cu-Ti brazing filler metal, Cu foil with 0.1mm thickness was used as the interlayer. For the case of Fe-Cr-Ni braze filler metal, the interlayer metal was Ni foil with 0.1mm thickness. The brazing temperature of Fe-Cr-Ni, 1070°C was near to copper's melting point, 1083°C, so the Cu foil could not be used for brazing with Fe-Cr-Ni brazing filler.

The Fe-Cr-Ni paste was spread between the interlayer metal foil and C/C composites plate and the interlayer metal and heat resistance metal. Molybdenum wires were also inserted there as spacers. The wire's diameter was Ø0.15 mm. The exploratory wetting test of the Fe-Cr-Ni on Inconel 600, Hastelloy C-276, and SUS304 had shown the immediate spreading and high flowability of the molten Fe-Cr-Ni alloy. On the other hand, the wetting of Fe-Cr-Ni on C/C composites had taken longer time. Of concern was the extrusion of the brazing filler from the interface to the metal sides. So the insertion of Mo wires was expected to keep the molten brazing filler in the interface by the capillary action or just by blocking of the flow. For the case of Ag-Cu-Ti brazing filler foil, the spacers were not used.

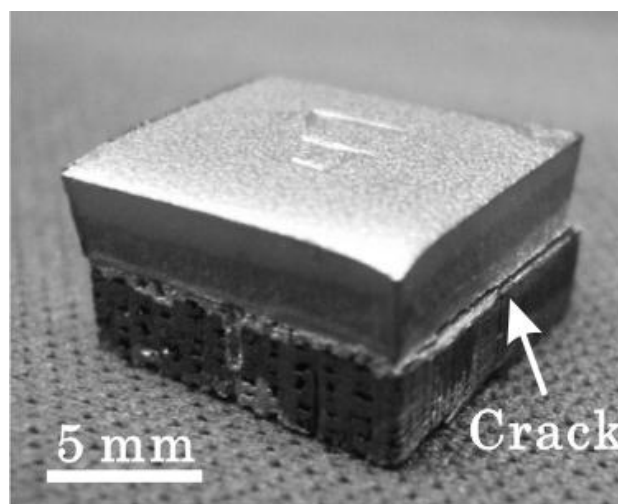


Fig. 2 Brazed joint of Inconel / Fe-Cr-Ni / C/C composites w/o interlayer.

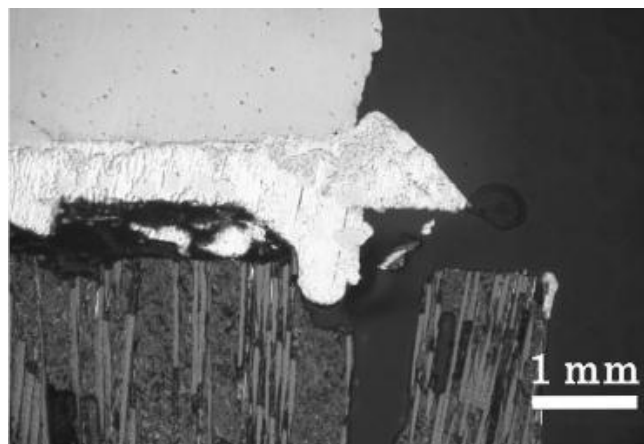


Fig. 3 Cross section of the brazed joint of Inconel / Fe-Cr-Ni / C/C composites w/o interlayer.

Table 2 Results of brazing tests.

	T _B	Interlayer	Inconel	Hastelloy	SUS304
Fe-Cr-Ni	1070	--	NA	NA	NA
		Ni foil	NA	NA	NA
Ag-Cu-Ti	830	--	NA	NA	NA
		Cu foil	OK	OK	NA

T_B : Brazing Temperature, °C

The brazing was conducted in a tube furnace under vacuum. The atmospheric pressure was approximately 2.7×10^{-3} Pa. The heating cycle had 2 dwell steps. The specimens were first heated up to 150°C in a time of 1800s, and held at this temperature for 600s. Then the furnace temperature was increased up to the final brazing temperature in 3600s. The brazing temperature was 1070°C for the Fe-Ni-Cr brazing filler, and 830°C for the Ag-Cu-Ti brazing filler. The final dwell time was 600s, after which the power of the furnace was turned off and the specimens were allowed to furnace cool to room temperature.

The brazed joints were cut to observe their cross sections. The cross section surface was polished with emery paper and alumina powder water suspension. The cross sections were

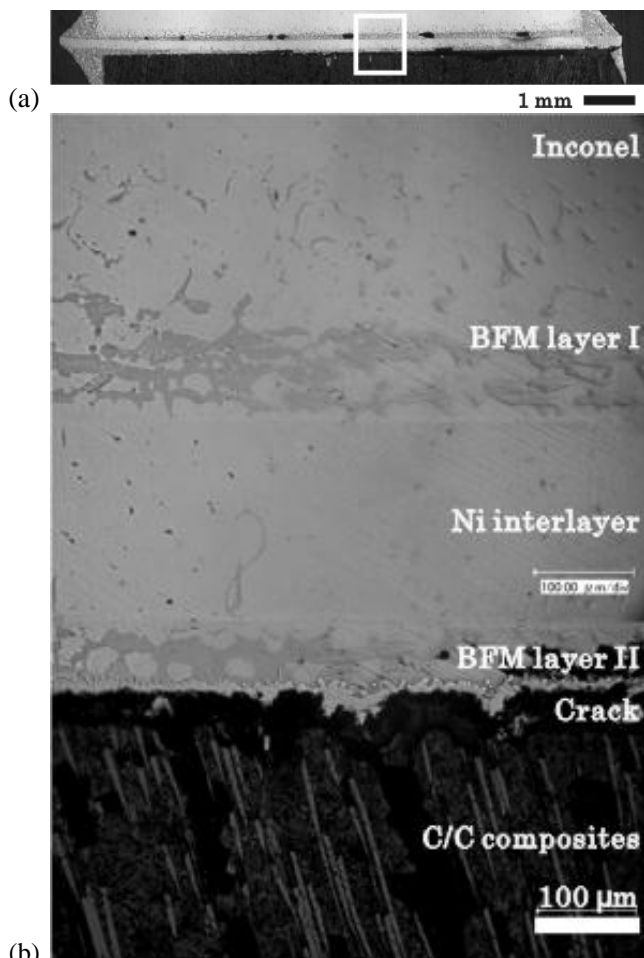


Fig. 4 Microstructure of the brazed joint of Inconel / Fe-Cr-Ni / C/C composites w/ Ni interlayer. (b)'s position is shown in (a).

observed by optical microscopy and SEM. Elemental mapping of the cross sections was also performed using EDX.

Results of Brazing Tests

Cracking at the Brazed Interface

The appearance of a brazed joint of C/C composites and Inconel using Fe-Cr-Ni brazing filler metal without an interlayer is shown in Fig. 2. On the left side of the picture, the joint appears well bonded. On the right side of the picture, a crack was observed at the interface of the C/C composites and Inconel. Its tip seemed to stop at the near side. So the crack might propagate from the far side of the picture to the near side.

The cross section of the brazed joint interfaces is shown in Fig. 3. This cross section was perpendicular to the crack propagation direction. The right side edge on the picture (Fig. 2) is shown in Fig. 3. Because the bottom shape of the brazing filler conforms to the shape of the C/C composites interface surface, the brazing filler metal seemed to wet well on the C/C composites. In the picture (Fig. 2), it was unclear, but the C/C composites appear to have been bonded to the brazing filler layer in Fig. 3. Therefore the crack would be formed during the cooling step of the brazing process after the formation of

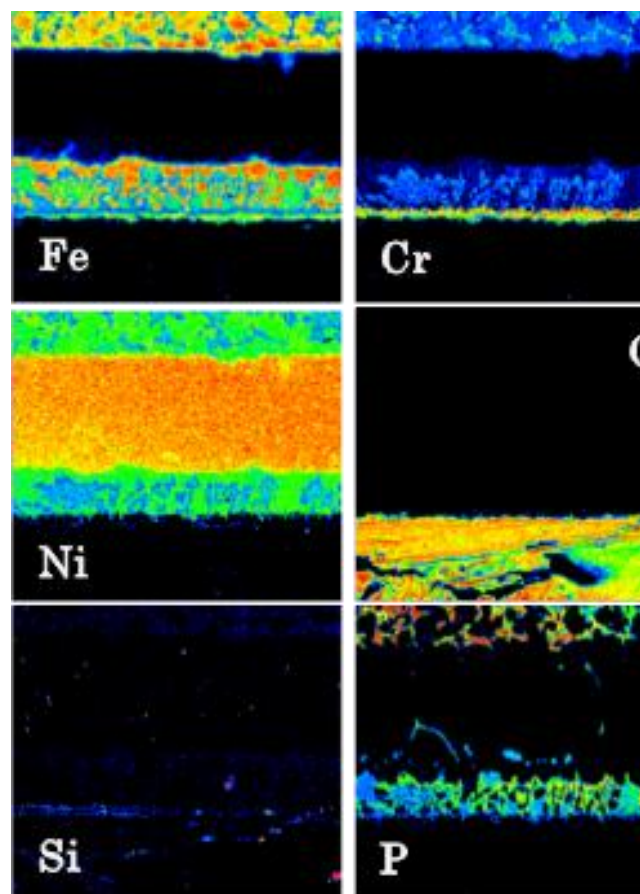


Fig. 5 EDX element mapping at the interface of the brazed joint of Inconel / Fe-Cr-Ni / C/C composites w/ Ni interlayer.

the bond between the C/C composites and brazing filler metal. The residual stress induced by the large discrepancy in the coefficient of thermal expansion (CTE) might have caused the cracking.

Most of the pairs of materials could not form the brazed joint due to similar cracking (Table 2). For the case of Fe-Cr-Ni brazing filler, a brazed joint was not formed even with the interlayer of 0.1 mm thick Ni foil. When Inconel and Hastelloy C-276 were brazed to C/C composites using Ag-Cu-Ti with Cu foil of 0.1 mm thickness, brazed joints were formed.

Brazed Joints with Fe-Cr-Ni Brazing Filler Metal

The microstructure of the brazed joint of the C/C composites and Inconel 600 using Fe-Cr-Ni brazing filler metal with Ni interlayer is shown in Fig. 4. Along the grain boundary of Inconel on the near side of the brazing filler metal layer, precipitation seemed to have occurred. The Ni interlayer did not change apparently. The brazing filler metal (BFM) layer on the lower side (BFM layer II) had a different microstructure than the upper side of Ni interlayer (BFM layer I). The initial precipitates of a spot shape were observed in the middle of the BFM layer II. Along the hem of the bottom of the BFM layer II, a thin layer was observed. To this layer, parts of C/C composites were bonded, though it was not clear on the photograph. Inside of the C/C composites, no severe infiltration was observed.

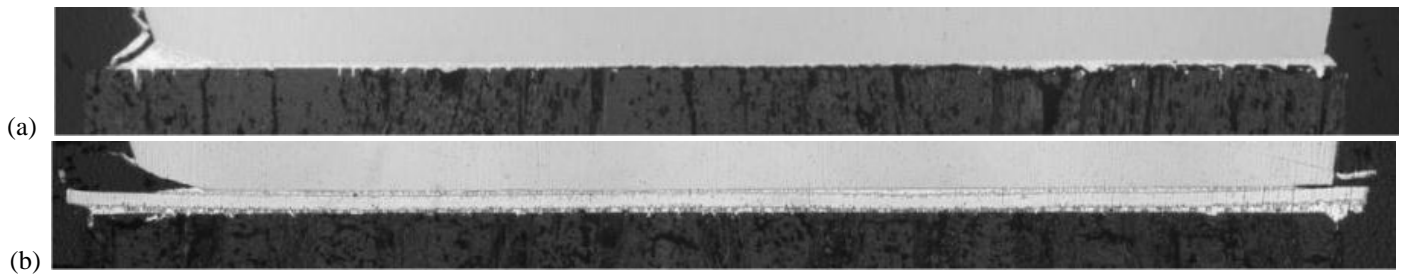


Fig. 6 Cross sections of the brazed joints. (a) Inconel / Ag-Cu-Ti / C/C composites w/o Cu interlayer. (b) w/ Cu interlayer.

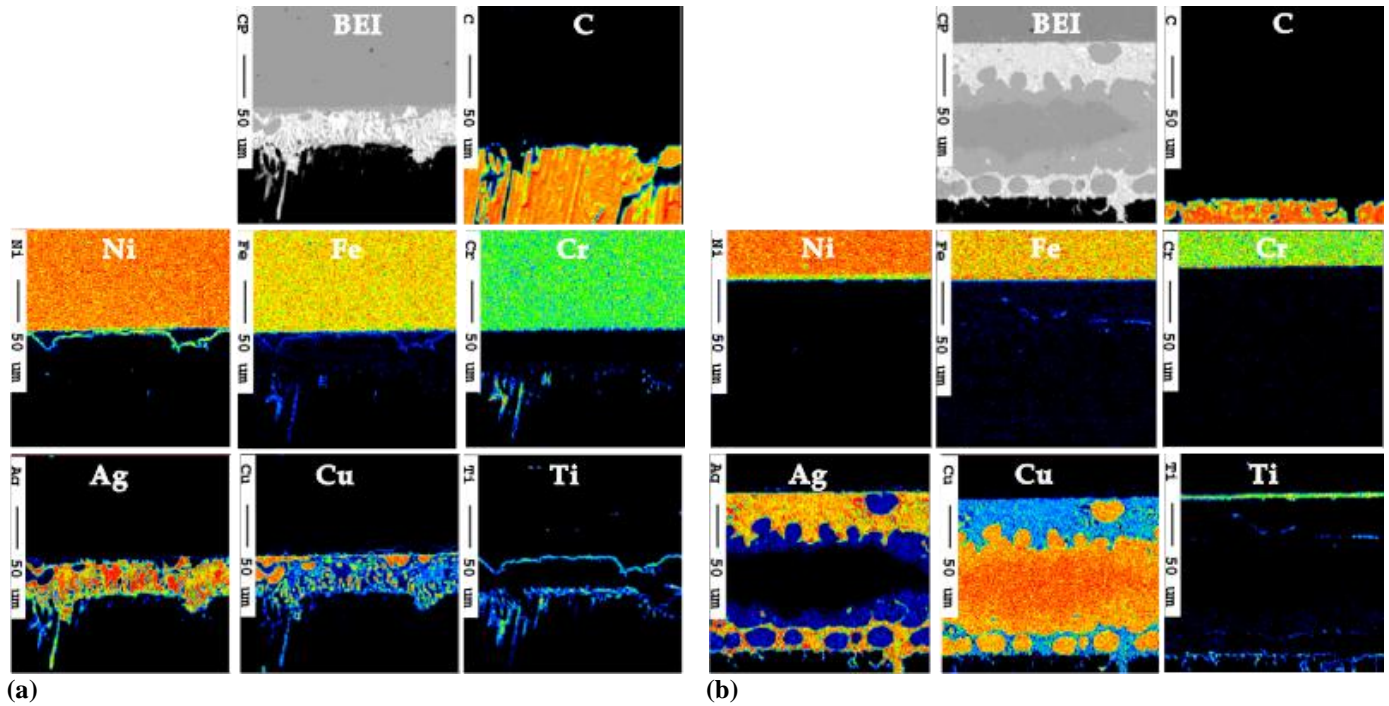


Fig. 7 EDX element mapping of at the interface of the brazed joints. (a) Inconel / Ag-Cu-Ti / C/C composites w/o Cu interlayer. (b) w/ Cu interlayer.

The EDX element mapping at the brazed joint interface is shown in Fig. 5. In the BFM layer I above the Ni interlayer, the microstructure divided into Ni rich phase and Cr rich phase. P coexisted with Cr. In the BFM layer II below the Ni interlayer, similar decomposition was observed. The initial precipitation spots were the Cr rich phase. Along the hem of the BFM layer II at the C/C composites side, the Cr-Fe layer was formed. Therefore, Cr seemed to have performed as an active element to form carbide on the C/C composites interface. At the hem, Si was also found and thus SiC might have formed at the C/C composites interface as well.

Brazed Joint with Ag-Cu-Ti Brazing Filler Metal

Without the Cu interlayer, the brazed joint of Inconel and C/C composites using Ag-Cu-Ti brazing filler metal had cracked from the edge to the middle of the interface (Fig. 6(a)). When the Cu interlayer was inserted and brazed, no crack was propagated along the brazing interface (Fig. 6(b)).

The EDX element mappings revealed the difference in the microstructure between the brazed joints without a Cu interlayer and with a Cu interlayer (Fig.7). Without a Cu interlayer the brazing filler layer was Ag/Cu eutectic phase. Ti was segregated along the interface with C/C composites and

the brazing filler layer, and so were Cr and Fe distributions. The elements capable to form carbides were segregated on the C/C composites. For the case that the Cu interlayer was inserted, Cu precipitation occurred in the brazing filler layer, which was basically Ag phase. Ti was segregated on the C/C composites and Inconel interface.

Discussions

The cracking at the brazing interface was due to the mismatch in the coefficient of thermal expansion (CTE). The value of CTE of Inconel® 600 is $11.5 \mu\text{m}/(\text{m}\cdot\text{K})$, for Hastelloy® C-276 it is $10 - 12 \mu\text{m}/(\text{m}\cdot\text{K})$, and for the austenitic stainless steel SUS 304, $17.3 \mu\text{m}/(\text{m}\cdot\text{K})$. The C/C composites have the anisotropy in CTE. Along the fiber direction, its value is approximately $0.5 \mu\text{m}/(\text{m}\cdot\text{K})$, and in the direction of the lamination or the direction perpendicular to the fibers, the value of CTE is $7\mu\text{m}/(\text{m}\cdot\text{K})$. The mismatch in CTE is larger in the fiber direction. Therefore, when the C/C composites were brazed to Inconel without interlayer, the crack propagated along the fiber direction as shown in Fig. 3. In the direction perpendicular to the fiber direction, a bonded part remained between the braze alloy and C/C/ composite. This is

considered due to the small difference in CTE mismatch and the compression strength of C/C composites in this direction.

The CTE value of copper is larger $16.5 \mu\text{m}/(\text{m}\cdot\text{K})$ as compared with that of nickel of $12.8\mu\text{m}/(\text{m}\cdot\text{K})$. The use of the Cu interlayer successfully formed the brazed joint, although the Ni interlayer could not. This is considered to be due to the lower brazing temperature and the difference in the elastic modulus. The elastic modulus of Cu is approximately 129 GPa, and that of Ni is approximately 210 GPa. So the Cu interlayer was softer than the Ni interlayer and capable to absorb the residual stress.

Conclusions

The brazing of Carbon/Carbon composites and Inconel, Hastelloy, and austenitic stainless steel SUS304 were attempted using a Fe-Cr-Ni brazing filler alloy and an Ag-Cu-Ti brazing filler alloy. Due to the large discrepancy in the coefficients of thermal expansion among those materials, the direct brazed joints were not obtained. But with insertion of copper foil in the brazed interface, and using Ag-Cu-Ti, C/C composites could be brazed to Inconel and Hastelloy C-276.

Acknowledgments

This research was subsidized by JKA through its promotion funds from KEIRIN RACE.

References

- [1] Aoyama, S., Yamamoto, S., Miyashita, Y., Mutoh, M. "Diffusion bonding of 0.5%Ti-0.07%Zr-Mo/Graphite for heat resistant structure material," *Quarterly Journal of the Japan Welding Society*, Vol.23, No.2 (2005) pp.337-343, in Japanese
- [2] Singh, M., G. N. Morscher, et al. "Active metal brazing of titanium to high-conductivity carbon-based sandwich structures," *Materials Science and Engineering A*, Vol. 498, No.1-2 (2008), pp.31-36.
- [3] Liu, J. Y., Chen, S., and Chin, B. A., "Brazing of vanadium and carbon-carbon composites to stainless-steel for fusion-reactor applications," *J. Nuclear Materials*, Vol.212 (1994), pp. 1590-1593.
- [4] Asthana, R., Singh, M., and Sobczak, N., "Wetting behavior and interfacial microstructure of palladium- and silver-based braze alloys with C-C and SiC-SiC composites," *Journal of Materials Science*, Vol.45, No.16 (2010), pp. 4276-4290.
- [5] Chen, B., Xiong, H. P., Mao, W., and Cheng, Y. Y., "Wettability and interfacial reactions of PdNi-based brazing fillers on C-C composite," *T Nonferr Metal Soc*, Vol.20, No.2 (2010), pp. 223-226.
- [6] Ishikawa, T., Hayashi, Y., Fukunaga, H., Matsushima, M., and Noguchi, T., "Experimental examination of theory of CTE (Coefficient of Thermal Expansion) control technology," *JSME International Journal Series I-*

Solid Mechanics Strength of Materials, Vol.34, No.2 (1991), pp. 178-186.

- [7] Ikeshoji, T.-T., Amanuma, T., Suzumura, A. and Yamazaki, T., "Shear Strength of Brazed Joint Between Titanium and C/C Composites With Various Cross-Ply Angles," *Journal of Solid Mechanics and Materials Engineering*, Vol.5, No.12 (2011), pp.1022-1028.