Microstructure Analysis of Brazed Sapphire to Inconel® 600 Using Porous Interlayer

The diffusion of Ti and Ni into a Cu/Ni porous composite and its influence on the braze/sapphire interface was investigated

BY T. ZAHARINIE, F. YUSOF, M. HAMDI, T. ARIGA, AND M. FADZIL

ABSTRACT

A Cu/Ni porous composite interlayer was used to enhance the brazing performance of sapphire to Inconel® 600. The porous interlayer was placed in between thin sheets of active brazing filler metal, BAg-8 with 2 wt-% titanium. It was expected that the porous interlayer would reduce the thermal coefficient mismatch, which can create unwanted residual stresses during cooling that may lead to weakened or failed joints. In this research, the effect of titanium (Ti), nickel (Ni), and copper (Cu) diffusion into the Cu/Ni porous interlayer was evaluated. The brazing process was conducted at 830°C for 30 min in a high-vacuum environment at a pressure of 1×10^{-4} Pa. The brazed interface was observed by SEM, and an elemental analysis was conducted using SEM-EDS. Microscopic observation has indicated the formation of a thin, black reaction layer on the sapphire side, which is believed a TiO_x compound. Elemental mapping was also conducted using EPMA to highlight the distribution of the elements. It was found that the Ti distribution on the sapphire interface was discontinuous and resulted in interdiffusion between Ti, Ni, and Cu, which subsequently reduced the thermodynamic activity between metal-ceramic interfaces. In the present study, a compound of Ni_3Ti was revealed to influence the formation of the thin reaction layer.

WELDING RESEARCH

Introduction

In recent years, there has been a growing interest in the joining processes for ceramics due to their excellent mechanical properties and unique applications, especially in the electronics industry. Typically, ceramics are characterized by low density, high strength, corrosion resistance, and ability to withstand high operating temperatures. However, ceramics are brittle and difficult to form or machine, which limits their direct use in product fabrications. To overcome this limitation, various the techniques for joining ceramics to metal have been proposed since the metal component is easily fabricated and both the properties of the material could be utilized in a single product (Refs. 1, 2). Furthermore, for most commercial applications, a metallic part is required to be joined to the ceramic component (Refs. 3, 4).

T. ZAHARINIE (rinie34@gmail.com), *F. YUSOF* (farazila@um.edu.my), *M. HAMDI* (hamdi@um.edu.my), *and M. FADZIL* (ibnjamaludin@um.edu.my) *are with Center of Advanced Manufacturing and Material Processing, Department of Engineering Design and Manufacture, Faculty of Engineering, University of Malaya, Kuala Lumpur. T. ARIGA* (ttariga@keyaki.cc.u-tokai.ac.jp) *is with Department of Materials Science, School of Engineering, Tokai University, Kanagawa, Japan.*

There are two main factors influencing the reliability of ceramic-to-metal mechanical joints: 1) coefficient of thermal expansion (CTE) mismatch between metal and ceramic (Refs. 5–8), and 2) the difference in the nature of interatomic bond (Refs. 3, 9–11). During the cooling process in a brazing cycle, residual stress can build up at the joint interface due to the mismatch of CTE and the difference in the mechanical response of ceramic and metal. For example, Valette (Ref. 12) brazed a system of alumina to CuNi using active filler metal made of Cusil-ABA® with 3.1 %Ti content. However, due to the discrepancy of thermal expansion between the materials, adhesion failure ensued during alumina/CuNi alloy assemble. Past studies have explored numerous techniques in order to reduce the CTE disparity during ceramic-metal brazing.

KEYWORDS

Brazing
Composites
Interlayer
Ceramics
Nickel
Titanium
Sapphire
Alumina

The use of interlayer for brazing has been proposed recently to reduce the CTE mismatch (Ref. 13). It was reported that the inclusion of a soft, low expansivity interlayer in the brazing could minimize the magnitude of residual stresses between ceramic and metal (Refs. 14–16). In reducing the residual stresses in the joint, Kim and Park (2000) (Ref. 17) reported an optimum copper interlayer thickness of 200 μm for use in the brazing of silicon nitride to stainless steel. In general, thin interlayers would have less plastic deformation, which results in high residual stresses in the ceramic and overall reduction in joint strength. Thicker interlayers showed a slight reduction in mechanical strength, but the joint is stronger than those of thinner interlayers. Finite element method (FEM) analysis of interlayer usage by Zhang et al. (Ref. 18) proves that a compliant metal layer between ceramic and metal can reduce residual stress and enhance bond integrity. A metallic interlayer in brazing is also thermally stable and may prevent the formation of brittle intermetallics that could result in joint failure during joining or servicing (Ref. 19).

This present work investigates the influence of a Cu/Ni porous composite interlayer in the brazing of sapphire to Inconel® 600. The evaluation focuses on the effect of diffusion by titanium (Ti) and nickel (Ni) into the Cu/Ni porous composite during joining, and the influences these elements have on the braze area/sapphire interface.

Experimental Procedure

A Cu/Ni porous composite was used as an interlayer in brazing sapphire to Inconel® 600. The sapphire (single-crystal, 99.999% purity) and Inconel® 600 were obtained from Yamatake Corp., Japan. The sapphire was prepared in a disc form measuring 0.7 mm thick with a diameter of 20 mm, while the Inconel® 600 sample size was 23×23 mm^2 with a thickness of 1 mm for the SEM analysis and 4 mm thickness for EPMA. The Cu/Ni porous composite interlayer is prepared from pure porous copper (Cu) and pure porous nickel (Ni) sheets. The porous Cu and Ni sheets were

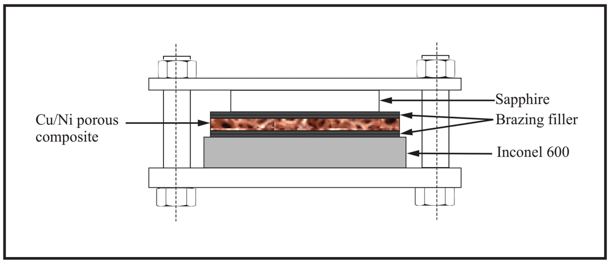

Fig. 1 — Diagram of sample preparation.

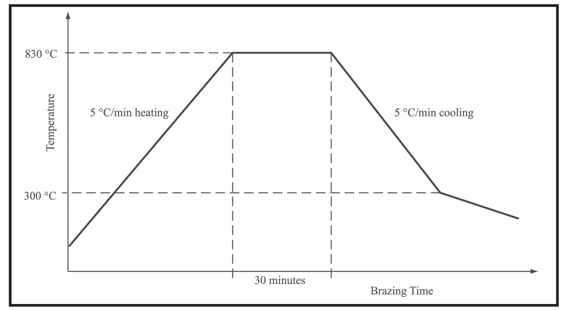

Fig. 2 — Temperature setup program for the brazing process.

stacked together and rolled to form a single composite layer of 0.4 mm thickness. Four sheets of a eutectic alloy 70Ag-28Cu-2Ti, each in the form of 0.1-mm-thick foil, was used as the filler metal. The brazing sample was prepared in a sandwich configuration, as shown in Fig. 1, and clamped using a suitable jig to hold them in place. The composite Cu/Ni interlayer was placed so that the Cu side faced the sapphire while Ni side faced the Inconel® 600. This configuration is significant to ensure Cu intimation with the sapphire during brazing. Two layers of the alloy were stacked on each side of the composite interlayer to ensure homogenous infiltration of the brazing filler metal into the Cu/Ni porous composite.

The brazing process was conducted under vacuum at 1×10^{-4} Pa pressure using a Tokyo vacuum furnace. Figure 2 shows the brazing cycle temperature profile used. The sample was directly heated to a brazing temperature of 830°C with a heating rate of 5°C/min. The brazing temperature was then kept constant for 30 min before cooling at a controlled rate of 5°C/min until it reached 300°C. Finally it was left to cool down to room temperature.

The cross section of the brazed specimen was analyzed using optical microscopy and SEM/EDS (using a Philips SEM-EDS XL40 for 500× magnification and JSM 5410LV for 2000× magnification). Evaluation using an electron probe microanalyzer (EPMA) was conducted using a Shimadzu EPMA-1600 on gold-coated specimens.

Results and Discussion

The effect of Ti/Ni diffusion into the Cu/Ni porous composites on the interface of brazed sapphire with Inconel® 600 was evaluated. Shirzadi (Ref. 20) recommends that the porous interlayer should be between 0.2 to 0.4 mm thick in order to control the strength of metallic bonding. Increasing porous interlayer thickness would lead to a reduction in shear strength. Thus, for this research, the 0.4 mm thickness of the Cu/Ni porous composite was obtained through a rolling process. The observation confirms that the porosity in the material was maintained even after the compressed rolling process. Figure 3 presents the optical micrograph of porous Cu/Ni composite (nickel side) showing the presence of open pores in the range of 100–200 μm.

Previous research has recognized the ability of a copper interlayer to absorb residual stresses in the brazing of ceramics to metal (Ref. 21). However, it was found that the diffusion of Cu is high, which may lead to the formation of microvoids in the brazed joint. Microvoids may reduce joint strength due to void propagation in the joining interface (Ref. 22). In this research, a Ni/Cu porous composite interlayer was used to enhance the joining process due to the presence of Ni and to generally improve the ability of residual stress absorption. A Ni interlayer is also preferable for high-temperature applications such as in the production of ceramic-to-metal seals for ultrahigh-vacuum equipment and pressure gas sensors (Ref. 22).

Physical examination of the brazed sample shows that an adequate strength joint was successfully obtained. However, during cross sectioning of the joint using a low-speed diamond saw, some of the sapphire tended to detach from the joint. This is probably due to the large impact force of the diamond on the cutting blade and the material being machined. Examinations of a detached portion of sapphire showed a very thin, black layer, which was subsequently identified as a reaction layer under microscopic observation. However, this layer is not observable using SEM, which agrees with past findings of the formation of an extremely thin reaction layer, not visible under SEM magnification (Ref. 21). This thin black layer is recognized in the literature as TiO_x, a compound resulting from possible reaction between Ti found in the active brazing filler metal and the oxide of the sapphire (Ref. 12).

The SEM micrographs of the joint cross section is shown in Fig. 4, while the micrographs of the braze area/sapphire interface at various magnifications are shown in Fig. 5. The microstructure within the brazing area is shown in Fig. 5A, indicating a significant presence of copper (dark gray

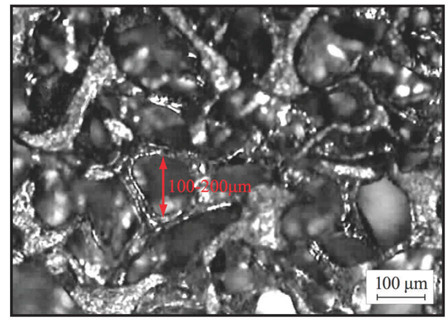

Fig. 3 — Micrograph of Cu/Ni porous composites (nickel side).

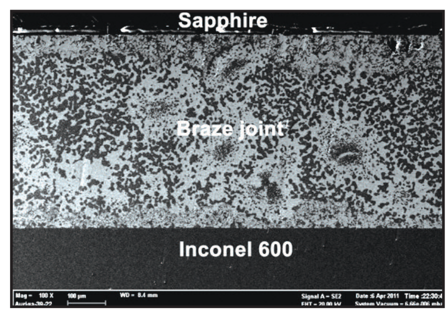

Fig. 4 — SEM micrograph showing a cross section of a brazed joint of sapphire/Cu/Ni porous composites/Inconel® 600.

Table 1 — EDS Analysis of SEM Micrograph of Brazed Joint/Sapphire Interface at 500× (at.-%)

Region	Ti	O	Al	Ag	Cr	Fe	Ni	Cu
A	2.22	58.71	9.45	3.99	0.4	3.47	3.59	18.17
B	2.09	75.3	5.09	1.49	0	0.73	4.54	10.77
C	46.63	31.66	0.3	5.01	0.34	0.79	4.05	11.21
D	0	95.6	1.99	0	2.41	0	0	0
E	2.32	44.58	3.17	13.69	0	0	9.34	26.89
F	0	73.82	0	1.8	0.76	1.52	6.97	15.13

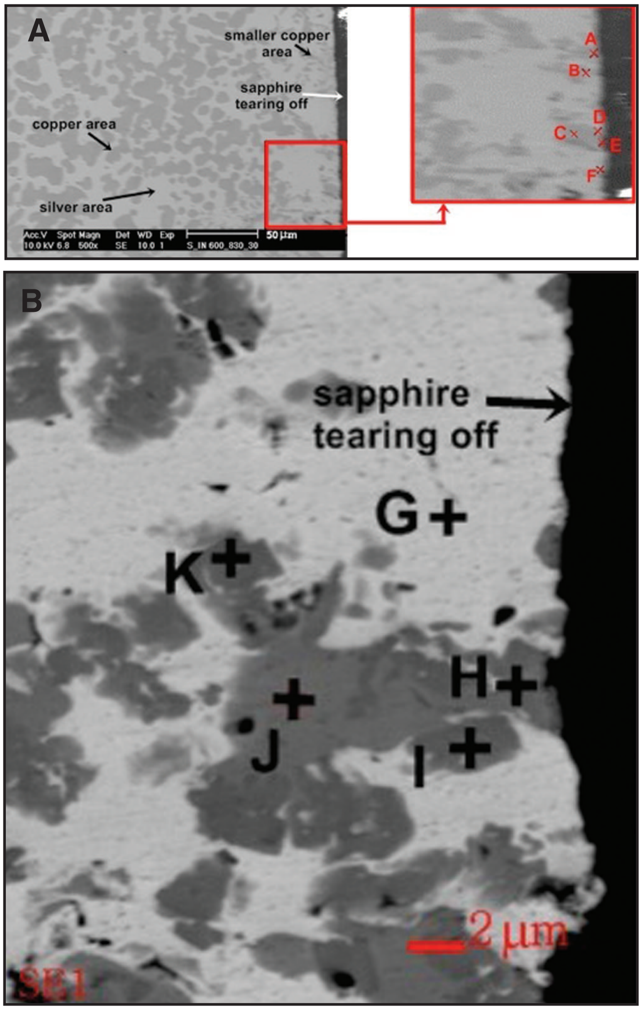

Fig 5 — SEM micrograph of brazed joint/sapphire interface at different magnifications. A — 500× magnification; B — 2000× magnification.

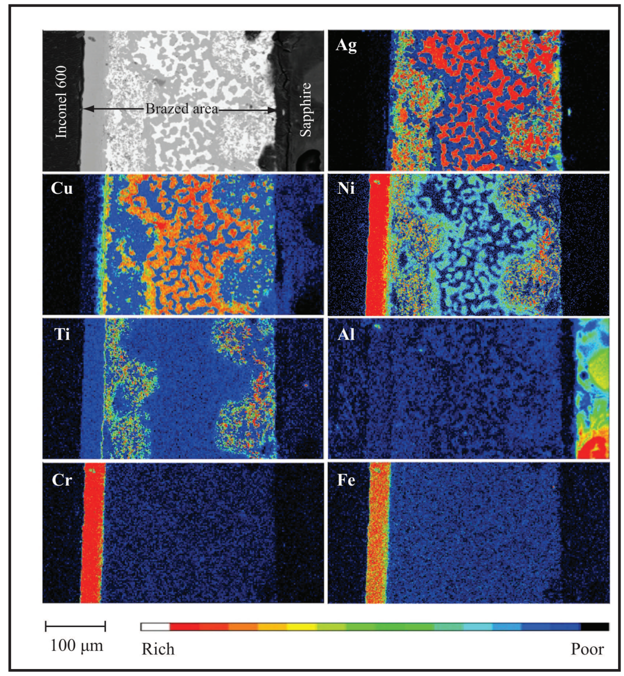

Fig. 6 — EPMA micrograph showing a cross section of a braze area/ sapphire.

area) and silver elements (light gray) from the Ni/Cu porous composite interlayer and the brazing filler metal. The EDS analysis was conducted within the vicinity of the braze area/sapphire interface, with the measurement taken at the points marked A to F as in Fig. 5A and G to K as in Fig. 5B. The complete EDS analysis is summarized in Tables 1 and 2.

It was observed that Ti tends to diffuse into the copper area. Since the Cu side of the porous interlayer faces the sapphire, the porous structure of the interlayer may have altered the adhesion behavior of active brazing filler metal by "entrapping" the titanium element (as an active element) within the Cu areas, as shown in Fig. 5A and Table 1. Very high concentrations of Cu, Ni, and Ti were detected in the interface with the sapphire, as shown in Fig. 5B and Table 2. Clustering of the copper region in close vicinity to the sapphire interface would be indicative of the adhesion process taking place although the regions of copper near the sapphire interface is smaller as compared to the middle of the brazed area. However, the presence of Ni mostly in the clustering of Cu may be attributed to the strong Ti-Ni affinity at the interface of the sapphire, which reduced the possibility for Ti to form a wettable compound with sapphire (Ref. 23). This strong affinity of Ti with Ni usually leads to the formation of a brittle intermetallic compound of Ni_3Ti as observed in the EDS point analysis of H–K (Table 2) (Ref. 24). This observation is in agreement with recent literature (Ref. 12). The strong Ti-Ni interaction subsequently reduces Ti reaction layer thickness and tends to alter layer of Ti compound type composition (Ref. 12). This phenomenon leads to the formation of a very thin reaction layer that weakens the joining interface, which may result in failure of the brazed sapphire interface.

There is also a "reduction phenomenon" of oxygen by Ti at the surface near the sapphire resulting in the formation of an intermetallic Ti_xO_y compound (Ref. 25). However, it appears that the oxygen content is very high compared to titanium in this zone. This may also suggest that high oxygen content could lead to the formation of a brittle intermetallic that would not accommodate the thermal expansion mismatch between joining sapphire with Inconel® 600 (Ref. 25).

An EPMA was conducted to map the constituent elements, especially the distribution of Ti at the brazed joint. Figure 6 shows the distribution maps with colored legends indicating the concentration of the elements. High concentration of Ag, Cu, and Ni were significantly observed in the middle of the brazed area. The rich Ag was isolated in the center of the braze layer, and it is believed that the Ag from the filler metal diffused into the porous layer (Cu and Ni) and formed wavelike structures. There was no trace of Ti element in the middle of the brazed area. However, a rich Ti element was significantly observed near the brazing interface. The wavelike struture of Ti (as indicated in the figure) formed on both sides of the brazing interface. This structure was almost identical with "lacework phase" revealed by Vianco et al. (Refs. 8, 26). In addition to the Ti element, the Cu and Ni elements were also traced in the wavelike structures, distributed in similar fashion to the rich Ti element. The EPMA analyses confirmed that the Ti dif-

Table 2 — EDS Analysis of Brazed Joint/Sapphire Interface at 2000× (at.-%)

Region	Al	Ag	Ti	Ni	Cu
G	2.42	89.52			8.06
H	0.53	11.9	12.5	38.71	25.86
I	1.06	2.28	21.5	60.2	14.97
J	1.05	1.99	12.83	38.31	46.08
K		1.16	23.04	69.67	6.15

fused toward the brazing interface, and it also had a strong affinity toward Cu and Ni elements. This observation is in agreement with the SEM-EDS analysis in the previous section. Similar observations also were reported by S. Mandal and Santella et al. (Refs. 27–29).

A high concentration of Ti was detected near the sapphire interface although it was inhomogeneously formed as that on the Inconel® 600 interface. Nevertheless, it was speculated that a very thin reaction layer formed along the brazing interface. In this work, the reaction layer was very thin (less than 1 μm) as compared to the reaction layer found by other researchers (Refs. 30, 31). The formation of a very thin reaction layer may be the result of strong interdiffusion between Cu, Ni, and Ti, which subsequently reduces the thermodynamic activity between metal-ceramic interfaces. It is also suggested that the reaction layer may contain several phases such as Ti-O, Ti-Cu-O, and Ti-Ni. According to the report by Santella et al. (Ref. 29), two main reaction layer phases could exist when brazing Al_2O_3 using Ag-Cu-Ti brazing filler metal, namely TiO and Ti_3Cu_3O. Both phases are very important to the bonding strength of the joint. The TiO itself would not be exerting thermal mismatch strains between the ceramic-metal joint due to a low CTE (9.2×10^{-6} °C^{-1}). The Ti_3Cu_3O may offer favorable transition in CTE and subsequently reduced the local strains with brazing alloys. The CTE of Ag, Cu, and Ti_3Cu_3O, Ni_3Ti are 19.2×10^{-6} °C^{-1}, 22×10^{-6} °C^{-1}, 15.1×10^{-6} °C^{-1}, and 9×10^{-6} °C^{-1}, respectively.

Conclusions

The effects of Ti, Ni, and Cu diffusion into a Cu/Ni porous composite as well as the influences on metallic bonding at the sapphire interface in sapphire brazed to Inconel® 600 were investigated. From the results, it appears that titanium (Ti) is an active element, well known for wetting the ceramic surface even in very small percentages. However, a strong Ti and Ni interaction rather than Ti and Cu during brazing have obstructed the thermodynamic activity of Ti. In this research, a Ni_3Ti compound was thought to be altering the thermodynamic activity in the brazing filler metal near the sapphire side and limiting the diffusion of Ti reacting with the oxide from the sapphire to form a reaction layer. As a result, only a very thin reaction layer was formed on the sapphire. The high-oxygen percentage at the sapphire interface contributed to the formation of a brittle intermetallic TiO_x layer.

The research has shown that the elements of the porous interlayer may alter the thermodynamic activity of the active filler metal. It is proposed that the composition of the porous interlayer should be carefully chosen to enhance, rather than weaken the brazed joint.

Acknowledgments

The authors would like to acknowledge the University of Malaya for providing the necessary facilities and resources for this research. This study was funded by the HIR Grant (HIR-MOHE-D000001-16001) from the Ministry of Higher Education, Malaysia.

References

1. Liu, G. W., Qiao, H. J., Wang, H. J., Wang, J. P., and Lu, T. J. 2011. Bonding mechanisms and shear properties of alumina ceramic/stainless steel brazed joint. *Journal of Materials Engineering and Performance* 20: 1563–1568.

2. Mizuhara, H., and Mally, K. 1985. Ceramic-to-metal joining with active brazing filler metal. *Welding Journal* 64(10): 27–32.

3. Blugan, D., Kuebler, J., Bissig, V., and Janczak-Rusch, J. 2007. Brazing of silicon nitride ceramic composite to steel using SiC-particle-reinforced active brazing alloy. *Ceramics International* 33: 1033–1039.

4. Feng, J. C., Liu, D., Zhang, L. X., Lin, X. C., and He, P. 2010. Effects of processing parameters on microstructure and mechanical behavior of SiO_2/Ti–6Al–4V joint brazed with AgCu/Ni interlayer. *Materials Science and Engineering A* 527(6): 1522–1528.

5. Cho, B.-R., Lee, J.-J., and Kang, S.-K. 2009. Effect of composition change on sintering and metallizing of alumina ceramics. *Journal of Ceramic Processing Research* 10(1): 121–123.

6. Ibrahim, A., and Hasan, F. 2011. Influence of processing parameters on the strength of air brazed alumina joints using aluminium interlayer. *Journal of Materials Science & Technology* 27(7): 641–646.

7. Zhong, Z., Zhou, Z., and Ge, C. 2009. Brazing of doped graphite to Cu using stress relief interlayers. *Journal of Materials Processing Technology* 209(5): 2662–2670.

8. Vianco, P., Stephens, J., Hlava, P., and Walker, C. 2003. Titanium scavenging in Ag-Cu-Ti active braze joints. *Welding Journal* 82(10): 268-s to 277-s.

9. Park, J.-W., Mendez, P. F., and Eagar, T. W. 2002. Strain energy distribution in ceramic-to-metal joints. *Acta Materialia* 50: 883–899.

10. Shamanian, M., Salehi, M., Saatchi, A., and North, T. H. 2003. Influence of Ni interlayers on the mechanical properties of Ti_6Al_4V/(WC-Co) friction welds. *Materials and Manufacturing Processes* 18(4): 581–598.

11. Passerone, A., and Muolo, M. L. 2000. Joining technology in metal-ceramics systems. *Materials and Manufacturing Processes* 15(5): 631–648.

12. Valette, C., Devismes, M.-F., Voytovych, R., and Eustathopoulos, N. 2005. Interfacial reactions in alumina/CuAgTi braze/CuNi system. *Scripta Materialia* 52(1): 1–6.

13. Lee, M. K., Lee, J. G., Choi, Y. H., Kim, D. W., Rhee, C. K., Lee, Y. B., and Hong, S. J. 2010. Interlayer engineering for dissimilar bonding of titanium to stainless steel. *Materials Letters* 64(9): 1105–1108.

14. Kar, A., Ghosh, M., Ashok, R. K., and Ajoy, R. K. 2008. Effect of interfacial thickness and residual stress on the mechanical property of the alumina-stainless steel braze joint interface. *Materials Science and Engineering A* 498(1–2): 283–288.

15. Tinsley, N. D., Huddleston, J., and Lacey, M. R. 1998. The reduction of residual stress generated in metal-ceramic joining. *Journal of Materials and Manufacturing Processes* 13(4): 491–504.

16. Miyazaki, H., Hotta, M., Kita, H., and Izutsu, Y. 2012. Joining of alumina with a porous alumina interlayer. *Ceramics Internationall* 38(2): 1149–1155.

17. Kim, T. W., and Park, S. W. 2000. Effects of interface and residual stress on mechanical properties of ceramic/metal system. *Key Engineering Materials* 183–187: 1279–1284.

18. Zhang, J. X., Chandel, R. S., Chen, Y. Z., and Seow, H. P. 2002. Effect of residual stress on the strength of an alumina–steel joint by partial transient liquid phase (PTLP) brazing. *Journal of Materials Processing Technology* 122: 220–225.

19. Abed, A., Jalham, I. S., and Hendry, A. 2001. Wetting and reaction between B'-sialon, stainless steel and Cu-Ag brazing alloys containing Ti. *Journal of the European Ceramic Society* 21: 283–290.

20. Shirzadi, A. A., Zhu, Y., and Bhadeshia, H. K. D. H. 2008. Joining ceramics to metals using metallic foam. *Materials Science and Engineering A* 496(1–2): 501–506.

21. Fang, F., Zheng, C., Lou, H. Q., Sui, R. Z., and Adamovskyy, A. A. 2001. Bonding of silicon nitride ceramics using Fe–Ni/Cu/Ni/Cu/Fe–Ni interlayers. *Materials Letter* 47: 178–181.

22. Sabetghadam, H., Hanzaki, A. Z., Araee, A., and Hadian, A. 2010. Microstructural evaluation of 410 SS/Cu difussion-bonded joint. *Journal of Materials Science and Technology* 26(2): 163–169.

23. Wan, C., Kritsalis, P., Drevet, B., and Eustathopoulos, N. 1996. Optimization of wettability and adhesion in reactive nickel-based alloys/alumina systems by a thermodynamic approach. *Materials Science and Engineering A* 207(2): 181–187.

24. Shen, Y., Li, Z., Hao, C., and Zhang, J. 2012. A novel approach to brazing C/C composite to Ni-based superalloy using alumina interlayer. *Journal of the European Ceramic Society* 32(8): 1769–1774.

25. Sciti, D., Bellosi, A., and Esposito, L. 2001. Bonding of zirconia to superalloy with the active brazing technique. *Journal of the European Ceramic Society* 21: 45–52.

26. Vianco, P. T., Stephens, J. J., Hlava, P. F., and Walker, C. A. 2003. A barrier layer approach to limit Ti scavenging in FeNiCo/Ag-Cu-Ti/Al_2O_3 active braze joints. *Welding Journal* 82 (9): 252-s to 262-s.

27. Bang, K., and Liu, S. 1994. Interfacial reaction between alumina and Cu-Ti filler metal during reactive metal brazing. *Welding Journal* 73(3): 54-s to 60-s.

28. Mandal, S., Rao, V., and Ray, A. K. 2004. Characterization of the brazed joint interface between Al_2O_3 and (Ag-Cu-Ti). *Journal of Materials Science* 39(16–17): 5587–5590.

29. Santella, M. L., Horton, J. A., and Park, J. J. 1990. Microstructure of alumina brazed with a silver-copper-titanium alloy. *Journal of the American Ceramic Society* 73(6): 1785–1787.

30. Laik, A., Bhanumurthy, K., Kale, G. B., and Kashyap, B. P. 2013. Microstructural evolution during reactive brazing of alumina to Inconel 600 using Ag-based alloy. *Acta Materialia* 6(1): 126–138.

31. Muolo, M., Ferrera, E., Morbelli, L., and Passerone, A. 2004. Wetting, spreading and joining in the alumina-zirconia-Inconel 738 system. *Scripta Materialia* 50(3): 325–330.