TEM ANALYSIS OF DIFFUSION-BONDED SILICON CARBIDE CERAMICS JOINED USING METALLIC INTERLAYERS

T. Ozaki[1], Y. Hasegawa[1], H. Tsuda[2], S. Mori[2], M. C. Halbig[3], R. Asthana[4], and M. Singh[5]

[1] Technology Research Institute of Osaka Prefecture, Osaka, Japan

[2] Graduate School of Engineering, Osaka Prefecture University, Osaka, Japan

[3] NASA Glenn Research Center, Cleveland, Ohio, USA

[4] University of Wisconsin-Stout, Menomonie, WI, USA

[5] Ohio Aerospace Institute, NASA Glenn Research Center, Cleveland, Ohio, USA

ABSTRACT

SiC fiber-bonded ceramics (SA-Tyrannohex™: SA-THX) diffusion-bonded with Ti/Cu metallic interlayers were investigated. Thin samples of the ceramics were prepared with a focused ion beam (FIB) and the interfacial microstructure of the prepared samples was studied by transmission electron microscopy (TEM) and scanning TEM (STEM). In addition to conventional microstructure observation, for detailed analysis of reaction compounds in diffusion-bonded area, we performed STEM-EDS measurements and selected area electron diffraction (SAD) experiments. The TEM and STEM experiments revealed the diffusion-bonded area was composed of only one reaction layer, which was characterized by TiC precipitates in Cu-Si compound matrix. This reaction layer was in good contact with the SA-THX substrates, and it is concluded that the joint structure led to the excellent bonding strength.

INTRODUCTION

Silicon carbide (SiC) composite materials are attractive materials for applications in high-temperature and extreme environments because of their excellent mechanical properties, oxidation resistance, and thermal stability. In particular, one robust ceramic SA-Tyrannohex™ (SA-THX), which has a structure of highly ordered, close-packed, hexagonal columnar fibers of crystalline β-SiC bonded with thin layers of interfacial carbon[1,2], is a promising material because of its good thermomechanical performance, high strength sustained up to 1600°C, and high fracture toughness (1200 J·m^{-2} at RT)[3]. Hence, SA-THX and related SiC-based ceramics are currently being developed and tested for a wide variety of applications in aerospace and energy[4,5]. However, the geometrical limitations of SiC ceramics prevent the fabrication of large or complex components *via* hot pressing, CVD, machining, or net-shape processing. To fabricate these components from brittle ceramics, simpler units must be joined and integrated. Various joining methods have been developed, such as reaction bonding[6-8] and brazing[9,10]. Diffusion bonding techniques have also been used and hold much promise[11,12].

We have applied diffusion-bonded to a variety of SiC parts with various metallic interlayers[13-16]. We also obtained good diffusion bonding in SA-THX through the use of a 10-μm-thick Ti interlayer and fibers parallel to the interlayer [15].

Recently, to reduce the temperature of diffusion bonding processes, we attempted to

use Ti/Mo and Ti/Cu foils as metallic interlayers[17,18]. In the case of Ti/Mo our process achieved metallurgically sound joints, but the results of a Knoop test suggested that the joint area contained some weak areas and microscale cracking was observed[17]. We also reported that the $Ti_5Si_3C_x$ phase generated by diffusion bonding had a large coefficient of thermal expansion (CTE), which contributed to the microscale cracking[16,18]. Conversely for the case of Ti/Cu no defects, such as microscale cracking, were observed around the diffusion-bonded area. Furthermore, the Knoop hardness of the joint area measured for Ti/Cu stability showed a higher strength than that based on Ti/Mo. The area diffusion bonded with Ti/Cu showed a different joint microstructure from that of Ti/Mo[17]. Therefore, to reveal the bonding mechanism, which exhibits a high strength in Ti/Cu interlayer, we investigated the microstructure around diffusion-bonded area.

For the microstructure observations by transmission electron microscopy (TEM) and scanning TEM (STEM), we prepared thin samples of the diffusion bond with focused ion beam (FIB) milling. In addition to conventional microstructure observations, we performed detailed analysis of the reaction compounds in the diffusion-bonded area with STEM-energy-dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAD). On the basis of the results obtained by TEM and STEM analysis, the process of formation of the joint microstructure was discussed.

EXPERIMENTAL

SA-Tyrannohex™ (SA-THX) SiC fiber-bonded ceramic was obtained from Ube Industries (Ube, Japan). The material was composed of SA-Tyranno fiber™ bundles in an eight-harness satin weave, with fibers oriented in parallel and perpendicular directions. Ti foil (10 μm) and Cu foil (5 μm) were obtained from Goodfellow Corporation (Glen Burnie, MD, USA). Before joining, all materials were ultrasonically cleaned in acetone for 10 min. Joints were diffusion bonded at 1200 °C for 4 hours under a pressure of 30 MPa in vacuum. For joints involving the Ti/Cu bilayers, three sheets of Cu foil were sandwiched by two sheets of Ti foil as illustrated in Fig. 6(a). Detailed fabrication procedures are reported elsewhere[17].

STEM and STEM-EDS measurements were performed with a Hitachi HD-2700. TEM and SAD were performed with a JEOL JEM-2000FX. All samples for TEM and STEM were prepared with a FIB (Hitachi FB-2200), which allowed us to examine precisely selected, clean, and diffusion-bonded areas with low-damage. Detailed conditions of the FIB process are described in the next chapter.

RESULTS AND DISCUSSION
Preparation of Thin Samples from Diffusion Bonding

We fabricated thin samples for TEM/STEM observation with a FIB micro-sampling technique. Fig. 1 shows scanning ion microscope (SIM) images of the diffusion-bonded area obtained from the FIB. The reacted layers and their boundaries are clearly shown in Fig. 1(a). No cracks or void were observed around the reacted layer. Similar microstructures were

imaged by SEM [17]. We selected a thin sample from the joint area which included the reaction layer and a part of the SA-THX substrate (Fig. 1(b)), and processed the sample to be thin enough for TEM observations.
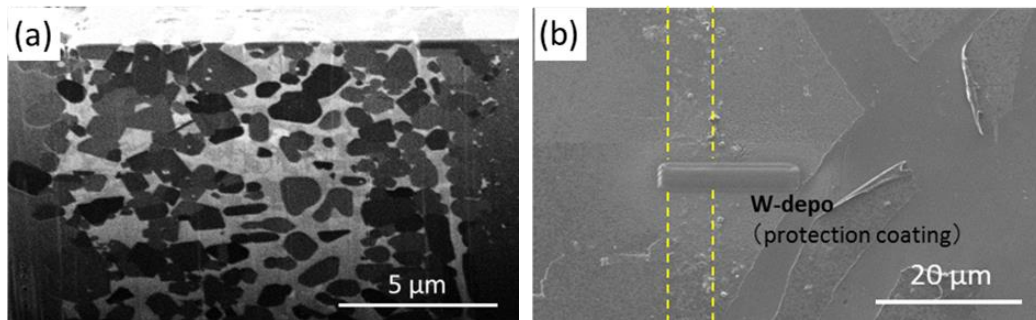

Figure 1. Scanning ion microscope (SIM) images of the diffusion bond obtained with the FIB. (a)Cross-sectional image and (b) image of the area where the thin sample was fabricated.

STEM Imaging

      Fig. 2 shows STEM images of the diffusion bond acquired in secondary electron (SE), bright-field (BF), and high angle annular dark-field (HAADF) STEM modes, respectively. The samples were thin enough to observe the microstructure of the entire diffusion-bonded area and the quality of the bonding appeared to be good. In the HAADF image, some dark contrast in SA-THX was attributed to residual carbon or fiber boundaries [18]; apart from the marks induced in the FIB process, no notable defects were observed. Some features should be noted in the diffusion bonded area. Several reaction layers were observed in the diffusion bonded Ti/Mo interlayer [17,18]; however, in the case of Ti/Cu, only one reaction layer was apparent in the diffusion bond. A part of the reaction compound leaked into the boundaries of the SA-THX, but no elemental diffusion from the reaction layer side into the SiC grains was observed. This result suggested that the diffusion bonding process with Ti/Cu interlayer proceeded mainly via a liquid state rather than diffusion in solid. Furthermore, the reaction layer was composed of grains of various sizes and a monolithic matrix, which filled the grains without gap. The reaction layer had few cracks or voids and formed a clean interface with the SA-THX substrate.
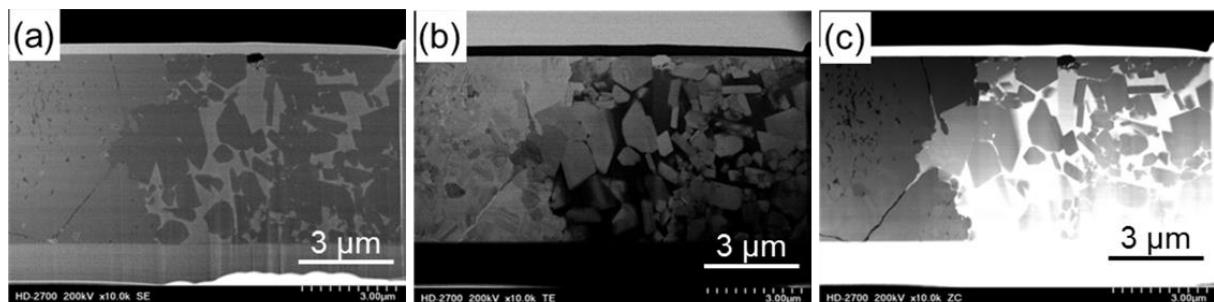

Figure 2. STEM images of diffusion bond: (a) SE STEM mode, (b) BF STEM mode, and (c) HAADF STEM mode.

STEM-EDS Mapping

        To investigate the elemental composition of the grains and the matrix in the reaction layer, we performed STEM-EDS mapping. As shown in Fig. 3, the elemental distribution of Si, Ti, and Cu could be clearly divided into two areas of the grains and the matrix. The grains appeared to contain more Ti and C whereas the matrix contained more Cu and Si. On the basis of these results, the reaction layer was likely composed of TiC grains and a matrix of a Cu-Si compound. Although the elemental distribution of C appeared not to differ much, carbon located in the nearby SA-THX substrate might have affected the EDS measurement or the matrix may have contained some carbon. Some previous research had reported that a certain amount of SiC can dissolve into melted copper and fine glassy carbon precipitates in Cu-Si solid solution[19].
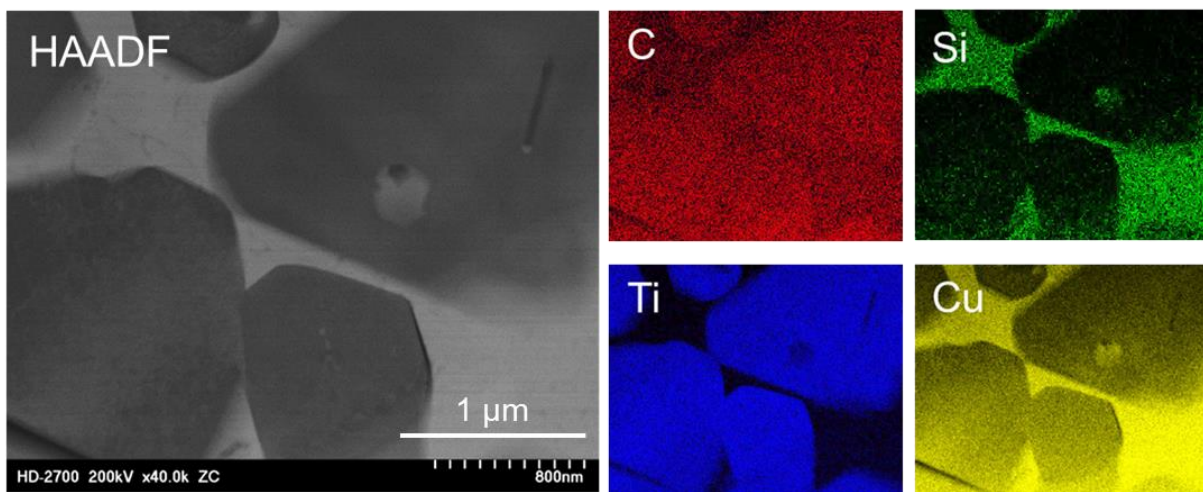

Figure 3. HAADF-STEM image of the reaction layer and elemental mapping images obtained by STEM-EDS.

TEM Imaging and SAD analysis

        For more detailed analysis of the reaction compound, we investigated its crystal structure by TEM. We acquired SAD patterns from regions of the grains and matrix in the reaction layer. Fig. 4 shows the TEM images and SAD patterns acquired from one grain, indicated by a circle. Each SAD pattern featured a reciprocal lattice pattern from a simple NaCl-type structure, which was consistent with the standard TiC structure.
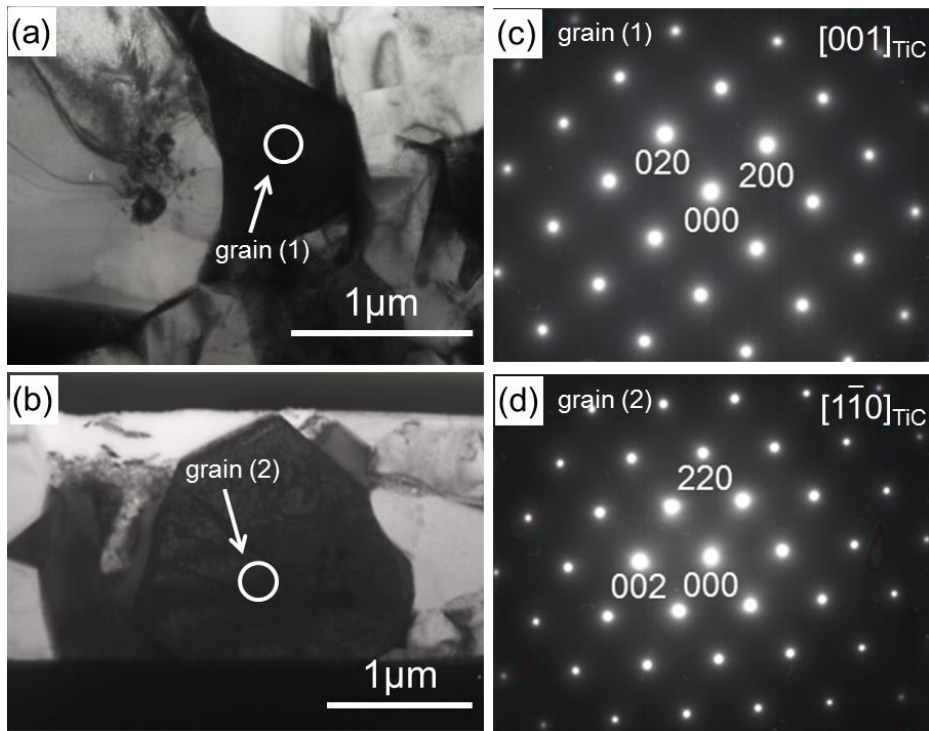
Figure 4. (a, b) TEM micrographs and (b, c) SAD patterns obtained from grains (1) and (2).

Although the crystal structure of the grains in the reaction layer was easily characterized it was more difficult to characterize the crystal structure of the matrix. As shown in Fig. 5, the SAD patterns acquired from the matrix region were complex. The results of the STEM-EDS suggested the matrix featured a Cu-Si system, and Cu_3Si is a potential candidate material. It has been reported that Cu_3Si has a long-period structure which appears as superlattice reflections in its SAD patterns[20,21]. The SAD patterns of the matrix were similar to those of Cu_3Si; however, further studies are required to clarify the matrix structure.
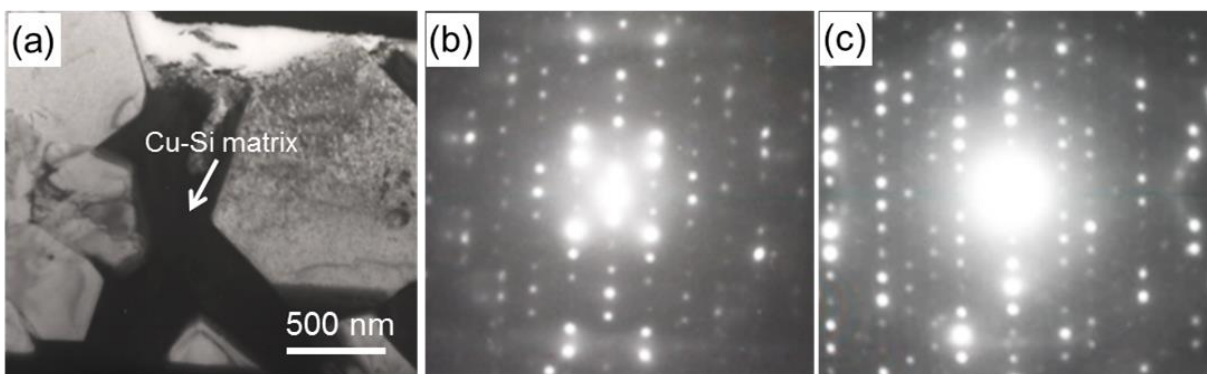

Figure 5. (a) TEM micrograph and (b, c) SAD patterns obtained from Cu-Si matrix region.

Formation of the Joint Microstructure

TEM and STEM analysis revealed the reaction layer of the diffusion bonding was composed of TiC precipitate in a Cu-Si compound matrix. The results described above also indicate the formation mechanism of the joint microstructure formed from the Ti/Cu interlayer.

At the maximum temperature in the diffusion bonding process, the Cu interlayer melts, and the titanium interlayer and SiC (SA-THX) substrate partially dissolve in the molten metal. In the cooling process, TiC grains precipitate from the molten metal, and as the temperature decreases the grains gradually grow by absorbing Ti and C atoms from the molten metal. At the end of the process, the molten metal completely solidifies becoming a monolithic Cu-Si compound. Thus the microstructure of TiC grains embedded in a monolithic Cu-Si compound was formed in this way.
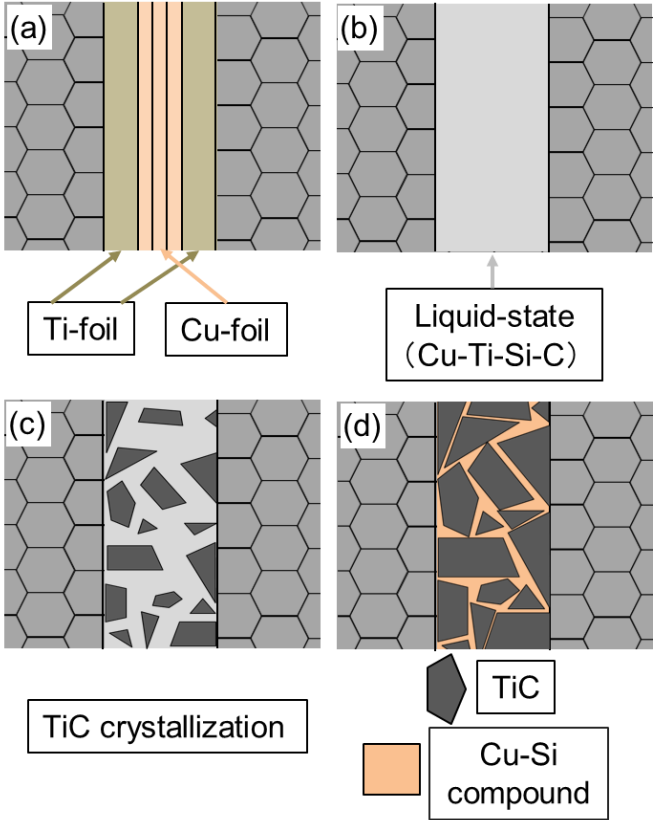

Figure 6. Change in the microstructure of interface of SA-THX/Ti/Cu/Ti/SA-THX (a) before processing, (b) at maximum temperature (1200°C), (c) in cooling, and (d) after processing

Considering the CTE value of the reaction compound, it is favorable for TiC grains to constitute most of interlayer because TiC has a CTE value relatively close to that of SiC. Furthermore, because TiC has a cubic crystal structure, TiC will expand and contract isotropically. Although the exact CTE value of the Cu-Si compound is not known, Cu metal generally exhibits relatively large CTE values. However, because Cu metal also exhibits a low Young modulus, the soft Cu-based compound formed in the matrix of the joint area may be advantageous for the diffusion bonding quality.

CONCLUSIONS

SA-THX was diffusion bonded with Ti-Cu foil interlayers. The diffusion bond regions were examined by TEM and STEM imaging for samples prepared by FIB. The results are summarized as follows.

(1) We selected thin samples from the bonded area of diffusion bonded SA-THX and processed these using a FIB micro-sampling technique. The prepared samples were sufficiently thin and showed low enough damage to allow detailed evaluation by TEM and STEM.

(2) The microstructure of the diffusion bonded area was observed by STEM and TEM. The composition and crystal structures of the reaction compound were investigated by STEM-EDS and SAD methods. The reaction layer of the diffusion bonding was composed of TiC precipitates in a Cu-Si compound matrix.

REFERENCES

[1] T. Ishikawa, S. Kajii, K. Matsunaga, T. Hogami, Y. Kohtoku, and T. Nagasawa, A Tough, Thermally Conductive Silicon Carbide Composite with High Strength up to 1600°C in Air, *Science*, **282**, 1265–1297 (1998).

[2] T. Ishikawa, Y. Kohtoku, K. Kumagawa, T. Yamamura, and T. Nagasawa, High-strength Alkali-Resistant Sintered SiC Fibre Stable to 2200°C, *Nature*, **391**, 773–775 (1998).

[3] T. Ohji, M. Singh, Engineered Ceramics: Current Status and Future Prospects, *Wiley*, **16**, Integration Challenges in Alternative and Renewable Energy Systems, 323 (2016).

[4] P. J. Lamicq, G. A. Bernhart, M. M. Dauchier, and J. G. Mace, SiC/SiC Composite Ceramics, *Am.Ceram. Soc. Bull.*, **65**(2), 336–338 (1986).

[5] M. Halbig, M. Jaskowiak, J. Kiser, and D. Zhu, Evaluation of Ceramic Matrix Composite Technology for Aircraft Turbine Engine Applications, *proceedings of the 51st AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition* (2013).

[6] M. Singh, A Reaction Forming Method for Joining of Silicon Carbide-based Ceramics, *Scr. Mater.*, **37**(8), 1151–1154 (1997).

[7] M. Singh, Joining of Sintered Silicon Carbide Ceramics for High Temperature Applications, *J. Mater. Sci. Lett.*, **17**(6), 459–461 (1998).

[8] M. Singh, Microstructure and Mechanical Properties of Reaction Formed Joints in Reaction Bonded Silicon Carbide Ceramics, *J. Mater. Sci.*, **33**, 1–7 (1998).

[9] V. Trehan, J. E. Indacochea, and M. Singh, Silicon carbide brazing and joint characterization, *J. Mech. Behav. Mater.*, **10**(5–6), 341–352 (1999).

[10] M. G. Nicholas, Joining Processes: Introduction to Brazing and Diffusion Bonding, *Kluwer*

Academic Publishers, Dordrecht, (1998).

[11]B. Gottselig, E. Gyarmati, A. Naoumidis, and H. Nickel, Joining of Ceramics Demonstrated by the Example of SiC/Ti, *J. Eur. Ceram. Soc.*, **6**, 153–160 (1990).

[12]M. Naka, J. C. Feng, and J. C. Schuster, Phase Reaction and Diffusion Path of the SiC/Ti System, *Metall. Mater. Trans. A*, **28A**, 1385–1390 (1997)**.**

[13]H. Tsuda, S. Mori, M. C. Halbig, and M. Singh, TEM observation of the Ti Interlayer between SiC Substrates during Diffusion Bonding, *Proceedings of ICACC 2012*, (2012).

[14]M. C. Halbig, M. Singh, and H. Tsuda, Integration Technology for Silicon Carbide-Based Ceramics for Micro-Electro-Mechanical Systems-Lean Direct Injector Fuel Injector Applications, *Int. J. Appl. Ceram. Tec.*, **9**, 677–687 (2012).

[15]H. Tsuda, S. Mori, M. C. Halbig, and M. Singh, Interfacial Characterization of Diffusion Bonded Monolithic and Fiber Bonded Silicon Carbide Ceramics, *Proceedings of ICACC 2013*, (2013).

[16]H. Tsuda, S. Mori, M. C. Halbig, M. Singh, and R. Asthana, Diffusion Bonding and Interfacial Characterization of Sintered Fiber Bonded Silicon Carbide Ceramics Using Boron-Molybdenum Interlayers, *Proceedings of ICACC 2014*, (2014).

[17]M. C. Halbig, M. Singh, and R. Asthana, Diffusion Bonding of SiC Fiber-Bonded Ceramics using Ti/Mo and Ti/Cu Interlayers. *Ceramics International*, **41**, 2140–2149, (2015).

[18] T. Ozaki, Y. Hasegawa, H. Tsuda, S. Mori, M. C. Halbig, M. Singh and R. Asthana, TEM Analysis of Interfaces in Diffusion-Bonded Silicon Carbide Ceramics Joined Using Metallic Interlayers, *Ceramic Engineering and Science Proceedings (CESP), Proceedings of the 40th International Conference on Advanced Ceramics and Composites*, (2016).

[19]K. Suganuma, K. Nogi, Interface Structure Formed by Characteristic Reaction between α-SiC Single Crystal and Liquid Cu, *J. Japan Inst. Met. Mater.*, **59**(12), 1292-1298 (1995).

[20]M. Heuer,T. Buonassisi, A. A. Istratov, and M. D. Pickett, Transition metal interaction and Ni-Fe-Cu-Si phases in silicon, *J. Appl. Phys.* **101**, 123510 (2007).

[21]C.-Y. Wen, F. Spaepen, In Situ Electron Microscopy of the Phases of Cu_3Si, *Phil. Mag.*, **87**(35), 5581-5599 (2007).