

# Microstructural Characterization and Mechanical Property Evaluation of SiC Coated Graphite – 304 Stainless Steel Brazed Joint

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**ABSTRACT:** SiC coated graphite is brazed to 304 stainless steel using 97(Ag28Cu)3Ti active filler alloy at 850, 900, 950 and 1000 °C under 1.962N dummy load. Thus developed interfaces of the brazed joints were characterized by SEM-EDS, EPMA and XRD analyses. Shear strength of the brazed joints along the graphite interface and micro hardness profile along both the interfaces for each sample have been evaluated. The sample brazed at 900 °C under 1.962N load exhibited maximum shear strength of about 50MPa. The nature of fracture was analyzed by SEM-EDS analysis. Micro hardness analysis along the interfaces reveals that there were minor variations in the nature of micro hardness profile along the brazed joint for all the specimens. The mechanical properties determined by shear tests for the specimens brazed under 1.962N load were compared with those of the specimens brazed under 0.981N load. It is observed that increasing the load on the braze assemble during brazing causes uniform interfacial diffusion throughout the joint area resulting in better joint strength. An attempt has been made for a comparative study on the effect of load applied, brazing temperature on the joint strength.

**KEYWORDS:** Joining, interfaces, diffusion, carbon.

## I. INTRODUCTION

Attractive properties of graphite like high heat and electrical conductivity, low density, high sublimation point, low thermal expansion and high emissivity makes it an extensively used material in nuclear, aerospace, automobile and medical industries [1, 2]. But its application as a structural material is restricted due to its low mechanical strength. To utilize the high temperature properties of graphite, it is often required to join the graphite with metallic parts [3-5]. A significant difference in the thermal and mechanical properties of graphite and the metals restricts its joining for wide spread applications [6-11]. Various reports are available for joining this type of system, however in most cases due to poor wettability of the graphite substrate by conventional brazing alloy and inherent porosities in graphite substrate the joint strength were found to be quite low (~10-15MPa) [3-4, 12]. Active metal brazing, which involves the use of chemically active elements such as Ti, Zr, Cr, Mo, is the extensively used method of joining ceramics with metals. Presence of small amount of these active elements enhances the wettability of ceramics as well as graphite by the filler alloy and thus improves the bonding between the graphite and metals [13-14]. These active elements have a strong affinity towards the ceramic or graphite surfaces [15]. During the joining of two dissimilar materials, many changes in the microstructural and mechanical properties in the vicinity of the joint region are observed [16]. Determination of a successful brazed joint depends upon the interfacial microchemistry. Thus it is necessary to identify the reaction products formed at the joint interfaces. Shear strength and micro hardness measurement give the bonding strength of the brazed joint. This paper aims to characterize the SiC coated graphite- 304 stainless steel joint interfaces brazed at an

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interval of 50 °C from 850 to 1000 °C under 1.962N dummy load. Also a comparative study on the mechanical properties of the samples brazed under different loads is done.

## II. EXPERIMENTAL PROCEDURE

SiC coating on graphite substrate was done by reaction bonding of Si and carbon of graphite. Water slurry of ~40µm sized Si was applied on a graphite plate by spin-coater. Si coated graphite was heated initially at 1450 °C. At this temperature the molten Si percolates into the open pores of graphite substrate; in the next step the temperature was raised to 1800 °C for the formation of reaction bonded SiC within the open pores as well as on the surface of graphite. The substrate materials, i.e. both 304 SS and SiC coated graphite were cut into rectangular pieces having the dimension of ~4mm (t) x 10mm (l) x 9mm (b). The surface of 304 SS was metallographically polished. Ag-Cu-Ti (3 wt% Ti in eutectic Ag-Cu) filler alloy having dimension of ~0.5 mm (t) x 9.5 mm (l) x 8.5 mm (b) was used as interlayer between 304 SS and SiC coated graphite. 304 SS and filler alloy were cleaned ultrasonically with acetone to remove any dirt, oil or grease over the faying surfaces. A dummy load of ~1.962N was applied over the braze assemble to maintain intimate contact among the substrates and the filler alloy as well as facilitating the interfacial reactions [7, 17-20].

The brazing process was carried out in a graphite resistance furnace (ASTRO Thermal Inc., USA) at a vacuum level of 30-40 mTorr. Prior to heating, the furnace was flushed 2-3 times with high purity argon gas to minimize the partial pressure of oxygen inside the furnace. The thermal cycle for brazing is depicted in Fig.1. The brazing was carried out at the temperatures of 850, 900, 950 and 1000 °C under 1.962N load and holding time at the peak temperature was maintained for 15 mins.

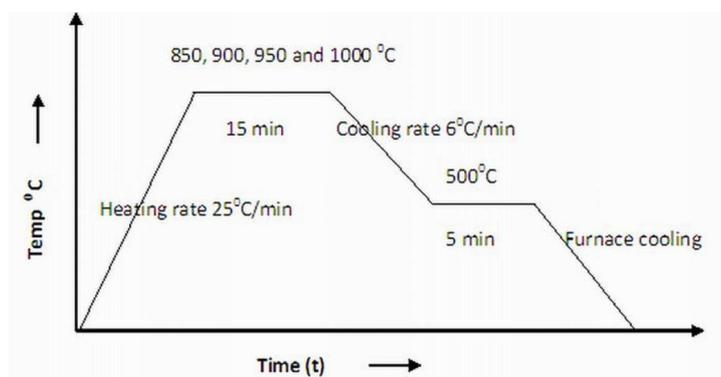


FIG.1. Schematic diagram of thermal cycle for brazing.

The brazed joints were characterized using Electron Probe Micro Analyzer with energy dispersive spectroscopy (EPMA, JXA 8230, Jeol Japan). WDS line profiles on the specimens brazed at 850, 900, 950 and 1000 °C were taken to understand the diffusion of various elements at the joint interfaces.

Since the reaction products/phases formed at the interfaces are mainly governed by brazing temperature, and the applied load showed minimum effect, earlier XRD results of 0.981N load [23] are taken into consideration for the phase identification in the present study.

Specimens of ~2 mm thickness were cut perpendicular to the brazed joint from each joint sample for shear tests. A Universal Testing Machine (H10K-S, Hounsfield, 10KN capacity) was used to evaluate the shear strength of brazed joint specimens. During the experiments, the cross head speed of 0.01 mm/min was maintained. Details of the specially designed shear test fixture used for shear test measurement, and the specimen placement technique are mentioned earlier [17- 22]. The load was applied on the joint perpendicularly and care was taken to ensure that the shear would take place exactly at the brazed joint. At least three shear tests were conducted for each specimen brazed at 850, 900, 950 and 1000 °C. The fractured surfaces were analyzed by SEM- EDS analysis.

The micro hardness tests were carried out using micro hardness tester (Leitz, RZD-DO, Germany). The measurements were carried out starting from 304 SS to SiC coated graphite across both the interfaces and the intermediate residual filler alloy. A load of 0.4905N on 304SS interface and filler alloy, 0.981N on SiC interface, and 0.24525N on the

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graphite region with holding time of 15sec for each indentation was applied. To minimize the interference of two consecutive indents, the centre to centre distance of two indents was maintained at least 2.5 times the diagonal of the indent [21]. The micro hardness profile was plotted against the respective positions. Based on the changes in the micro hardness values at different regions, the interfaces were identified in the hardness-distance plots.

### III. RESULTS AND DISCUSSION

While brazing with uncoated graphite, the liquid filler alloy percolated into the open pores of the graphite substrate resulting in severe stress generation at the graphite surface, causing peeling off of a thin layer of graphite from the bulk graphite substrate. Thus in order to avoid this problem, SiC coating on the graphite substrate was done. This reduces or restricts (i) the penetration of the liquid filler alloy into the pores of graphite, and (ii) also the formation of excessive amount of the reaction products at the interface. Since the interfaces in any brazed joint are formed as a result of the reaction of molten filler alloy with the substrate material, identification of these reaction products, their relative positions along the interface is of utmost importance. For any brazed joined system, it is practically not possible to alter the relative positions of the reaction products formed at the interface with respect to either the substrate or filler alloy. However, the quantity/volume fraction (i.e. the layer thickness) can be controlled by changing the brazing temperature, holding time and the applied pressure/load on the joint assembly [22].

The phases such as TiC,  $Ti_5Si_3$  and  $Ti_3SiC_2$  along with SiC, Cu, Ag at the interface of graphite side and FeTi and  $Fe_{35}Cr_{13}Ni_3Ti_7$  at the SS side interface were identified by XRD analyses [21-22]. The volume fraction (layer thickness) and the relative positions of these phases are carefully determined by SEM-EDS (Fig. 2(a)-(c)) and EPMA line profile analyses (Fig.3(a)-(b)). The results show that TiC is formed near the SiC layer, and next to SiC  $Ti_5Si_3$  is formed. In case of specimen brazed at 900 °C the formation of  $Ti_5Si_3$  is found to be maximum, whereas at 950 °C or above,  $Ti_3SiC_2$  phase starts forming at the cost of  $Ti_5Si_3$  phase.

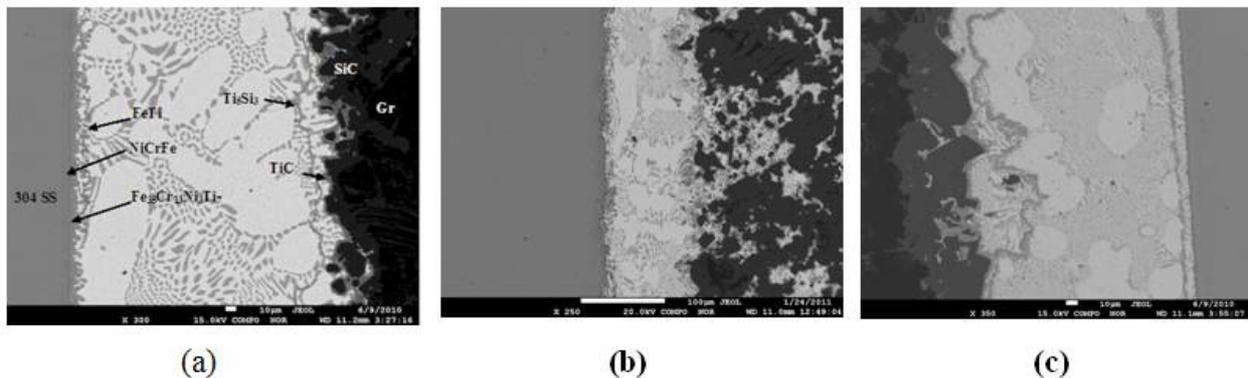


FIG.2. SEM images of (a) 900, (b) 950, (c) 1000 °C .

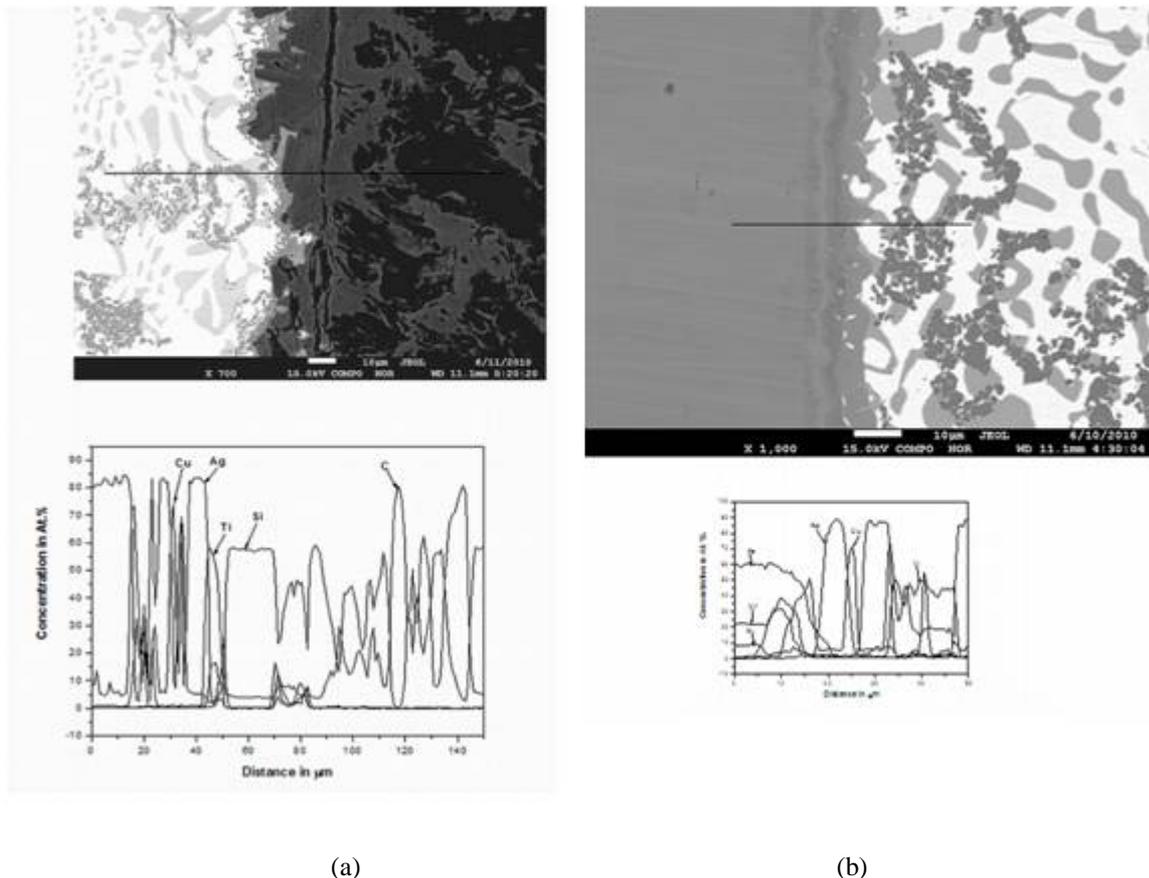


FIG.3. WDS line analysis along (a)SiC coated graphite side interface, (b) 304 SS side interface for the sample brazed at 900 °C under 1.962N load.

It was reported that a reaction product having low coefficient of thermal expansion (CTE) between two phases of higher CTE provides good joint strength [21- 23]. The CTE of  $Ti_5Si_3$ , SiC, TiC,  $Ti_3SiC_2$  and Ag/Cu are 2.7, 4.3, 7.4, 8.5 - 11.4 and  $21/18 \times 10^{-6}/^\circ C$  respectively [22]. In case of sample brazed at 900 °C, the presence of  $Ti_5Si_3$  between SiC/TiC and the residual filler alloy (Ag/Cu) resulted in higher shear strength. This is because a layer having lower CTE ( $Ti_5Si_3$ ) acts as a buffer layer or thermal shock absorbing layer to reduce stresses. Whereas the samples brazed at 950 and 1000 °C showed low shear strength owing to the formation of  $Ti_3SiC_2$  phase having higher CTE than  $Ti_5Si_3$ . There would be two opposite effects while the applied load over the brazed assemble is changed, that is, (i) change in amount of residual filler alloy and (ii) amount of reaction products formation at the interface. For example, at 900 °C under 1.962N load, some part of filler alloy will be squeezed out – causing reduced residual filler alloy; whereas due to better contact between the filler alloy and substrate there is possibility of formation of more reaction products than the sample brazed under 0.981N load at the same temperature. Similarly, under the same load, increasing the brazing temperature would result in (i) more amount of reaction products and (ii) formation of detrimental reaction product ( in this case  $Ti_3SiC_2$ ). Therefore, to achieve best possible joint strength one has to look into these factors – and in the present study 900 °C under 1.962N load was found to be the best brazing condition.

For the specimen brazed at 850 °C, although the filler alloy did not melt properly, it was only for higher load (i.e. 1.962N) there was better contact, which resulted in some diffusion of the filler alloy to form the joint; and the joint strength was found to be 18MPa (Fig.4); in case of 0.981N load there was no joining at 850 °C.

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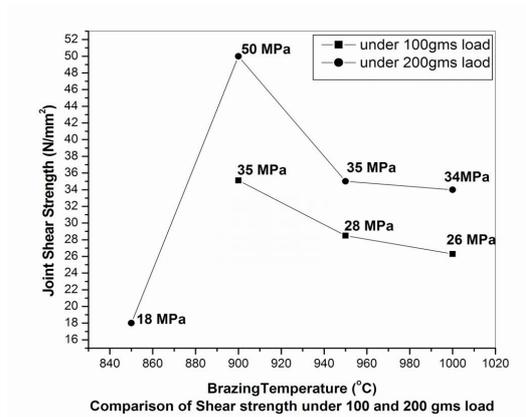


FIG.4. Comparison of shear strengths of the samples brazed at 850, 900, 950 and 1000 °C under 0.981N and 1.962N.

In the present study, for the specimen brazed at 900 °C the joint strength is found to be 50MPa, this is due to better diffusion of the filler alloy at higher temperature. Similar observation, ie. the effect of brazing temperature was reported by Yeh et al. [24]. However, for the specimens brazed at 950 and 1000 °C under 1.962N, even though the diffusion at the interfaces was more, a part of the molten filler alloy squeezed out. Thus the amount of overall Ti responsible for the formation of reaction products reduced. Thus the shear strength was found to be 35 and 34MPa for the specimens brazed at 950 and 1000 °C respectively (TABLE. I).

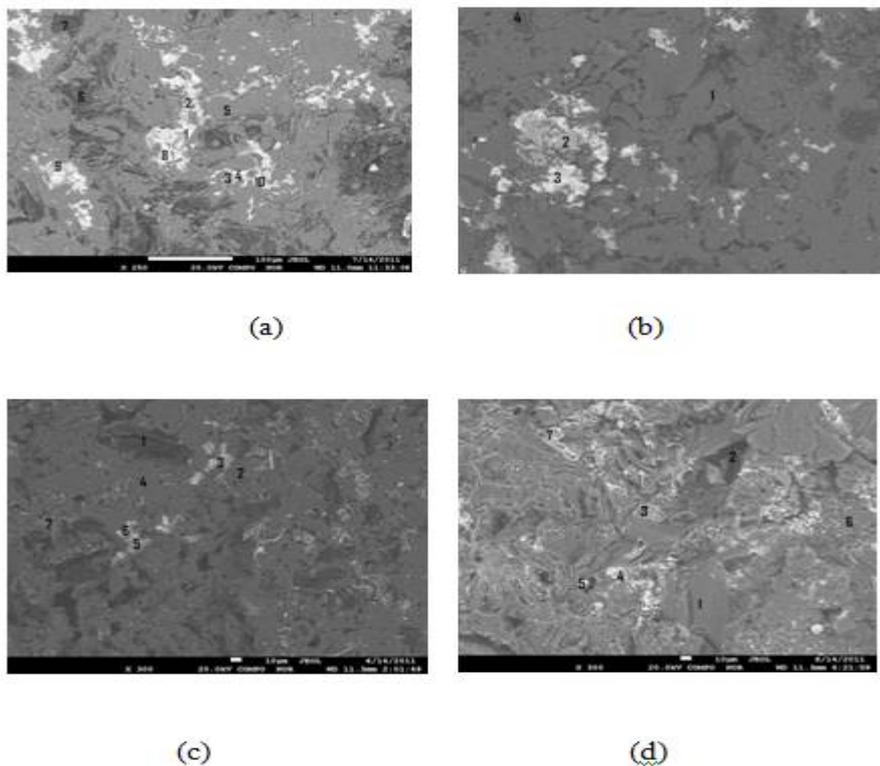


FIG.5. SEM images of fracture surfaces of (a) 850, (b) 900, (c) 950 and (d) 1000 °C

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**TABLE.I.** Variation of shear strength with brazing temperature.

Load applied (g)	Brazing temperature	Shear strength (MPa)	Remarks
1.692N	850 °	C 18	(i) the filler alloys only Softened but not Melted, very little Diffusion under the Influence of load. (ii) Formation of brittle <u>TiC</u>
1.692N	900 °C	50	(i) Due to the increased Load, greater amount Of diffusion occurred. (ii) Presence of $Ti_5Si_3$ - Very good joint Strength
1.692N	950 °C	35	(i) Formation of $Ti_3SiC_2$ starts; (ii) Under load during Heating part of molten filler alloy squeezed out.
1.692N	1000 °C	34	(i) More amount of $Ti_3SiC_2$ . (ii) molten filler alloy squeezed out.

Fractured surfaces were characterized by SEM-EDS analysis (Fig.5 (a)-(d)). In case of specimen brazed at 850 °C under 1.962N load, both EDS point and overall map (not shown) analyses suggest that there could be only TiC formation which provided weak bond strength (i.e. 18MPa). Apart from SiC there could be  $Ti_5Si_3$  as well as TiC at the fractured surface of the specimen brazed at 900 °C. While the specimens brazed at 950 and 1000 °C showed highly brittle fracture, which might be due to the presence of TiC and  $Ti_3SiC_2$  phases. These phases were identified considering both XRD and EDS analyses.

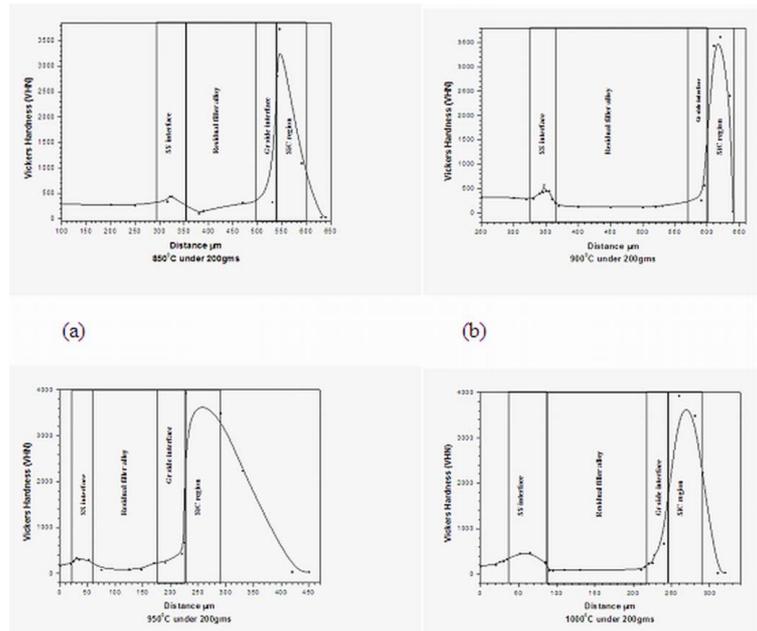


FIG.6. Micro hardness profiles for (a) 850, (b) 900, (c) 950 and (d) 1000 °C.

Micro hardness test was conducted on the brazed joint specimens starting from 304 SS to graphite passing through the interfaces and also the residual filler alloy. As the hardness of SS, interfaces, residual filler alloy, SiC and graphite varied widely, the applied load was changed for measurable indents. A load of 50g on SS and filler alloy, 0.981N on SiC region and 25g on the graphite was applied to make the indents. Micro hardness analysis (Fig.6) along the interfaces reveals that the SS interface (330-530VHN) is harder than SS substrate (260VHN). Similarly at the graphite side, the interface (570-730VHN) exhibits more hardness than the graphite substrate (37-48VHN). Due the presence of harder TiC,  $Ti_5Si_3$  and  $Ti_3SiC_2$  phases, the filler alloy near the SiC interface was harder than that near the SS interface. Considering the measured micro hardness, it is clear that apart from lower strength of graphite, due to presence of different brittle and hard phases at the graphite side interface the fracture should occur at the graphite side, which is observed while shear tests were carried out.

#### IV. CONCLUSION

Using Ag-Cu-Ti filler alloy for joining 304 SS and SiC coated graphite, it has been observed that not only the brazing temperature but also the applied load over the braze assemble is responsible for the variation of joint strength. There are two competitive factors for load variation, and two factors for temperature variations have been noticed. Considering these effects, an optimum condition, i.e. 900 °C under 1.962N load has been identified for brazing the above system. The fracture for all the samples occurred at the graphite side due to the presence of brittle phases like TiC,  $Ti_3SiC_2$  and also SiC. Presence of  $Ti_5Si_3$  having low CTE caused better joint strength for the sample brazed at 900 °C.

#### REFERENCES

- [1] Li Yingquan, Zhang Zhengde, Den Chaoquan and Su Yusheng, Investigation of [Brazing Structure of Bulk Graphite to a W-Re Substrate](#), Mat. Characterisation, 44 (2000), p.425- 429.
- [2]R. Staffler, Kneringer. E. Kny, N. Reheis, [Metal/graphite-composites in fusion engineering](#), IEEE Thirteenth Symp. on Fusion Engg., 2(1989), p. 955-958.
- [3] E. Fitzer, The Future of Carbon/Carbon Composites, Carbon, 25(20) (1987), p. 163-190.
- [4] F. Delannay, L. Froyen and A. Deruyttere, The wetting of solids by molten metals and its relation to the preparation of metal matrix composites, *J. of Mat. Sc.* 22(1987) p.1-16.

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- [5] P.B. Abel, A.L. Korenyi-Both, F.S. Honey, and S.V. Pepper, Study of copper on graphite with titanium or chromium bond layer, *J. of Mat. Res.* 9 (1994) p. 617-624.
- [6] J. W. Park, P. F. Mendez, T. W. Eager, [Strain Energy Release in Ceramic-to-Metal Joints by Ductile Metal Interlayers](#), *Scripta Materialia* 53 (2005)p. 857.
- [7] G. J. Qiao, C. G. Zhang, Z. H. Jin, Thermal Cyclic Test of Alumina/Kovar Joint Brazed by Ni-Ti Active Filler, *Ceramics International* 29 (2003) p. 7-11.
- [8] A. K. Jadoon, B. Ralph, P. R. Hornsby, [Metal to ceramic joining via a metallic interlayer bonding technique](#), *J. of Mat. Processing Tech.* 152 (2004) p. 257.
- [9] W. Tillmann, E. Lugscheider, R. Xu, J. E. Indacochea, Kinetic and microstructural aspects of the reaction layer at ceramic/metal braze joints, *J. of Mat. Sc.* 31 (1996) p. 445.
- [10] J. Y. Kim, J. S. Hardy, K. S. Weil, Novel Metal-Ceramic Joining for Planar SOFCs, *J. of the Electrochem. Soc.* 152 (6) (2005) p. J52 –J58.
- [11] K. S. Weil, J. Y. Kim, J. S. Hardy, Reactive Air. Brazing: A novel Method of Sealing SOFCs and Other, *Electrochem. and Solid State Letters* 8 (2) (2005) p. A316.
- [12] Chen Ji Chun, Hao Chuan Yong and Zhang Jin Song, [Interfacial microstructure and mechanical strength of ferritic stainless steel and silicated graphite joints bonded with Cu/Ni composite interlayers](#), *Scripta Materialia* 54 (2006) p. 553– 557.
- [13] D.A. Mortimer, M. Nicholas, The Wetting of Carbon by Copper and Copper Alloys, *J. of Mat. Sc.* 8 (2004) p. 640-648.
- [14] Arroyave R, Eager T. W, [Metal Substrate Effects on the Thermochemistry of Active Brazing Interfaces](#), *Acta Mater.* 51 (2003) p. 4871-4880.
- [15] Naka M, Tsuyoshi M, Okamoto I, Ti-precoating Effect on Wetting and Joining of Cu to SiC, *ISIJ International* 30 (1990) p. 1108-1113.
- [16] Sudipta Mandal, Ph.D Thesis, Jadavpur University, Kolkata, India, 2004.
- [17] A. Kar, A. K. Ray, Characterization of Al<sub>2</sub>O<sub>3</sub>-304 stainless steel braze joint interface, *Mater. Lett.* 61(2007) p. 2982-2985.
- [18] J. Krautkramer and H. Krautkramer, *Ultrasonic Testing of Materials*, 4<sup>th</sup> ed. Springer, Germany, (1993) p. 467.
- [19] M. Brochu, M.D. Pugh, R. A. L. Drew, Joining silicon nitride ceramic using a composite powder as active brazing alloy, *Mater. Sc. and Engg. A* 374 (2004) p. 34.
- [20] J. Beraes, A. Polar, J. E. Indacochea, Proceedings of the 3<sup>rd</sup> International Brazing and Soldering Conference, San Antonio, Texas, 24-26 April, (2006) p. 125.
- [21] Ajoy K. Ray, Abhijit Kar, S. A. Kori, L.C. Pathak, A. N. Sonnad, Graphite to 304SS braze joining by active metal brazing technique - Improvement of mechanical properties, *JMEP* (Manuscript submitted and accepted for publication).
- [22] Abhijit Kar, Studies on interfacial characterization of ceramic-ceramic/metal brazed joints, Ph.D. thesis, Jadavpur University, Kolkata, India (2004).
- [23] Abhijit Kar, Mainak Ghosh, Ashok Kumar Ray and Ajoy Kumar Ray, Effect of interfacial thickness and residual stress on the mechanical property of the alumina-stainless steel braze joint interface, *Mater. Sci. Engg. A* 498 (2008) p. 283-288.
- [24] [M. S. Yeh](#) and [T. H. Chuang](#), Effects of applied pressure on the brazing of superplastic INCONEL 718 super alloy, [Met. and Mat. Trans. A](#) 28,1367-1376.