DEVELOPMENT AND CHARACTERIZATION OF Ag-Cu-Ti ALLOYS FOR CERAMIC BRAZING

Sudipta Mondal, L. C. Pathak, K. Venkateswarlu, S. K. Das and Ajoy Kumar Ray
National Metallurgical Laboratory, Jamshedpur 831 007, India

ABSTRACT

In the present investigation, silver and copper base alloys with varying compositions of Ag:Cu = 72:28, 60:40, 50:50 and 30:70 (by wt%) are prepared. In each set, 1, 2 and 3wt% of active filler element, i.e. titanium is incorporated by powder metallurgical route. The samples are characterised by XRD, DTA-TGA, SEM and EDX. The XRD results show that titanium and its related phases are not present due to the lower concentration of Ti in these samples. Energy dispersive X-ray analyses reveal that most of the titanium is present in the copper rich phase and very little in the silver rich phase. The rolled brazing alloys are used for joining the alumina to alumina, that showed excellent joining characteristics.

Key Words : Brazing, Active filler alloy, Ceramics, EDX and Phase analysis.

INTRODUCTION

Ceramics find their applications in electronic, aerospace, nuclear, automotive industries, batteries, integrated circuits, cutting-tools and biomaterials due to their excellent strength, wear, heat and corrosion resistances at elevated-temperatures [1]. In recent years, the requirements of joining graphite to itself and to the common structural metals have significantly increased because of the excellent properties of graphite, such as resistance to thermal shock, corrosion resistance, electrical or thermal conductivity.

With the development of new ceramic materials, including those for structural application, there is an increasing demand for joining of ceramic components to metal/ ceramic. Ceramic-to-metal/ ceramic joints have an important role in industries, where, the components made from monolithic or composites. In order to exploit these potential materials, strong and reliable joining methods and technologies are in demand. Besides, the joining of ceramic to themselves, the question of joining the ceramic to metals is of particular interest for various important applications where the joint components will behave as functionally gradient material [2].

Soldering or brazing represents as one of the several methods for joining of solid materials. These two methods can produce smooth and rounded fillets at the periphery of the joints. It involves the use of a non-ferrous filler alloy with liquidus temperature exceeding 450^0C but lower than the melting points of the components to be joined. Bulk of the brazing alloys, which are widely used in electrical and electronics industries are based on nickel, copper and silver based alloys. The silver brazing alloys of the AWS (American Welding Society) BAg (Brazing Silver) classification are best suited as filler metals for joining of iron, copper, nickel and silver-based alloys [3-5]. Most of those industrial silver brazing alloys are derived from the Ag-Cu system, either as Ag-Cu eutectic alloy or in combination with other elements.

However, Ag-Cu eutectic alloys are not suitable for joining of ceramic to metal or ceramic to ceramic, because they do not wet the ceramic surfaces easily. In the present investigation, an attempt has been made to modify the Ag-Cu brazing alloy to join ceramic to metal or ceramic to ceramic components. One of the basic problems in brazing ceramics lies their poor wetting by conventional brazing alloys. The wetting of ceramic surfaces by liquid metals has long been the subject of study and it is well known that in many systems the wetting process depends on the chemical reaction occurring at the solid/liquid interface [6]. The widely used method of joining ceramic to metal is the multi-step moly-manganese process (Fig.1), where a moly/manganese coating is applied on the ceramic surface to induce wetting properties and the assembly is joined by brazing [7,8]. This process is time consuming and expensive [7,9]. Also, complex bonding methods tend to be somewhat troublesome where the nature of the work changes frequently. The pre-metallizing feature is also undesirable for many nuclear reactor applications, since the commonly used intermediate metals such as manganese, exhibit poor corrosion and oxidation resistance to many of the reactor environment.

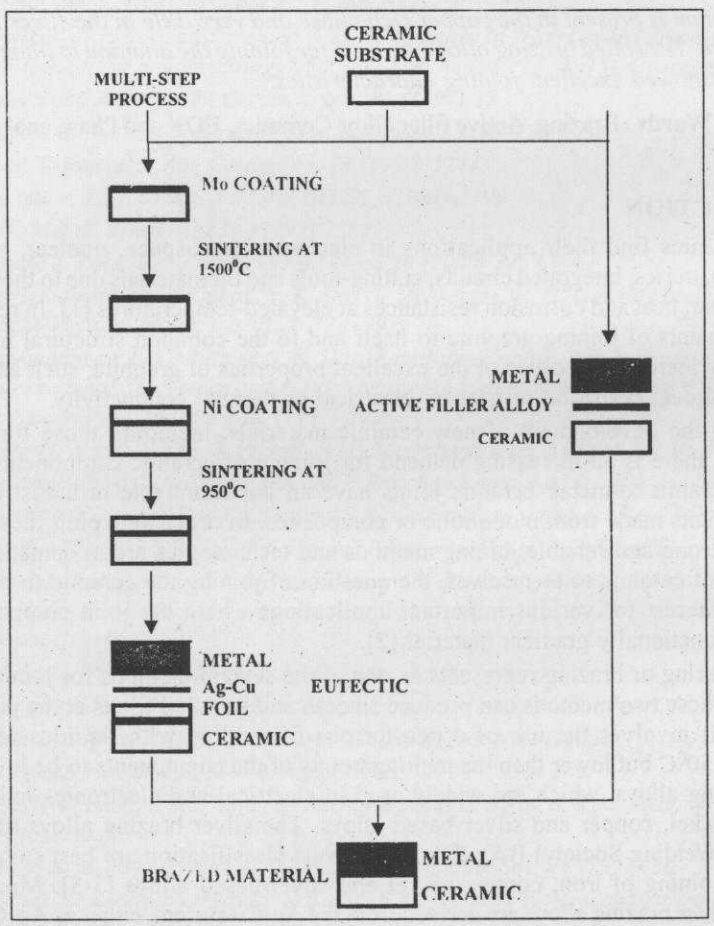

Fig. 1 : Methods of ceramic to metal joining

Ag-Cu eutectic type filler metals containing one or more strong carbide forming reactive elements, such as Ti, Zr, Be,Ta etc. have been developed for joining graphite to itself [10]. Ceramic is joined directly to metal with an active brazing alloy by one-step process (Fig. 1). This process is simple, less sensitive to process variable and inexpensive than the moly-manganese process [9]. The active filler alloy for direct joining contain reactive additive elements such as Ti, Zr, Be, Ta etc., that enable the surface of the ceramic to be wetted during brazing, which is the primary criteria for a good joint [11-13]. In this paper an attempt has been made to incorporate various amount (1–3wt.%) of titanium as reactive element in silver-copper based alloys with different composition of 72Ag28Cu, 50Ag-50Cu and 30Ag-70Cu. The samples were characterized using SEM, EDX and XRD.

EXPERIMENTAL DETAILS

Silver (99.99%) and copper (electrolytic, 99.9% purity), were taken for the base alloy (Ag-Cu) preparation. In this process the alloys were prepared by melting the metals in a graphite crucible with borax as flux in a programmable temperature controlled pit type resistance-heating furnace. The melt was held for a period of 15 minutes for homogenization. Subsequently, the melts were cast in graphite moulds. The base alloy was re-melted in a graphite crucible at temperatures at least 50^0C above the melting point of the particular alloy. The solidified samples were divided into four parts to which Ti (1–3wt.%) was added [14]. The above-mentioned alloys were polished with 0.5mm diamond paste. SEM (JEOL JSM 840A, Japan) and EDX analyses of the samples were carried out in for the microstructure and compositional analysis. XRD (Scifert, PTS 3003, Germany) analysis were carried out (2q from 20 to 80^0 with Co Ka radiation at the speed of 2^0/min) to identify the phases present at the interface of brazed joint samples. Image analysis of the base alloys and as well as the alloy containing Ti were carried out in an optical microscope attached with an Image Analyser, (Metal Power, India). Quantitative and X-ray dot mapping of aluminum, titanium silver and copper were carried out with the help of Electron Probe Micro Analysis (EPMA),JEOL JXA - 8600M, Japan. A hot stage optical microscope (Leitz, Germany), was used to measure the melting point of each base alloy.

RESULTS AND DISCUSSION

The melting point measurements of the base alloys by Leitz Heating microscope are in agreement with the same as obtained from Ag-Cu phase diagram. The measured melting point of 72Ag28Cu, 60Ag40Cu, 50Ag50Cu and 30Ag70Cu alloys is 780, 820, 870 and 950^0C respectively. The accuracy of the measurement was $\pm 2^0$C in all the cases. In these alloys, Ti addition temperatures were kept at about 50^0C above the respective base alloys to get homogenous composition. EPMA dot mappings of the alloys show the uniform distribution of titanium in the alloy (Fig. 2). Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) analysis show that in case of 72Ag-28Cu series the observed amount of titanium is lower than that of it was added in the base alloy, e.g. 0.5, 0.6 and 0.5 titanium are found when 1, 2 and 3%titanium is added respectively (Fig.3). Titanium has much higher solubility in copper than in silver. The solubility limit of titanium in copper at 1150^0C is 67%, whereas it is only 3% in silver at the same temperature [15]. Therefore, in case of 72Ag28Cu it is difficult to incorporate more titanium.

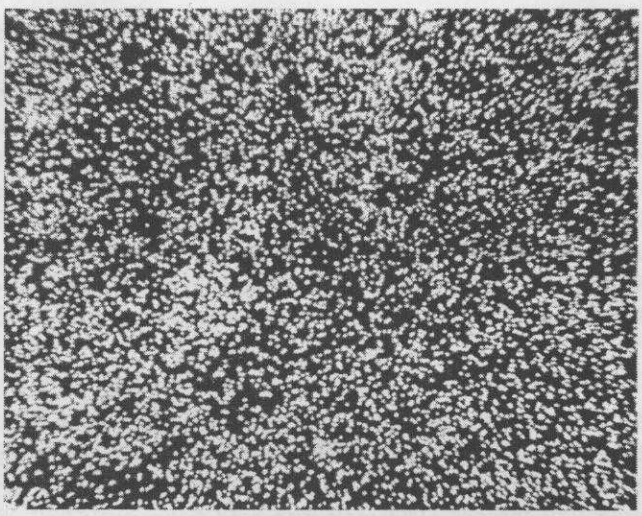

Fig. 2 : EPMA Ti dot mapping of (72Ag28Cu)3Ti, x400

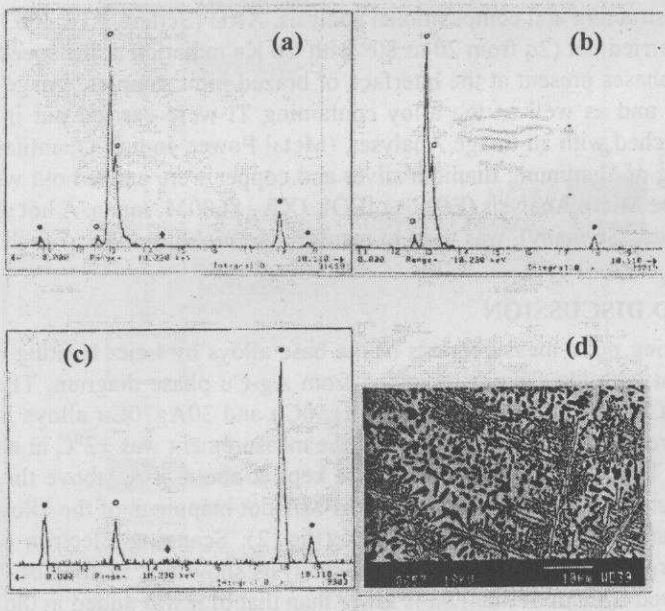

Fig.3 : EDX analyses of (72Ag28Cu)2Ti alloy, o – Ag, - Cu and - Ti. (a) average, (b) at the silver rich bright phase (c) at the copper rich dark phase and (d) back scattered SEM image.

It was further observed that in case of 30Ag-70Cu base alloy, even though the Cu is high in percentage, the amount of titanium was found lower in the alloy than it was added (Table 1). During addition of titanium in the 30:70 base alloy (m.p. 950^{0}C) for proper mixing of titanium and proper casting, the temperature was kept ~1000^{0}C. The titanium metal under goes a phase transition at 882^{0}C from hcp to bcc. In general, metal having bcc crystal structure is more reactive than hcp. Therefore, in case of 30:70 base alloy titanium at 1000^{0}C is highly reactive towards carbon of the crucible. Hence, in this alloy titanium was found low. In case of 50Ag-50Cu base alloy the amount of Cu rich phase was enough to dissolve 3% titanium and the temperature during addition of titanium (~920^{0}C) was not much higher than the phase transition temperature of titanium.

Table 1 : EDX analysis of Ag-Cu-Ti alloys

Wt.% (as added)	Wt.% (obtained)		
	Average	Bright Phase	Dark Phase
(30Ag70Cu)	25Ag75Cu	65Ag35Cu	7Ag93Cu
(30 Ag70Cu)1Ti*	24Ag75.1Cu0.9Ti	89.5Ag10.3Cu0.2Ti	7.7Ag91.0Cu1.3Ti
(30 Ag70Cu)2Ti	24.0Ag74.1Cu1.9Ti	89.1Ag10.4Cu0.5Ti	7.7Ag89.9Cu2.4Ti
(30 Ag70Cu)3Ti	25.8Ag73.7Cu0.5Ti	87.7Ag12.1Cu0.3Ti	8.3Ag89.4Cu2.3Ti
(50 Ag50Cu)	54.4Ag45.6Cu	72.5Ag27.5Cu	8.7Ag91.3Cu
(50 Ag50Cu)1Ti	55.9Ag43.4Cu0.7Ti	85.6Ag14.1Cu0.3Ti	40.6Ag58.3Cu1.1Ti
(50 Ag50Cu)2Ti	52.9Ag45.2Cu1.9Ti	88.7Ag10.8Cu0.5Ti	7.8Ag87.7Cu4.5Ti
(50 Ag50Cu)3Ti	44.0Ag52.9Cu3.0Ti	89.6Ag10.1Cu0.3Ti	8.3Ag84.9Cu6.8Ti
(72 Ag28Cu)	72.6Ag27.4Cu	72.0Ag28.0Cu	18.5Ag81.5Cu
(72 Ag28Cu)1Ti	72.5Ag27.0Cu0.5Ti	69.9Ag29.8Cu0.4Ti	33.1Ag66.1Cu0.8Ti
(72 Ag28Cu)2Ti	74.2Ag25.2Cu0.6Ti	90.7Ag9.1Cu0.3Ti	15.7Ag83.3Cu1.0Ti
(72 Ag28Cu)3Ti	73.7Ag25.8Cu0.5Ti	90.3Ag9.5Cu0.2Ti	15.9Ag83.0Cu1.1Ti

*1% Ti was added in 99% (30Ag70Cu)

Irrespective of amount of Ag and Cu present in the base alloys, two types of phases having different contrasts are observed during SEM studies. The SEM-EDX analysis of the alloys also reveals that most of the titanium is associated with copper rich dark phase (Fig.4).

Very little titanium was found in the silver rich bright phase of alloys containing Ti (Fig. 5). On an average, irrespective of composition (with or without Ti, the ratio of Ag and Cu in the dark phase was found to vary between 1:5 to 1:13 (by weight). Whereas in the sample without Ti, the bright phase the ratio varies in between 2:1 to 2.7:1, but in the samples containing Ti, the same ratio varies from 7:1 to 10:1. Again, in the bright phase the Ag:Ti ratio is not more than 1:0.005. This is due to the formation of some intermetallic phases in the Cu-Ti system, e.g. Cu_3Ti. In some higher concentration of Ti added sample (10 wt.%), Cu_3Ti phase formation has been confirmed from the XRD analysis (Fig. 4). Image Analysis of the alloys, with and without Ti are in agreement with the results obtained from EDX analysis. These analyses were carried out from the backscattered compositional images of SEM.

As the alloys are more or less homogeneous, the area fractions obtained by image analysis were assumed to be same as the volume fractions. Even in the case of 3 wt.% titanium alloys it is very difficult to identify the presence of titanium either in free state or as compound / intermetallics by XRD (Fig. 4).

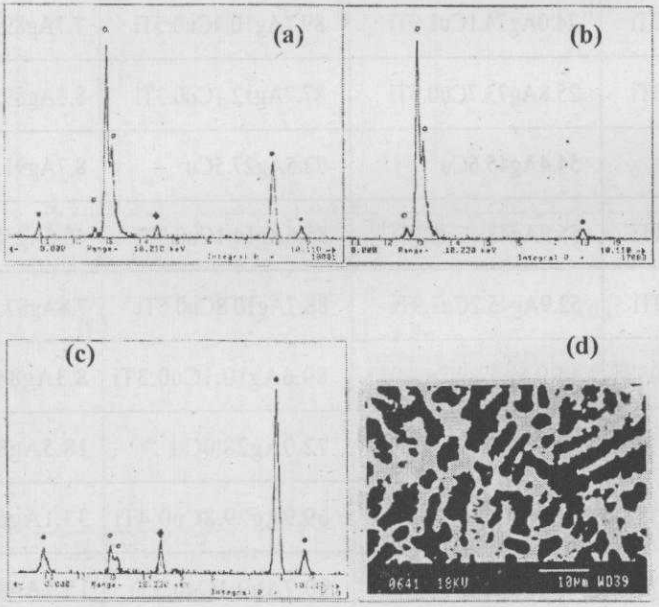

Fig.4 : EDX analyses of (50Ag50Cu)2Ti alloy, o – Ag, · - Cu and ¨- Ti. (a) average, (b) at the silver rich bright phase (c) at the copper rich dark phase and (d) back scattered SEM image.

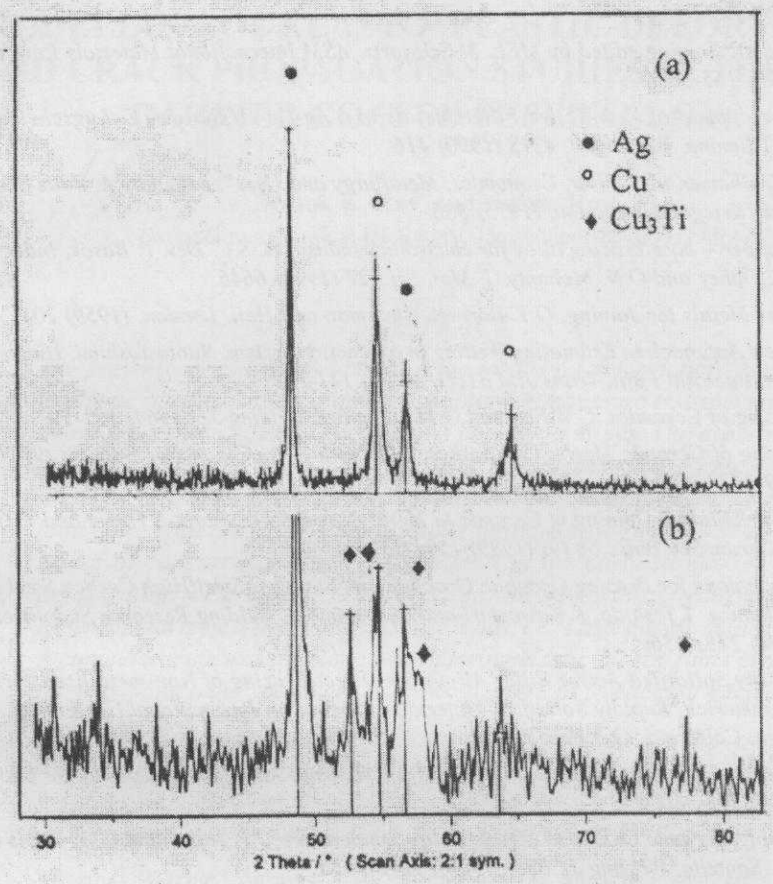

Fig.5 : X-ray diffraction of (a) 50Ag50Cu)2Ti and (b) (50Ag50Cu)10Ti brazing alloys

CONCLUSIONS

An attempt has been made to prepare Ag-Cu-Ti brazing alloys. It has been observed that Ti has higher affinity towards Cu. For example, irrespective of the composition of base alloys (Ag-Cu), the approximate ratio of Ag : Ti in the Ag rich bright phase is only 1 : 0.005. Rest of the Ti remains with Cu rich dark phase. The ratio of Ag and Cu in the bright phase is in between 2 : 1 to 2.7 : 1 in the alloys without Ti (only the base alloys), whereas it is 7 : 1 to 10 : 1 when Ti is present in the alloys. Again the same ratio in the dark phase is in between 1 : 5 to 1 : 13 by weight.

It has also been observed that it is difficult to incorporate Ti in the high Ag (72%) base alloys. Again when the percentage of Ag is low (i.e. 30%) the melting point of the alloys is well above the hcp to bcc transition temperature (882^{0}C) of Ti, as a result during Ag-Cu-Ti alloy preparation some of the Ti reacts with carbon of the melting crucible. Whereas can easily be incorporated in 50Ag50Cu base alloy.

REFERENCES

[1] Ceramic Joining edited by MEL. M.Schwartz, ASM International Materials Park Ohio (1990) 165-168.

[2] Development of New Active Filler Metals in a Ag-Cu-Hf System, E. Lugscheider and W. Tillmann, Welding J., 421S (1990) 416.

[3] E. S. Chamer, in " Silver, Economics, Metallurgy and Uses", edited by A. Butts and C. D. Coxe (Krieger, Hintington, (1975) 386.

[4] A copper – base brazing alloy for electronics industries, S.C. Dev, P. Basak, Inder Singh, R.K. Dubey and O.N. Mohanty, J. Mat. Sci., 27 (1992) 6646.

[5] Filler Metals for Joining, O.T. Barnett, Chapman and Hall, London, (1959) 205.

[6] A New Approach to Estimating Wetting in a Reaction system, Naoto Yoshimi, Hideo Nakae and Hidetoshi Fujii, Trans JIM 31(2), (1990) 141-147.

[7] Brazing of Ceramics, C.W.Fox and G.M.Slaughter, Welding J., (1964) 591-597.

[8] Joining of Ceramic Matrix Composites, J.D.Cawley, Am.Ceram.Soc.Bull, 68 (9) (1989) 1619-1623.

[9] High- Reliablity Joining of Ceramic to Metal, Howard Mizuhara, E.Hubel and T. Oyama, Am.Ceram.Soc.Bull., 68 (9) (1989) 1591-1599.

[10] A Technique for Brazing Graphite/Graphite and Stainless Steel/High Carbon Steel Joints, H.Ohmura, T.Yoshida, K.Kawashiri and O.Yoshimoto, Welding Research Suppliment, (1994) 249s-256s.

[11] Rapidly Solidified Active Filler Alloys for Direct Brazing of Non-metallized ceramics, K. Emmerich, Rapidly Solidified Materials- Proc. of an International Conference, San Diego, Calfornia, (3-5 Feb. 1986).

[12] Joining of Ceramics, R.E. Loehman and A.P. Tomsia, Am. Ceram. Bulletin, 67 (2), (1988) 375-380.

[13] Brazing Ceramic Oxides to Metals at low temperature, J.P. Hammond, S.A. Davis and M.L. Santella, Welding J., (Oct. 1998), 227S-232S.

[14] A. K. Ray, S. Mondal, K. Venkat applied for Patent

[15] Principles of Soldering and Brazing, Hunpston and Jacobson, March (1993) 167.