

## BRAZE AND CARBIDE INTERACTIONS

Ravi K. Enneti, Neal Myers, and Randall M. German  
Pennsylvania State University  
Center for Innovative Sintered Products  
P/M Lab, 147 Research West  
University Park, PA 16803

### ABSTRACT:

Brazing is popular method of joining carbides to steel structures. Wetting behavior of the braze alloy on the ceramic plays an important role in this process. Active brazing uses an active element like Ti, Zr, Cr etc. in the braze alloy to react with the ceramic and improve the wetting behavior of the braze alloy. In this paper preliminary results of wetting study of Ni based braze alloys, a Co based alloy and a Fe based alloy on different carbides is presented. 3wt% Ti is added to the braze alloys and the effect of Ti on the wetting behavior of the brazes is studied. Thermodynamic approach is used to analyze the wetting behavior and effect of Ti addition to the braze alloys.

### INTRODUCTION:

In recent years, due to the advancement of engineering technology, ceramics are finding extensive use in automotive, aerospace and electronic industrial applications (1,2). Due to the brittle nature of ceramics, their application as structural components with complex geometries is limited. Combinations of ceramics and metals can be used in such cases. One of the important applications of ceramic-metal joining is in the structures of moving parts that must withstand high stress and temperature gradients (3).

Brazing is uniquely suited and foremost method for fabrication of ceramic to metal joints and seals (4). For successful brazing of metals to ceramics, the braze must wet the workpiece, spreading over the surface and entering through the capillary gaps (5). The braze alloy must react and reach chemical equilibrium at the metal-ceramic interface. Metals generally are wetted by the braze alloys (6). Ceramics on the other hand, due to their high chemical stability and strong atomic bonding are not easily wetted by most of the conventional braze alloys (7).

Active brazing is a widely used process for joining ceramics to metals. In active brazing process an active metal such as Ti, Cr, Zr etc is used to react and improve the wettability of braze alloy

with the ceramic (8). Many researchers have studied the reactive brazing processes for different ceramic-metal joining (9-19).

In this paper the preliminary results about the wetting behavior of braze alloys on different carbides is presented. The affect of addition of 3 wt% Ti to the braze alloys on the wetting behavior is also studied. A thermodynamic approach to explain the stability and wettability of the carbides is presented

#### EXPERIMENTAL PROCEDURE:

Six different carbides, designated A-F, with particle sizes of 1-5 $\mu$ m were used in the present study. Braze alloys included two nickel based braze alloys; a nickel based hardfacing alloy, Co based hardfacing alloy; and an iron containing intermetallic. The particle distribution for the braze alloys is shown in Table I. Each braze was mixed with a binder and pressed at 15 TSI into a 6 mm x 6mm cylinder. Braze mixtures were also prepared with 3wt% admixed titanium. Each carbide was mixed with a binder and pressed at 20 TSI into a 12 mm square block.

Five sets of sintering experiments were performed to observe wetting behavior and interactions of braze alloys with carbides. Pressed braze alloy pieces were placed on the top of the pressed carbide pieces. The samples were sintered in 1-5 mTorr vacuum. The brazing temperatures for different braze alloys are shown in Table I. The samples were then metallographically prepared and examined under a Nikon Epiphot microscope. The penetration depth of the braze in the carbide was qualitatively observed from the metallography.

Table I.  
Particle size distributions of braze alloys.

<b>Sample Name</b>	<b>D<sub>10</sub> (<math>\mu</math>m)</b>	<b>D<sub>50</sub> (<math>\mu</math>m)</b>	<b>D<sub>90</sub> (<math>\mu</math>m)</b>	<b>Brazing temperature (<math>^{\circ}</math>C)</b>
Ni Braze A	8	18	34	1200
Ni Braze B	19	36	69	1030
Ni Hardface	17	26	41	1100
Co Hardface	12	21	42	1350
Fe Intermetallic	9	21	38	1263

## RESULTS AND DISCUSSION:

The ideal (standard) Gibbs free energy for the formation of carbides at different brazing temperatures is shown in Table II.

Table II.  
 $\Delta G^\circ$  values for the formation of carbides.

	$\Delta G^\circ$ (kJ/mole)				
Brazing temperature	1303 K (Ni24Cr10P)	1373 K (Deloro 50)	1473 K (AMS 4777)	1536 K (Fe <sub>2</sub> Al <sub>5</sub> )	1623 K (Stellite 694)
Carbide					
Carbide A	-35	-34	-34	-34	-34
Carbide B	-93	-93	-93	-93	-92
Carbide C	-169	-168	-167	-166	-164
Carbide D	-143	-144	-143	-144	-144
Carbide E	-59	-59	-60	-25	-27
Carbide F	-110	-111	-113	-114	-116

A chemical reaction resulting in a stable product will increase the wetting behavior of the braze on the carbide. Addition of Ti to the braze will result in Ti reacting with the carbide to form TiC thus improving the wettability of the braze.  $\Delta G^\circ$  values for the reaction will provide an indication about the feasibility of the reaction.  $\Delta G^\circ$  values for Ti reaction with different carbides is given in Table III.

Table III.  
 $\Delta G^\circ$  values for the Ti reaction with different carbides.

	$\Delta G^\circ$ (kJ/mole)				
Brazing temperature	1373 K Ni Braze A	1303 K Ni Braze B	1373 K Ni Hardface	1536 K Fe Intermetallic	1623 K Co Hardface
Carbide					
Carbide A	-134	-135	-134	-132	-130
Carbide B	-75	-76	-75	-73	-72
Carbide D	-25	-26	-25	-22	-21
Carbide E	-109	-111	-109	-141	-137
Carbide F	-57	-59	-57	-51	-48

As observed from Table III, the  $\Delta G^\circ$  values are negative for the reactions of Ti with the different carbides at the brazing temperatures indicating the feasibility of chemical reaction and thus improvement in the wetting behavior of the braze. It was not possible to measure a well-defined wetting angle for any of the braze/carbide system because the braze alloys infiltrated the carbides in most cases. All the brazed samples were analyzed by metallography. The microstructures were evaluated for the bonding integrity between the braze alloy and carbide and penetration depth of the braze alloy into the carbide.

### Ni based braze alloys:

Ni based braze alloys A and B and the Ni hardfacing alloy showed a similar kind of behavior. Except for carbides E and F all other carbides showed good bonding behavior. The penetration depth of the braze inside the carbide was found to relate with the stability of the carbide. Low stability carbides such as carbide A showed higher penetration of the braze whereas high stable carbides such as carbides B, C, and D showed a low penetration depth. There was an anomaly in the behavior with carbides E and F. E has lower stability than F but showed lower penetration than F. Some anomalies were observed in the case of Ni braze B. The braze showed a high penetration into carbide B, but did not even bond to carbide C. Further analysis is being carried out by using X-ray diffraction and energy dispersive X-ray spectroscopy techniques to understand these anomalies.

Addition of Ti showed little effect in the wetting behavior of the Ni alloys. This behavior can be explained by considering the solution enthalpy of Ti in liquid Ni. The solution enthalpy of Ti in liquid Fe, Co, Ni, is -82, -140, -170 kJ/mol respectively. Thus there is a higher tendency for Ti clustering in liquid Fe than in liquid Ni or Co (20). Due the high solubility of Ti in the liquid Ni, there will be less reaction between the Ti and the carbide and thus there will not be any increase in the wettability of the braze. Fig 1a-1d are some micrographs of the interfaces between various Ni based brazes and the carbides.

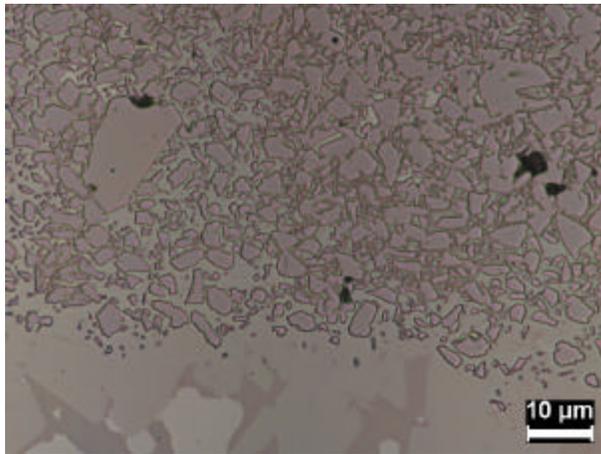


Fig 1a Interface between Ni braze B (bottom) and carbide B (top)

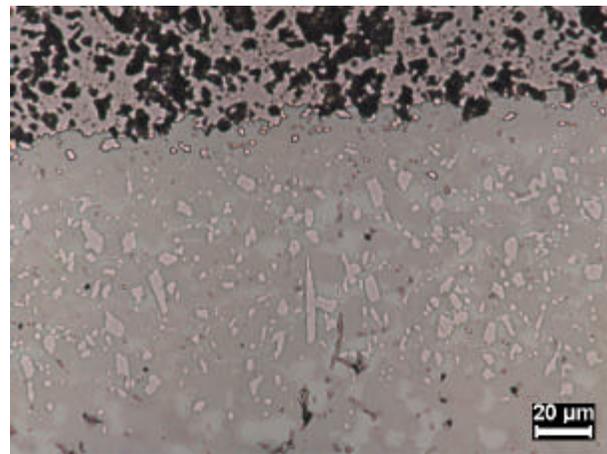


Fig 1b Interface between Ni braze B+3Wt%Ti (bottom) and carbide B (top)

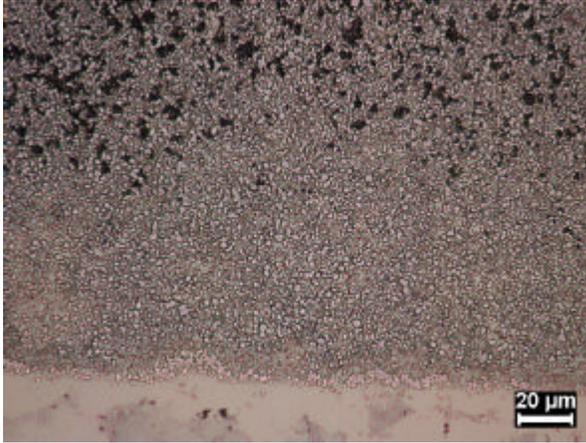


Fig 1c. Interface between Ni braze A (bottom) and carbide A (top)

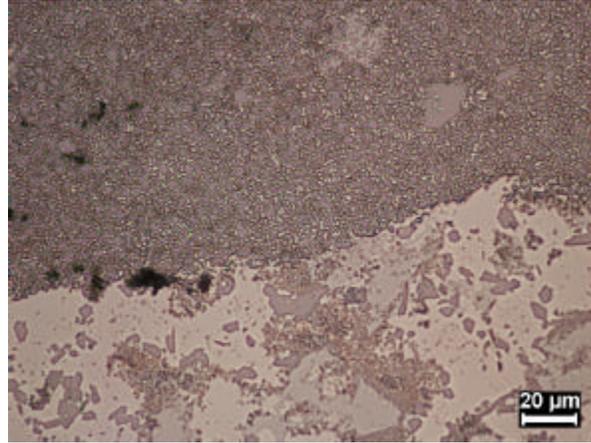


Fig 1d. Interface between Ni braze A +3wt%Ti (bottom) and carbide C (top)

### Co hardfacing alloy:

The Co hardfacing alloy showed fairly consistent results in bonding and penetration. With the exception of carbide F the braze bonded well with all carbides. There was no direct relation between the penetration depth and the stability of the carbides. Most of the carbides showed considerable amount of penetration. The good bonding and penetration of the braze is may be due to the high brazing temperature. Addition of Ti to braze did not have much effect on the wetting behavior. This may be due to the low solution enthalpy of Ti in liquid Co (20). Further analysis is in progress. Fig 2a and 2b show some micrographs of the interface between the Co hardfacing alloy and carbides.

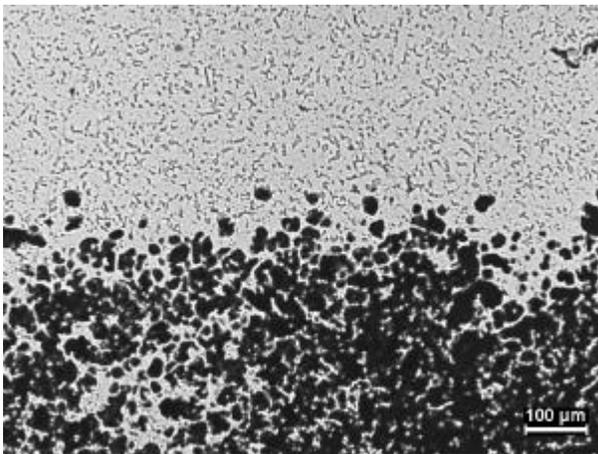


Fig 2a. Interface between Co hardface and carbide F

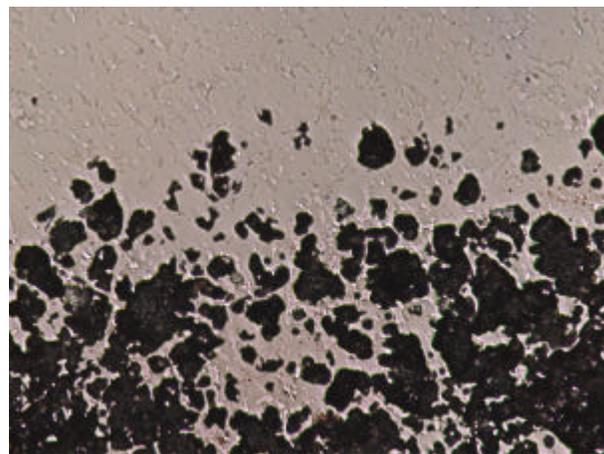


Fig 2b. Co hardface+3wt%Ti (center) and infiltrated carbide D (surrounding)

### Iron intermetallic alloy:

The iron intermetallic alloy showed no bonding to any of the carbides. The penetration depth of the braze alloy was also low. Addition of Ti had a great effect on the wetting behavior of the alloy. The intermetallic with 3wt% Ti bonded well with all the carbides except for carbide E. The improvement in the wetting and bonding behavior may be attributed to the high activity of Ti in liquid Fe (20). Due to the low solution enthalpy of Ti in liquid Fe, Ti reacts with the carbides and

improves the wetting behavior of the braze alloy. Fig 3a and 3b show the micrographs of the interface regions between the intermetallic and carbide D. It is clearly seen that addition of Ti to the intermetallic improves the wetting behavior on the carbide.

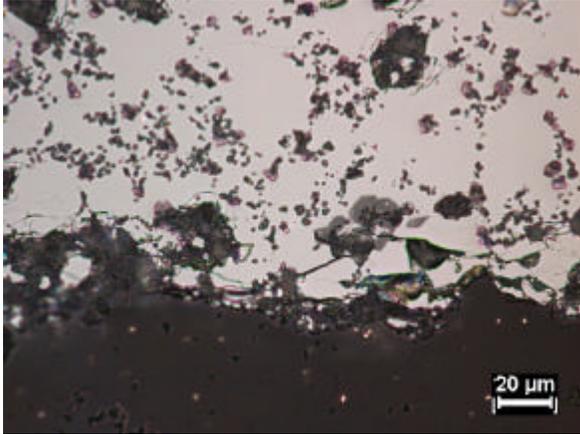


Fig 3a. Interface between Fe intermetallic (top) and uninfiltrated carbide D (bottom)

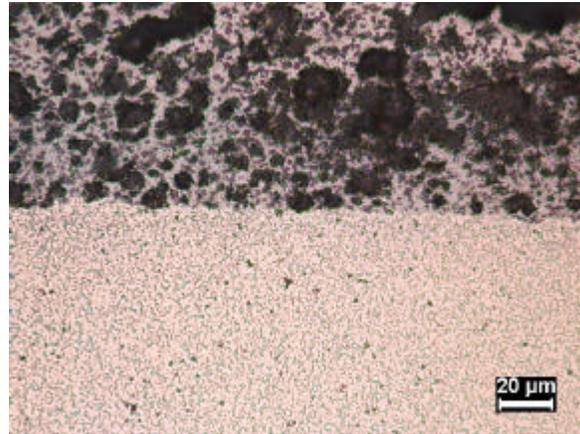


Fig 3b. Interface between Fe intermetallic +3wt%Ti (top) and infiltrated carbide D (bottom)

#### CONCLUSIONS:

Preliminary studies showed that the bonding and penetration behavior of Ni based brazed alloys were related to the stability of the carbides. Low stable carbides showed high penetration whereas high stable carbides showed low penetration of the braze alloy. Exception to this behavior was observed in carbides E and F. Ti addition to the Ni based and Co based braze alloys had a little effect on their wetting ability on the carbides. This may be due to the high solution enthalpy of Ti in liquid Ni and Co. Addition of Ti to the iron intermetallic had a great effect on the wetting and bonding behavior to various carbides. This may be attributed to low solution enthalpy of Ti in liquid Fe. Further analysis using X-ray diffraction and energy dispersive X-ray techniques are being carried out to attain a better understanding of the wetting behavior of brazes on various carbides.

#### REFERENCES:

1. R.XU and J.E.Indacochea, "Silicon nitride - stainless steel braze joining with an active filler metal", Journal of materials science, V 29, 23, Dec 1, 1994, pp. 6287 - 6294.
2. Y.H.Chai, W.P.Weng and T.H.Chuang, "Relationship between wettability and interfacial reaction for Sn10Ag4Ti on Al<sub>2</sub>O<sub>3</sub> and SiC Substrates", Ceramics International, V 34, 1998, pp. 273-279.
3. W.Tillmann, E.Lugscheider, R.Xu, J.E.Indacochea, "Kinetic and microstructural aspects of the reaction layer at ceramic / metal braze joints", Journal of Materials Science, V 31, 1996, pp. 445-452.
4. Mel M. Schwartz, Ceramic joining, ASM international, Materials park, Ohio, 1990, pp. 75-110
5. M.G.Nicholas, "Material aspects of ceramic-ceramic and ceramic-metal bonding", Advanced joining technologies, edited by T.H.North, Chapman and Hall, 1990, pp. 160-171.

6. Mel M. Schwartz, Ceramic joining, ASM international, Materials park, Ohio, 1990, pp. 17-37.
7. Chia-Chin Lin, Rui-Bin Chen, Ren-Kae Shiue, " A wettability study of Cu/Sn/Ti active braze alloys on alumina", Journal of materials science, Vol 36, 2001, pp 2145-2150.
8. R.M.do Nascimento, A.E.Martinelli, A.J.A.Buschinelli and A.N.Klein, " Brazing sintered materials", Materials science forum, vol 299-300, 1999, pp. 254-262.
9. Yasuhiro Morizono, Minoru Nishida and Akirachiba, " Joining of chromized carbon-steel and  $Si_3N_4$ ", Journal of ceramic society of Japan, Intl edition, Vol 101, pp. 1327-1332.
10. A.K.Chattopadhyay, H.E.Hintermann, " On brazing of cubic boron nitride abrasive crystal to steel substrate with alloys containing Cr or Ti", Journal of Materials science, V28, n21, Nov 1, 1993, pp.5887 - 5893.
11. R.XU and J.E.Indacochea," Reaction layer characterization of the braze joint of silicon nitride to stainless steel", Journal of materials engineering and performance, Vol 3(5), Oct 1994, pp. 596-605.
12. R.XU and J.E.Indacochea, "Silicon nitride - stainless steel braze joining with an active filler metal", *Journal of materials science*, V 29, 23, Dec 1, 1994, pp. 6287 - 6294.
13. W.Tillmann, E.Lugscheider, R.Xu, J.E.Indacochea, " Kinetic and microstructural aspects of the reaction layer at ceramic / metal braze joints", Journal of materials science, Vol 31, 1996, pp.445-452.
14. Huaping Xiong," Effect of metallurgical behavior at the interface between ceramic and interlayer on the  $Si_3N_4$  / 1.25Cr-0.5Mo steel joint strength", Journal of materials science technology, Vol 14, 1998, pp. 20-24
15. Abdulrahman Abed, Issam S jalham, Alan Hendry, " Wetting and reaction between  $\beta^1$ -sialon, stainless steel and Cu-Ag brazing alloy containing Ti," Journal of European ceramic society, V 21, 2001, pp. 283-290.
16. Y.C.Yoo, J.H.Kim, K.Park, " Microstructural characterization of  $Al_2O_3$  / AISI 8650 steel joint brazed with Ag-Cu-Sn-Zr alloy", Materials letters, Vol 42, March 2000, pp. 362-366.
17. Peter Batfalsky," Interfacial reaction during active brazing process on metal-ceramic (SiC) joints", Interfaces in new materials, edited by P.G. Range and B.Delmon, Elsevier applied science, London and Newyork, 1991, pp.229-238.
18. Rajendra U. Vaidya, Andrew H.Bartlett, Sameul D.Conzone and Darryl P.Butt, " Investigation into the joining of  $MoSi_2$  to 316L stainless steel",Ceramic joining, edited by Ivar E.Reimans, Charles H.Henager Jr., Antoni P.Tomsia, Ceramic transactions, American ceramic society, Ohio, Vol 77, pp 63-74.
19. Tae-woo Kim, Sang-Whan Park," Development of interlayer system for high strength ceramic / metal joint",Ceramic joining, edited by Ivar E.Reimans, Charles H.Henager Jr., Antoni P.Tomsia, Ceramic transactions, American ceramic society, Ohio, Vol 77, pp 177-184.
20. Huaping Xiong, Wei Mao, Yaoyong Cheng, Xiaohong Li, Wanlin Guo, " Effect of elements Cr and Ti in the newly-designed  $CoFeNi(Si, B)$ -Cr-Ti system brazing alloys on the wetting behavior of the alloys on  $Si_3N_4$ ", Journal of Materials Science Letters,20,2001,pp 1681-1684.