ELSEVIER

Materials Science and Engineering A 407 (2005) 154–160

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Diffusion bonding of commercially pure titanium to 304 stainless steel using copper interlayer

S. Kundu [a], M. Ghosh [b], A. Laik [c], K. Bhanumurthy [c], G.B. Kale [c], S. Chatterjee [a],*

[a] *Department of Metallurgy and Materials Engineering, Bengal Engineering and Science University, Shibpur, Howrah 711103, West Bengal, India*
[b] *Materials Science & Technology Division, National Metallurgical Laboratory, Jamshedpur 831007, India*
[c] *Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

Accepted 15 July 2005

Abstract

Diffusion bonding was carried out between commercially pure titanium (cpTi) and 304 stainless steel (304ss) using copper as interlayer in the temperature range of 850–950 °C for 1.5 h under 3 MPa load in vacuum. The microstructures of the transition joints were revealed in optical and scanning electron microscopy (SEM). The study exhibits the presence of different reaction layers in the diffusion zone and their chemical compositions were determined by energy dispersive spectroscopy. The occurrence of different intermetallic compounds such as $CuTi_2$, CuTi, Cu_3Ti_2, Cu_4Ti_3, FeTi, Fe_2Ti, Cr_2Ti, T_2 ($Ti_{40}Cu_{60-x}Fe_x$; $5 < x < 17$), T_3 ($Ti_{43}Cu_{57-x}Fe_x$; $21 < x < 24$) and T_5 ($Ti_{45}Cu_{55-x}Fe_x$; $4 < x < 5$) has been predicted from the ternary phase diagrams of Fe–Cu–Ti and Fe–Cr–Ti. These reaction products were confirmed by X-ray diffraction technique. The maximum bond strength of ∼318 MPa (∼99.7% of Ti) was obtained for the couple bonded at 900 °C due to better coalescence of mating surface. With the rise in joining temperature to 950 °C, decrease in bond strength occurs due to formation of brittle Fe–Ti bases intermetallics. At a lower joining temperature of 850 °C, bond strength is also lower due to incomplete coalescence of the mating surfaces.

Keywords: Diffusion bonding; Interlayer; Intermetallic compounds

---

1. Introduction

In recent years, the diffusion bonded components consisting of commercially pure titanium (cpTi) and 304 stainless steel (304ss) have several applications in chemical and nuclear industries [1–3]. Diffusion couple consisting of these two dissimilar materials suffers from poor mechanical properties due to the formation of brittle intermetallics in the diffusion zone and residual stress generation caused by mismatch in linear expansion coefficient [4].

Solid solubility of iron in titanium and vice-versa is limited at room temperature; the previous investigations by the present author depicts that, direct bonding between cpTi and 304ss promotes the formation of σ, χ, λ, FeTi, β-Ti and Fe_2Ti_4O phases in the reaction zone as during diffusion mass transfer occurs across the bond line [5,6]. All these brittle intermetallic compounds impair the mechanical properties of the transition joints; hence, the use of soft interlayer has come into limelight to eradicate the limitation and to improve the mechanical properties. In the previous attempt, nickel has been used as an intermediate material to produce the transition joints and the results indicate an improvement in bond strength (∼256 MPa) with respect to the direct bonding (∼217 MPa) due to lowering in volume fraction of Fe–Ti intermetallic compounds [2,7,8]. In this respect, copper can also be considered as a potential candidate to be used as interlayer to further improve the joint quality. Copper does not form any intermetallics with iron. Moreover, the melting point of the copper is lower with respect to Ti, Fe and Ni; so, increase in the flow-ability of the same at higher temperature (>$0.5T_m$, T_m melting point in K) will encourage a good contact between the faying surfaces. Though binary phase diagram of Cu–Ti indicates the occurrence of Cu_2Ti,

---

* Corresponding author.
E-mail address: schatterjee46@yahoo.com (S. Chatterjee).

0921-5093/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2005.07.010

Cu_3Ti_2, CuTi and $CuTi_2$ with increasing Cu content, however, improved contact area may have some beneficial effect on the bond strength of the diffusion-welded joints [9].

The present study reports diffusion bonding of commercially pure titanium and 304 stainless steel using copper as interlayer in the temperature range of 850–950 °C under uniaxial load. The investigation projects the influence of bonding temperature on the interface microstructure and tensile properties of the bonded assemblies.

2. Experimental

The cylindrical samples of cpTi and 304ss with the dimensions of 15 mm diameter and 30 mm length were used for diffusion couple preparation. The chemical compositions and room temperature tensile properties of the parent materials are given in Tables 1 and 2, respectively.

The mating surface of the cylinders were prepared by conventional grinding and polishing techniques by final polishing on 1 μm diamond paste. The copper foil (300 μm thick, 99.95% purity) was used as intermediate material and both the surfaces of the interlayer were polished in the same fashion. The faying surfaces were cleaned in acetone and dried in air. The cpTi–Cu–304ss assembly was kept in contact in a fixture and was inserted in a vacuum chamber. The diffusion bonding was carried out at 850, 900 and 950 °C for 1.5 h in vacuum. Uniaxial load of 3 MPa was applied along the longitudinal direction of the sample. Heating was done at a constant rate of 14 °C min^{-1} at the time of processing and after the operation the samples were allowed to cool in vacuum.

The diffusion bonding joints thus formed were cut longitudinally and prepared by usual techniques for metallographic observation. The titanium side was etched in an aqueous solution (88 ml H_2O) of 4 ml HF and 8 ml HNO_3. The stainless steel side was etched by a mixture of HNO_3 (10 ml), HCl (40 ml) and glycerol (50 ml). A solution containing $FeCl_3$ (5 g), HCl (2 ml) and ethanol (96 ml) was used for etching pure copper. The structural change owing to diffusion was observed in a light microscope (Correct SDME TR5). Polished samples were also examined in scanning electron microscope (JEOL JXA 840A) using back-scattered mode (SEM-BSE) to reveal the reaction layers near the diffusion-welded interface. The composition of the reaction layers was determined in atomic percent using energy dispersive spectroscope (Kevex). The presence of intermetallic phases in the reaction zone was confirmed by carrying out X-ray diffraction study (Philips PW 1840) on the fracture surfaces of the couples using a copper target. The scanning span of 30°–80° with a step size of 0.01° (=2θ) was used during the investigation. Evaluation of bond strength at room temperature was performed in tensile testing machine (Instron 4204) using sub-size specimens as per ASTM specification (Vol. 03.01 E8M-96) at a crosshead speed of 0.05 mm min^{-1}. The interlayer was at the center of the gauge length. Four samples were tested at each process parameter to check the reproducibility of the results.

Table 2
Tensile properties of the base metals at room temperature

Alloy	0.2% Proof stress (MPa)	Ultimate tensile strength (MPa)	Fracture elongation (%)
cpTi	205 ± 2	319 ± 3	23 ± 0.9
304ss	740 ± 4	822.5 ± 6	42 ± 2

3. Results and discussion

The optical microstructure of the bonded assemblies is shown in Fig. 1. It is observed that, certain amount of diffusion occurs between the interlayer and the two substrates. The stainless steel–copper bonding interface is planar in nature and a thin diffusion layer was revealed for all the assemblies. Ti–Cu interface is characterized by the presence of a lightly shaded reaction zone and the Widmanstatten α–β titanium structure. Atomic migration of copper (strong β-stabilizer element) in titanium lattice lowers the eutectoid transformation temperature of titanium and α–β phase aggregate forms by the decomposition of β-Ti during cooling [10,11]. In the temperature interval of 850–950 °C, copper and stainless steel both have close packed fcc structure hence, the extent of diffusion of these elements across the bond line is limited. On the contrary, below 882 °C, Ti has two-phase structure, i.e. α(hcp) + β(bcc) and above β-transus it transforms to beta. Owing to more open crystallography of bcc matrix, copper atoms can travel longer distance in titanium lattice than vice-versa [12].

The SEM-BSE images of the transition joints are given in Fig. 2. Both stainless steel–copper (ss–Cu) and copper–titanium (Cu–Ti) interfaces are resolved at higher magnification. The composition of the chemical species was determined near the two bond lines.

For the ss–Cu interface at 850 °C joining temperature (Fig. 2(a)), a deeply shaded reaction layer has been observed near the stainless steel side, which is enriched with Fe (∼65.8 at%) and Cr (∼28.8 at%) with a small quantity of Ti (∼2.7 at%), Ni (∼2.2 at%) and Cu (bal.); hence, the composition indicates the phase mixture of $\lambda + \chi$ [10–12]. Close to the

Table 1
Chemical compositions of the base metals (wt%)

Alloy	C	Fe	Ti	Mn	Si	S	P	Cr	Ni	O	N	H
cpTi	0.02	0.10	Balance	–	–	–	–	–	–	0.15	0.02	0.0011
304ss	0.06	Balance	–	1.38	0.37	0.013	0.03	18.15	8.50	–	0.005	–

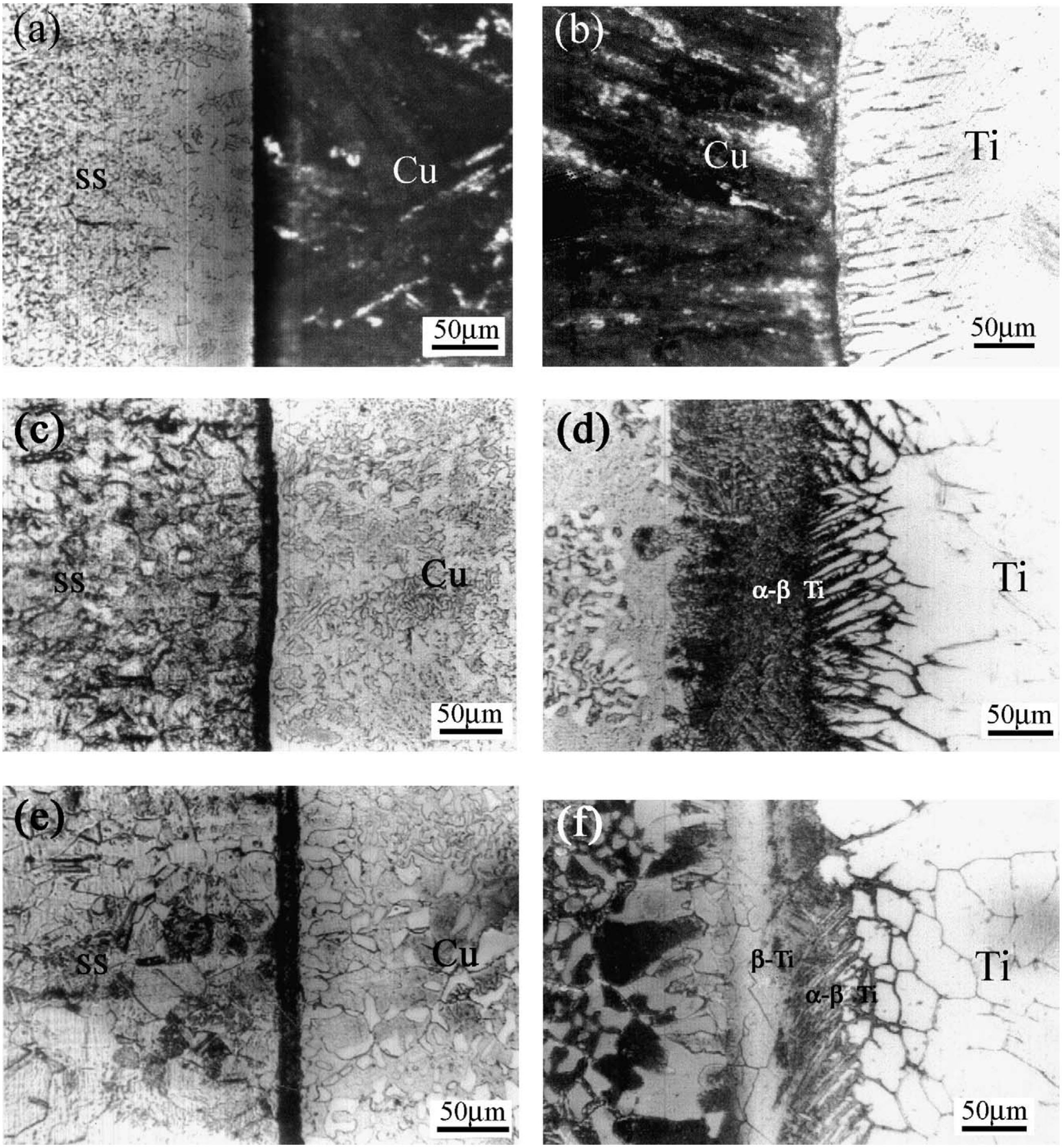

Fig. 1. Optical microstructure of the diffusion bonded assemblies joined at: (a) 850 °C, ss–Cu interface, (b) 850 °C, Cu–Ti interface, (c) 900 °C, ss–Cu interface, (d) 900 °C, Cu–Ti interface, (e) 950 °C, ss–Cu interface and (f) 950 °C, Cu–Ti interface.

$\lambda + \chi$ region, the thin bright region consists of Fe (~57.6 at%) and Ti (~20.11 at%) in association with Cr (~19.1 at%), Ni (~2.4 at%) and Cu (bal.); hence, the composition perhaps is the phase mixture of $\lambda + Fe_2Ti$ [13]. The shaded matrix with irregular shaped bright islands (arrows in Fig. 2(a)) has been observed in Cu interlayer. The composition of the shaded matrix is Ti (~47.5 at%), Fe (~22.5 at%), Cu (~25.33 at%), Ni (~3.45 at%) and Cr (bal.). The bright islands contain Ti (~43.72 at%) and Cu (~46.03 at%) with a small amount of Fe (~8.32 at%), Ni (~1.93 at%) and Cr (bal.). Hence, bright islands and shaded matrix are T_5 (T_5 is $Ti_{45}Cu_{55-x}Fe_x$; $4 < x < 5$) and FeTi + T_5 + Cu, respectively [14]. In Cu–Ti diffusion zone, two distinct reaction layers have been observed (Fig. 2(b)). The light shaded band is enriched with Ti (~61.36 at%) and Cu (bal.); hence, the Ti–Cu binary phase diagram indicates the formation of $CuTi_2$ + CuTi phase mix-

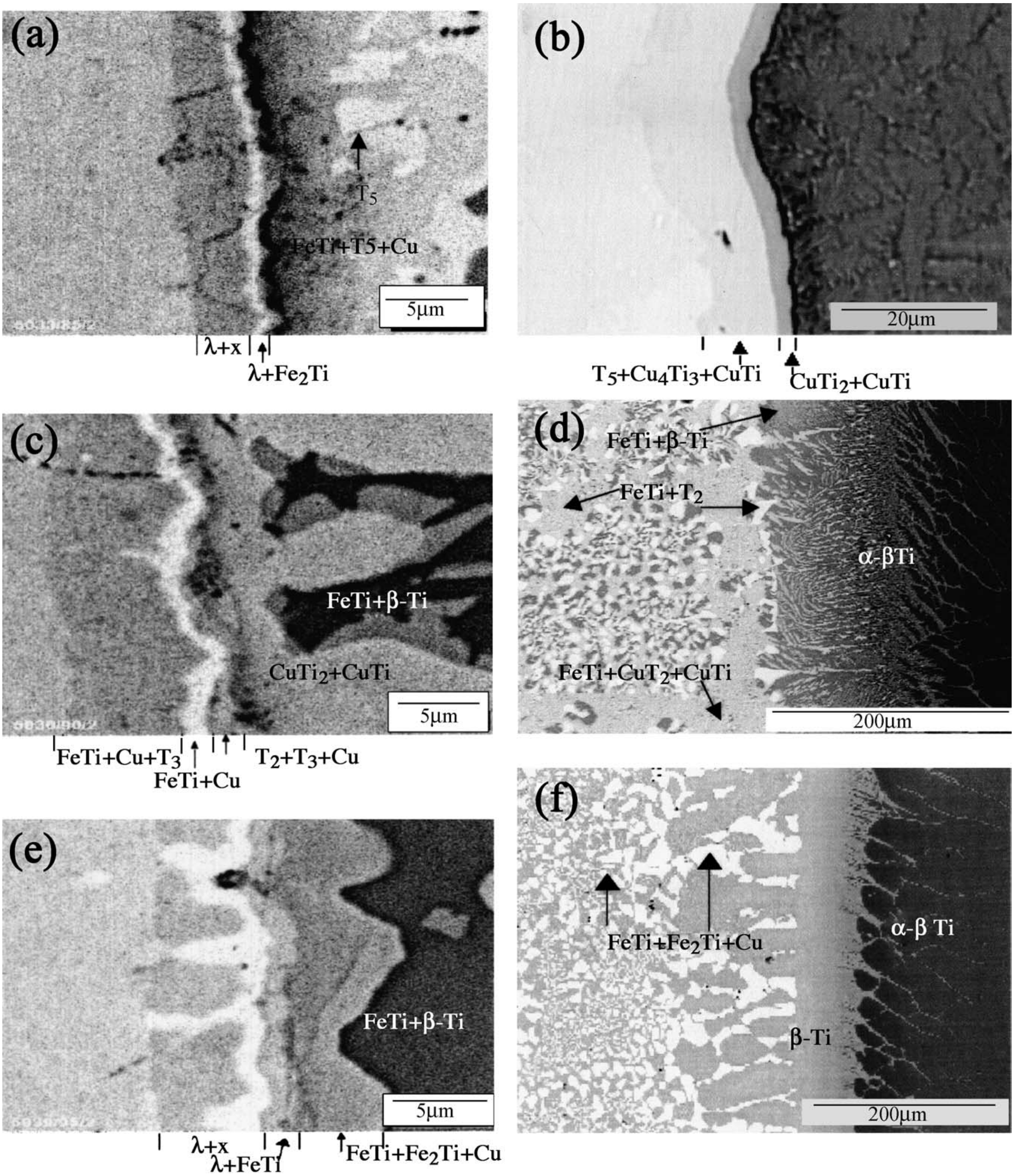

Fig. 2. SEM-BSE images of the transition joints processed at: (a) 850 °C, ss–Cu interface, (b) 850 °C, Cu–Ti interface, (c) 900 °C, ss–Cu interface, (d) 900 °C, Cu–Ti interface, (e) 950 °C, ss–Cu interface and (f) 950 °C, Cu–Ti interface.

ture [14]. Close to copper, the light shaded reaction layer contains Ti (∼44.7 at%), Fe (∼2.35 at%) and Cu (bal.). The isothermal section of Fe–Cu–Ti ternary phase diagram indicates the presence of phase mixture $T_5 + Cu_4Ti_3 + CuTi$ (T_5 is $Ti_{45}Cu_{55-x}Fe_x$; $4 < x < 5$) in this layer [14,15].

At 900 °C joining temperature, the deeply shaded area has been noticed (arrow in Fig. 2(c)) near stainless steel, containing Ti (∼45.76 at%), Fe (∼20.2 at%) and Cu (∼27.24 at%) with a small amount of Cr (∼1.8 at%) and Ni (bal.). This region is presumably the phase mixture of $FeTi + Cu + T_3$.

T_3 is $Ti_{43}Cu_{57-x}Fe_x$; $21 < x < 24$ having structure closely related to Ti_3Cu_4 [14]. Adjacent to FeTi + Cu + T_3, the river like bright reaction band consists of Ti (∼39.73 at%), Fe (∼18.44 at%) and Cu (∼36.94 at%) with a small amount of Cr (∼1.6 at%) and Ni (bal.), which perhaps is a phase mixture of FeTi + Cu. van Beek et al. reported that nearly 38 at% Cu could be dissolved in FeTi [15]. A lightly shaded region is found in between FeTi + Cu and ss–Cu interface, consisting of Ti (∼44.4 at%) and Cu (∼36 at%) in association with Fe (∼16.2 at%), Cr (∼1.9 at%) and Ni (bal.). This reaction layer is a phase mixture of $T_2 + T_3$ + Cu. T_2 phase is $Ti_{40}Cu_{60-x}Fe_x$; $5 < x < 17$ with structure resembled to Ti_2Cu_3 [15]. Near $T_2 + T_3$ + Cu the region contains Ti (∼61.7 at%), Cu (∼36 at%), Fe (∼2.01 at%), Cr (∼0.3 at%) and Ni (bal.); hence, the phase mixture of $CuTi_2$ + CuTi may be present. Irregular distribution of reaction products occur at the Cu–Ti interface (Fig. 2(d)). The shaded area with composition of Ti (∼61.1–55.4 at%), Fe (∼2.14–9.43 at%), Cu (∼36.6–34 at%), Cr (∼0.2–1.36 at%) and Ni (∼bal.), is the phase mixture of FeTi + $CuTi_2$ + CuTi. The β-Ti forms as bright needles with the composition of Ti (∼81 at%), Fe (∼7.8 at%), Ni (∼2.4 at%), Cr (∼1.5 at%) and Cu (bal.) [16]. The bright islands have been found within the FeTi + $CuTi_2$ + CuTi phase, containing Ti (∼50.2 at%), Fe (∼12.5 at%), Cu (∼34 at%), Cr (∼1.4 at%) and Ni (bal.); hence, the composition indicates the FeTi + T_2 phase mixture.

The dark area in Fig. 2(c–e) is enriched with Ti (∼75.7–75.5 at%) and Fe (∼10.3–10.9 at%) with a small amount of Cu (8.7–10.5 at%), Cr (∼3.3–3.1 at%) and Ni (∼bal.); hence, the composition indicates the stabilized FeTi + β-Ti [16].

At 950 °C processing temperature at ss–Cu interface (Fig. 2(e)), a combination of bright and shaded region appeared adjacent to ss side. The shaded area contains Fe (∼64 at%), Ti (∼3.4 at%), Cr (∼27.93 at%), Ni (∼3.13 at%) and Cu (bal.). The composition of the bright region is Fe (∼60.2 at%), Ti (∼9.9 at%), Cr (∼24.9 at%), Ni (∼3.5 at%) and Cu (bal.). Hence, the bright and shaded region indicates $\lambda + \chi$ phase mixture. The shade difference occurs owing to difference in the concentration of Ti, Cr and Fe. Close to the $\lambda + \chi$, a lightly shaded layer exists, which consists of Fe (∼55.4 at%), Ti (∼21.7 at%), Cr (∼17 at%), Ni (∼4.11 at%) and Cu (bal.). Presumably, the phase combination is λ + FeTi in this area [10–12]. Next to λ + FeTi, the shaded region with irregular boundary has been found in Fig. 2(e), containing Ti (∼50.6 at%), Fe (∼23.8 at%), Cu (∼19.34 at%), Ni (∼2.14 at%) and Cr (bal.). So, this composition is the phase mixture of FeTi + Fe_2Ti + Cu. At Cu–Ti interface (Fig. 2(f)), the shaded area is enriched with Ti (∼86.01 at%) and Fe (∼7.6 at%) with a small amount of Cr (∼2.22 at%), Cu (∼4.2 at%) and Ni (bal.). This composition is stabilized β-Ti [16]. The bright islands in β-Ti phase (arrow in Fig. 2(f)), is enriched with Ti (∼50.2 at%), Fe (∼24.4 at%) and Cu (∼19.9 at%) with a small amount of Cr (∼3.6 at%) and Ni (bal.); hence, the phase mixture of FeTi + Fe_2Ti + Cu may be present.

The intermetallic compounds in the diffusion zone have been confirmed by X-ray diffraction technique and are given in Fig. 3. The study indicates the occurrence of CuTi, $CuTi_2$, Cu_2Ti, Cu_4Ti_3, Cu_3Ti_2, FeTi, Fe_2Ti, Cr_2Ti, χ, α-Fe, α-Ti and β-Ti. The λ phase (solid solution of Fe_2Ti and Cr_2Ti) is identified separately in the X-ray diffraction study. The occurrence of Cu_3Ti_2 and Cu_2Ti phases has not been observed in SEM-BSE micrograph perhaps due to its low volume fraction. However, these phases could be observed by cross-sectional transmission electron microscopic technique.

In the bonding temperature range of 850–950 °C, the flow-ability of copper becomes high as bonding temperature, especially 950 °C, is close to the melting point of copper. Diffusion of chemical species becomes easier, i.e. through interlayer Ti can migrate to ss side and Fe, Cr and Ni can move to Ti side. So, 300 μm copper intermediate material cannot hinder the formation of Fe–Ti intermetallics.

The tensile properties of the diffusion-annealed samples are shown in Table 3. At a low bonding temperature of 850 °C, the bond strength and breaking strain of the diffusion couple is low. At this joining temperature, the flow-ability of copper is substantial yet yield strength of the base materials still remains high which, leads to an incomplete coalescence of the mating surfaces. Hence, tensile properties become poor.

Diffusion welding temperature of 900 °C results in a considerable improvement in UTS (∼99.7% of that of cpTi) and breaking strain (∼37% of that of cpTi). Such high strength with good ductility have not been reported in earlier investigations for diffusion couple of these two dissimilar materials joined directly or with interlayer [2,5,7,13]. Diffusion welding temperature of 900 °C promotes mass transfer of the alloying elements across the interface, which is responsible for the increase in volume fraction of the reaction products; hence, causes more embrittlement to the joints with respect to the couples processed at 850 °C. However, plastic collapse of the mating surface asperities leads to intimate contact, which counterbalances the embrittlement phenomena due to intermetallic phases; bond strength naturally improves and attains its maximum value. Beyond 900 °C diffusion annealing temperature, the width of brittle intermetallics considerably increases and the embrittlement effect over-balances the positive effect obtained due to betterment in coalescence of faying surfaces. So, the bond strength drops. Moreover, it is observed that the embrittlement effect of Cu–Ti and Cu–Ti–Fe base intermetallics is probably less with respect to Fe–Ti intermetallic in lowering the bond strength.

It is to be noteworthy that beside the presence of Cu–Ti intermetallics, the tensile properties of the transition joints

Table 3
Tensile properties of the transition joints processed for 1.5 h

Bonding temperature (°C)	Ultimate tensile strength (MPa)	Breaking strain (%)
850	225.6 ± 6	3.2 ± 0.7
900	318.2 ± 7	8.5 ± 0.9
950	244.4 ± 2	4.7 ± 0.6

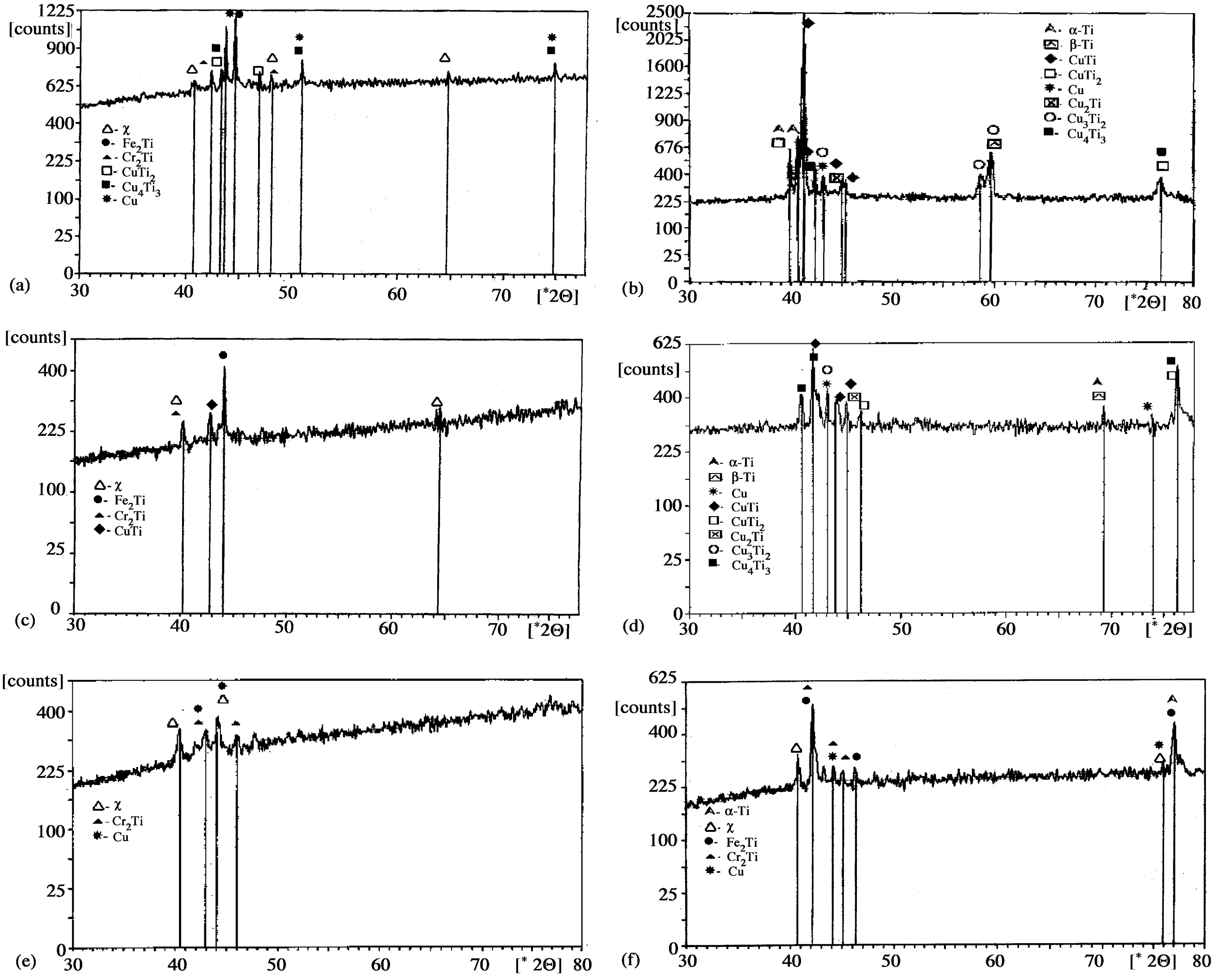

Fig. 3. X-ray diffraction analysis of the fracture surfaces of the couples bonded at: (a and b) 850 °C, (c and d) 900 °C and (e and f) 950 °C.

improve substantially in comparison to direct bonding of the same dissimilar materials; hence, it can be inferred that embrittlement effect of Cu–Ti intermetallics is lower than the Fe–Ti intermetallics. Moreover, formation of intermetallics in the diffusion zone of Cu–Ti also deteriorates the bond strength as failure takes place from the above interface during tensile loading. Despite the presence of the brittle reaction products in the diffusion zone, the use of copper as intermediate materials improves the joint quality by eradicating voids formation near interface, which were observed for the direct bonding of titanium–stainless steel due to differential mass transfer across the bond line [11,12].

4. Conclusions

The solid-state diffusion bonding was carried out between commercially pure titanium and 304 stainless steel using 300 μm copper interlayer. Bonding was carried in the temperature range of 850–950 °C for 1.5 h under 3 MPa uniaxial load in vacuum. The characterization of the transition joints revels the following:

SEM-BSE images exhibit that the Fe–Cu–Ti ternary products (T_2, T_3 and T_5) are formed in both the diffusion interfaces at the joining temperature of 850 and 900 °C. Whereas, at 950 °C bonding temperature, Fe–Cu–Ti and Cu–Ti bases intermetallics are not formed in the diffusion interfaces.

However, it is evident from the study that copper interlayer cannot block the diffusion of Fe, Cr and Ni to Ti side and Ti to 304ss side. Maximum bond strength of ∼318 MPa and ductility of ∼8.5% has been obtained for the diffusion joint processed at 900 °C due to better coalescence of mating surface. With the rise in joining temperature to 950 °C, bond strength drops due to the enhanced volume fraction of brittle intermetallics. At a lower joining temperature of 850 °C, bond strength is also poor owing to incomplete coalescence of the mating surfaces.

References

[1] P. He, J.H. Zhang, X.Q. Li, Mater. Sci. Technol. 17 (2001) 1158–1162.
[2] M. Ghosh, S. Chatterjee, Mater. Charact. 48 (2002) 393–399.

[3] H. Kato, S. Abe, T. Tomizawa, J. Mater. Sci. 32 (1997) 5225–5232.
[4] P. He, J. Zhang, R. Zhou, X. Li, Mater. Charact. 43 (1999) 287–292.
[5] M. Ghosh, K. Bhanumurthy, G.B. Kale, S. Chatterjee, J. Nucl. Mater. 322 (2003) 235–241.
[6] M. Ghosh, S. Chatterjee, B. Mishra, Mater. Sci. Eng. A 363 (2003) 268–274.
[7] S. Kundu, M. Ghosh, S. Chatterjee, ISIJ Int. 44 (2004) 1891–1896.
[8] G.R. Kamat, Weld. J. 67 (1988) 44–46.
[9] T.B. Massalaki, Binary Alloy Diagram, vol. 2, second ed., ASTM International, 1996, p. 1735.
[10] B. Aleman, I. Guitterrez, J.J. Urcola, Mater. Sci. Technol. 9 (1993) 633–641.
[11] M. Ghosh, K. Bhanumurthy, G.B. Kale, S. Chatterjee, Trans. Indian Inst. Met. 56 (2003) 197–203.
[12] M. Ghosh, S. Chatterjee, Mater. Sci. Eng. A 358 (2003) 152–158.
[13] V. Raghavan, Phase Diagrams of Ternary Iron Alloys, Part 1, ASM International, Materials Park, Ohio, 1987, p. 43.
[14] V. Raghavan, J. Phase Equilib. 23 (2002) 172–174.
[15] J.A. van Beek, A.A. Kodentsov, F.J.J. van Loo, J. Alloys Compd. 217 (1995) 97–103.
[16] M. Eroglu, T.I. Khan, N. Orhan, Mater. Sci. Technol. 18 (2002) 68–72.