Reactive Diffusion Bonding Between Commercially Pure Titanium and 304 Stainless Steel Using Nickel Interlayer

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Diffusion bonding was carried out between commercially pure titanium and 304 stainless steel using nickel as interlayer in the temperature range of 800–900°C for 5.4 ks under 3 MPa load in vacuum. The transition joints thus formed were characterized in optical and scanning electron microscopes. TiNi_3 , TiNi and Ti_2Ni are formed at the Ni–Ti interface whereas, 304 ss–Ni diffusion zone is free from intermetallic compounds at 800 and 850°C processing temperatures. At 900°C, Ni–Ti interface exhibits the presence of α – β Ti discrete islands in the matrix of Ti_2Ni and the phase mixture of α -Fe+ λ + χ occurs at the ss–Ni interface. Nickel is able to inhibit the diffusion of Ti to 304 ss side up to 850°C; however, becomes unable to restrict the migration of Ti to stainless steel at 900°C. Highest bond strength of 80 % of that of titanium has been obtained for the diffusion couple processed at 850°C owing to the better coalescence of the mating surfaces and failure takes place from Ni–Ti interface. At higher joining temperature, the formation of Fe–Ti intermetallics reduces the bond strength and failure in tensile loading occurs from ss–Ni interface.

KEY WORDS: diffusion bonding; intermetallic compounds; intermediate material.

1. Introduction

Diffusion bonding of commercially pure titanium (cp Ti) and 304 stainless steel (304 ss) has emerged as an improved fabrication technique for producing primary and secondary components for application in nuclear, aerospace and chemical industries.^{1,2)} However, direct bonding of these materials promotes residual stress at the interface region caused by mismatch of thermal expansions between bonding materials and the formation of the intermetallic phases in the diffusion zone.³⁾

The interdiffusion and structure-properties relationship study between cp Ti and 304 ss exhibit that atomic migration of chemical species across the bond line promotes the formation of σ , χ , λ , FeTi, β -Ti and $\text{Fe}_2\text{Ti}_4\text{O}$ phases in the reaction zone.^{4–6)} All these brittle intermetallics impair the mechanical properties of the transition joints. Consequently, diffusion bonding of these two materials using intermediate material is increasing importance. In this context, Nickel can be considered as an useful intermediate material for its satisfactory corrosion resistance. Ni has substantial extent of solid solubility in iron and in Ni-stainless steel diffusion couple no intermetallic formation has been reported.⁷⁾ However, an ordered compound of Ni–Cr is formed at 22–32 at% Cr at $\sim 600^\circ\text{C}$ and another compound of Fe–Ni occurs for 74–84 at% Ni at $\sim 500^\circ\text{C}$.^{8,9)} On the other hand, binary phase diagram of Ni–Ti shows that, the mode of intermetallics formation changes from Ti_2Ni to TiNi_3 via TiNi with increasing Ni content.^{10,11)} It is also established that, Ni–Ti intermetallic phases have higher plasticity than

that of Fe–Ti intermetallics.

The informations concerning the diffusion bonding of cp Ti and 304 ss using Ni as an interlayer is scanty and makes it difficult to optimize the processing parameters to obtain a joint of satisfactory quality. Moreover, it has been illustrated earlier that, direct bonding between these dissimilar materials results in maximum bond strength of $\sim 70\%$ of that of titanium.¹²⁾ Hence, the present investigation aims at improving the bond strength further with the use of interlayer. The bonding temperature was varied to observe its effect on the interface microstructure, which in turn will alter the strength of the diffusion bonds.

2. Experimental

The chemical compositions and room temperature tensile properties of commercially pure titanium and 304 stainless steel are given in **Tables 1** and **2** respectively. Both of them were received in the form of rod having 20 mm diameter. From the base materials, cylinder of 15 mm diameter $\times$ 30 mm length was machined. The faying surfaces of the samples were prepared by metallographic technique with the surface roughness of $\sim 2.5\ \mu\text{m}$. 300 μm thick nickel foil (purity 99.5 at%) was used as intermediate material and both the surfaces was polished using 1 μm diamond. The assembly was placed in a fixture under 3 MPa uniaxial load, applied along the longitudinal direction of the specimen and was inserted in the chamber. Diffusion bonding was carried out at the temperatures of 800, 850 and 900°C for 5.4 ks in $(6\text{--}8)\times 10^{-5}$ mbar vacuum. Heating was done at

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

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

Table 2. Tensile properties of the base metals at room temperature.

Alloy	0.2% proof stress (MPa)	Ultimate tensile strength (MPa)	Fracture elongation (%)
cp Ti	205	319	23
304 ss	740	822.5	42

Fig. 1. Optical microstructure of the diffusion bonded assemblies joined at a) 800°C, b) 850°C, c) 900°C, 304 ss-Ni interface, d) 900°C, Ni-Ti interface.

the rate of 14°C/min at the time of processing and after the operation the sample was allowed to cool in vacuum.

From the bonded couples, a transverse section was taken and prepared by conventional grinding and polishing technique. The titanium side was etched with an aqueous solution (85 mL) containing HNO₃ (8 mL) and HF (4 mL). The stainless steel was etched by a mixture of HNO₃ (10 mL), HCl (40 mL) and glycerol (50 mL). A solution consisting of glacial acetic acid (50 mL) and concentrate HNO₃ (50 mL) was used for etching pure nickel. The structural changes at both the interfaces, were observed in a light microscope. Finer structure details in the diffusion zone were revealed in scanning electron microscope using back-scattered mode (SEM-BSE). The composition of the reaction layers was determined in atomic percent using energy dispersive spectroscopy. Tensile properties of the transition joints were evaluated in a tensile testing machine (Instron 4204) at a crosshead speed of 5×10⁻² mm/min at room temperature. Cylindrical tensile specimens were machined as per ASTM specification (Vol. 03.01 E8M-96) with gauge diameter and length of 4 and 20 mm respectively. The interface was at the

center of the gauge length. Four samples were tested at each process parameter to check the reproducibility of results. The presence of intermetallic phases on the fracture surfaces was confirmed by X-ray diffraction technique using copper target. The scanning span of 20–80° with a step size of 0.01° (=2θ) was used during diffraction study.

3. Results and Discussion

The optical microstructure of the bonded assemblies is shown in **Fig. 1**. From the photographs, it is observed that, certain amount of diffusion occurs between the interlayer and the two substrates. The stainless steel–nickel bonding interface is planar in nature and a thin diffusion layer was revealed for the processing temperatures of 800 and 850°C. At the same joining temperatures the Ti–Ni interface is characterized by the presence of a lightly shaded reaction zone and the Widmanstätten α–β Ti structure. As a β-stabilizing element, nickel atoms, after migration in titanium lattice lowers the eutectoid transformation temperature of titanium and the acicular α–β Ti occurs from the decomposi-

Fig. 2. SEM-BSE images of the transition joints processed at a) 800°C, 304 ss–Ni interface, b) 800°C, Ni–Ti interface, c) 850°C, 304 ss–Ni interface, d) 850°C, Ni–Ti interface, e) 900°C, 304 ss–Ni interface, f) 900°C, Ni–Ti interface.

tion of β -Ti during cooling.^{13,14)} A rise in processing temperature to 900°C leads to form deeply shaded diffusion zone at both the interfaces. The total diffusion zone at the Ni–ss interface is smaller than the Ni–Ti interface. At 800–900°C, nickel and stainless steel both have fcc crystallography and being the close packed structure, the extent of diffusion of chemical species 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 titanium. Owing to more open crystallography of bcc structure, nickel atoms can travel a longer distance in titanium matrix with respect to titanium in nickel lattice.¹⁵⁾

An increment in the joining temperature from 800 to 850°C results in grain growth of nickel interlayer (~ 128 and $\sim 174 \mu\text{m}$ at 800 and 850°C respectively) and at 900°C shaded islands ($\sim 21 \mu\text{m}$) appear within the nickel matrix.

The SEM-BSE images of the transition joints are given in **Fig. 2**. Both Ni–ss and Ni–Ti interfaces are resolved at higher magnification. The composition of the chemical species was determined near the two bond lines.

In the mutual diffusion layer at stainless steel–nickel in-

terface, the composition changes gradually for Fe, Cr and Ni. For 800 and 850°C joining temperatures, the diffusion zone is free from reaction products and the observation is in agreement with the earlier investigation.³⁾ Presence of Fe (~ 6.8 – 10.7) and Cr (~ 1.5 – 3.4) in the Ni side indicates substantial diffusion of the two alloying elements at the bonding temperatures of 800–850°C to nickel side. Similarly, Ni also migrates to the 304 ss substrate in adequate quantity (~ 28.4 – 44.9) at the same temperature range. When the bonding temperature is enhanced to 900°C, a marked change has been noticed in ss–Ni interface. The region is characterized by the presence of a bright reaction product containing Ti (~ 12), Cr (~ 21.2), Ni (~ 2.6) and Fe (bal). Nickel concentration is low enough to form any nickel bearing intermetallic; hence ignoring the effect of nickel, from the ternary isotherm of Fe–Cr–Ti, it can be predicted that the region contains the phase mixture of α -Fe + λ + χ having $\sim 1.1 \mu\text{m}$ width (Fig. 2(e)).^{16,17)} This continuous bright phase is embedded in a lightly shaded region which is depleted in Ni (~ 5.4) and Ti (~ 4) and enriched with Cr (~ 24.7) and Fe (bal). Adjacent to the lightly shaded

region, the deeply shaded zone indicates the existence of pure Ni(~ 90) containing Fe, Cr and Ti in solid solution.

At the Ni–Ti interface, for 800–850°C processing temperature three distinct reaction layers have been observed (Figs. 2(b) and 2(d)). At the nickel side the faint area contains Ni(~ 79.8 – 80.3) and Ti(bal) and corresponds to TiNi_3 intermetallic.¹⁰⁾ Close to titanium base metal the deeply shaded region is enriched with Ti(~ 59.7) and depleted in Ni(bal); hence indicates the formation of Ti_2Ni intermetallic compound.¹⁸⁾ Between TiNi_3 and Ti_2Ni , another lightly shaded reaction band TiNi is present having the composition of Ti(~ 42.4) and Ni(bal).¹⁰⁾ Increment in diffusion welding temperature to 900°C results in disappearance of layer wise reaction products at Ni–Ti interface; rather between the pure nickel and titanium, the area is the combination of bright and shaded regions. The average composition of the bright matrix is Ti(~ 52.3), Ni(~ 37.6), Fe(~ 8) and Cr(bal) and that of the shaded island is Cr(~ 3.5), Fe(~ 3.9), Ni(~ 8.5) and Ti(bal). Hence, the former is Ti_2Ni intermetallic compound and the latter is the phase aggregate of Widmanstätten α – β titanium.

From the electron micrographs, it is evident that, the rise in joining temperature encourages profuse diffusion of chemical species across the bond line. The thickness of Ti_2Ni , TiNi and TiNi_3 is ~ 3.4 , ~ 4.8 and $\sim 1.7 \mu\text{m}$ at 800°C and increases to ~ 3.7 , 4.9 and $2.1 \mu\text{m}$ at 850°C processing temperature respectively. At ss–Ni interface the same trend is also observed as the presence of Fe and Cr in nickel matrix and enrichment of nickel concentration in stainless steel side increase at 850°C in comparison to 800°C.

From the results of energy dispersive spectroscopy for the transition joint processed at 900°C, it has been observed that, at this bonding temperature the lowering of yield stress of the interlayer results in irregular shaped residual nickel at the 304 ss–Ni interface. Moreover, 300 μm thick nickel intermediate layer is unable to block the diffusion of titanium to stainless steel side and this phenomenon has been divulged by the existence of α -Fe + λ + χ phase mixture at the Ni–ss reaction layer. The enhanced atomic transport of Ti at 900°C is also responsible for prevailing non-equilibrium situation to cause the absence of Ni–Ti intermetallics as continuous layer at the Ni–Ti interface; rather acicular α – β titanium occurs in the form of islands surrounded by Ti_2Ni phase.

The tensile properties of the diffusion-annealed samples are illustrated in **Fig. 3**. At low bonding temperature like 800°C, both the bond strength and the breaking strain of the diffusion couple is low because at this temperature yield strength of the bonded material is still high. The deformation of the base metals at the interfaces and the extent of diffusion of alloying elements is limited at both the interfaces. Moreover, diffusion of Ni and Ti promotes intermetallics formation in the diffusion zone and lowers the bond strength. During tensile loading failure takes place from Ni–Ti interface and X-ray diffraction analysis indicates the formation of NiTi_2 , Ni_3Ti and NiTi at the fracture surfaces (**Figs. 4(a) and 4(b)**). With the rise in diffusion annealing temperature to 850°C, the bond strength is enhanced as the plastic deformation of the master alloy increases owing to the lowering in the yield stress of the same. On the other hand, 850°C processing temperature

Fig. 3. Tensile properties of the diffusion bonded assemblies.

also promotes atomic diffusivity of the chemical species, which in turn is accountable for the increment in the width of the reaction products at the Ni–Ti interface. Though the volume fraction of Ni–Ti intermetallic phases emanates at 850°C with respect to 800°C bonding temperature yet, the plastic collapse of the faying surface asperities steers the betterment in bond strength and ductility of the transition joints. The UTS value exhibits a substantial improvement in bond quality (in terms of UTS, 80% of that of titanium) with respect to earlier reported values of directly bonded cp Ti–304 ss joint.^{2,4,12,18)} Fracture takes place once again through Ni–Ti interface as the XRD analysis exhibits the occurrence of NiTi_2 , Ni_3Ti and NiTi in the reaction zone (**Figs. 4(c) and 4(d)**). So, in the temperature range of 800–850°C, the presence of Ni–Ti intermetallics at nickel–titanium interface plays a key role for failure in tensile testing.

A further rise in processing temperature to 900°C decreases the bond strength and ductility of the diffusion bonded couples. SEM-BSE images (**Figs. 2(e) and 2(f)**) unveil that, at the Ni–Ti interface no layer wise intermetallic is formed yet, ss–Ni interface is characterized by the presence of α -Fe + λ + χ phase aggregate. λ phase is a solid-solution of (Fe,Cr)₂Ti having hexagonal structure. Both of them are hard and very brittle in comparison to Ni–Ti intermetallics. So, failure occurs through this phase mixture and the fracture surface is denoted by the manifestation of α -Fe, σ , χ , Fe_2Ti and Cr_2Ti compounds. The occurrence of σ phase has not been found in SEM-BSE micrographs perhaps due to its small volume fraction. The σ phase principally contains Fe and Cr. Ti migration in 304 ss lattice decreases the activity of Cr. Hence, diffusion takes place down the activity gradient rather than the concentration gradient. Cr enrichment occurs due to uphill diffusion of the same and during cooling the chromium enriched region transforms to the s phase.¹⁵⁾ The formation of α -Fe in 304 ss matrix supports the findings of previous investigation where, it has been stated that, ~ 0.8 at% of Ti in austenite matrix promotes the formation of bcc ferrite.²⁰⁾ It can be also inferred that Fe–Ti intermetallics are more pernicious than Ni–Ti intermetallics in deteriorating the bond strength and breaking strain of the diffusion bonded joints.

4. Conclusions

Solid state diffusion bonding was carried out in vacuum

Fig. 4. X-ray diffraction analysis of the fracture surfaces of the couples bonded at a) and b) 800°C, c) and d) 850°C, e) and f) 900°C.

between commercially pure titanium and 304 stainless steel using 300 mm nickel as interlayer. Processing parameters were 800–900°C temperature, 5.4 ks time and 3 MPa load. Characterization of the transition joints reveals the following:

304 ss–Ni interface is free from any reaction product at the joining temperatures of 800 and 850°C yet, α -Fe + λ + χ phase aggregates was formed in the diffusion zone of the same region at 900°C bonding temperature.

At Ni–Ti interface inter-diffusion between Ni and Ti encourages layer wise formation of Ni₃Ti, NiTi and Ni₂Ti in the diffusion zone at 800–850°C joining temperature; however their presence has not been found at 900°C bonding temperature. Between pure nickel and titanium, α – β Ti exists as discrete islands in the matrix of Ti₂Ni at 900°C.

A rise in processing temperature promotes atomic migration of chemical species across both the bond lines; yet, up to 850°C joining temperature 300 μ m Ni interlayer can completely inhibit the diffusion of Ti to 304 ss side. However, at 900°C titanium atoms can cross the nickel matrix to form Fe–Ti intermetallics at ss–Ni interface.

Highest bond strength ($\sim$ 257 MPa) with substantial ductility has been obtained for the diffusion couple processed at 850°C due to the better coalescence of mating surfaces and failure occurs from Ni–Ti interface. Similar trend has been observed for the specimens bonded at 800°C though, UTS is lower than the previous value owing to the limited plastic deformation of mating surface asperities. With the rise in joining temperature to 900°C the fracture occurs from ss–Ni interface due to formation of brittle Fe–Ti intermetallics resulting in decrease in bond strength.

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