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Structure and properties of diffusion bonded transition joints between commercially pure titanium and type 304 stainless steel using a nickel interlayer

Sukumar Kundu · Subrata Chatterjee

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Abstract The solid-state diffusion bonding was carried out between commercially pure titanium and Type 304 stainless steel using nickel as an interlayer in the temperature range of 800–900 °C for 9 ks under 3 MPa load in vacuum. The transition joints thus formed were characterized in the optical and scanning electron microscopes. The inter-diffusion of the chemical species across the diffusion interfaces were evaluated by electron probe microanalysis. $TiNi_3$, TiNi and Ti_2Ni are formed at the nickel–titanium (Ni–Ti) interface; however, the stainless steel–nickel (SS–Ni) diffusion interface is free from intermetallic compounds up to 850 °C temperature. At 900 °C, the Ni–Ti interface exhibits the presence of α-β Ti discrete islands in the matrix of Ti_2Ni and $\lambda + \chi + \alpha$-Fe, λ + FeTi and λ + FeTi + β-Ti phase mixtures occur at the SS–Ni interface. The occurrence of different intermetallics are confirmed by the x-ray diffraction technique. The maximum tensile strength of ~276 MPa and shear strength of ~209 MPa along with 7.3% elongation were obtained for the diffusion couple processed at 850 °C. At the 900 °C joining temperature, the formation of Fe–Ti base intermetallics reduces the bond strength. Evaluation of the fracture surfaces using scanning electron microscopy and energy dispersive spectroscopy demonstrates that failure takes place through Ni–Ti interface up to 850 °C and through the SS–Ni interface of the joint when processed at 900 °C.

S. Kundu (✉) · S. Chatterjee
Department of Metallurgy and Materials Engineering,
Bengal Engineering and Science University,
Shibpur, Howrah 711103, India
e-mail: erskundu@yahoo.com

S. Chatterjee
e-mail: schatterjee46@yahoo.com

Introduction

Diffusion-bonded joints of titanium to stainless steel have wide applications in the chemical processing, aerospace and nuclear industries [1, 2]. Conventional fusion welding of these materials can result in segregation of chemical species, stress concentrations and the formation of brittle intermetallics at the bond interface. The superplastic deformation offers an advantage in the processes of diffusion bonding because it is possible to break the oxide film and fill the voids on the bond interface. The superplastic joining is generally conducted by using a diffusional phase transformation and thermal cycling through the transformation temperature under a compressive stress [3].

Reports in the literature show that inter-diffusion between titanium and stainless steel occurs across the bond interface and promotes the formation of χ phase, FeTi, Fe_2Ti, Cr_2Ti, TiC, β-Ti and Fe_2Ti_4O phases in the reaction zone. These brittle intermetallics deteriorate the mechanical properties of the transition joints [4–8]. Chatterjee et al. reported that solid state diffusion bonding of titanium to stainless steel has been performed at 850 °C for 30 min and that a maximum bond strength of ~235 MPa (~73% of Ti) was achieved [2]. Kato et al. achieved bond strength of 70% of that of titanium and $\leq 2.2\%$ breaking strain for a 927 °C processing temperature for the same transition joint [8]. The use of appropriate intermediate materials can minimize the brittle intermetallics, which, in turn, further increase strength properties of the diffusion bonded joint. In this context, nickel can be considered as a useful intermediate material due to its satisfactory corrosion resistance. Nickel has substantial solid solubility in iron and Kamat et al. reported that the nickel-stainless steel diffusion couple is free from intermetallics [9]. However, Ni–Cr can form an ordered compound of 22–32 at.% Cr at

~600 °C, and another compound of Fe–Ni occurs for 74–84 at.% Ni at ~500 °C [10, 11]. The binary phase diagram of Ni–Ti shows that intermetallic formation changes from Ti_2Ni, to $TiNi_3$ via TiNi with increasing Ni content [11, 12]. He et al. reported that Ni–Ti type intermetallic phases have higher plasticity than that of Fe–Ti base intermetallics [13]. The purpose of the present work is to demonstrate the feasibility of producing diffusion joints of titanium to stainless steel with a nickel interlayer, with a focus on the interface microstructure and strength of the diffusion bonded joints.

Experimental procedure

The commercially pure titanium (CP Ti) and Type 304 stainless steel (304 SS) used in this investigation, had dimensions of 25 mm diameter × 400 mm length and $150 \times 150 \times 900$ mm^3, respectively. Chemical compositions and room temperature mechanical properties are given in Tables 1 and 2, respectively.

Cylindrical specimens of 15 mm diameter × 30 mm length were machined from the base metals. The mating surfaces of the cylinders were prepared by conventional grinding and polishing techniques with final polishing on 1 μm diamond paste. A 300 μm thick nickel foil (purity 99.5 at.%) was used as an intermediate material, and both surfaces were polished in the same fashion. Faying surfaces were cleaned in acetone and dried in air. The Ti–Ni–SS assembly was placed in a fixture under 3 MPa uniaxial load applied along the longitudinal direction of the specimen, and was inserted in a vacuum chamber. Diffusion bonding was carried out in the temperature range of 800–900 °C for 9 ks in $(3–5) \times 10^{-3}$ Pa vacuum. During processing, the constant heating rate was 0.24 °Cs^{-1} and after the joining operation, samples were furnace-cooled in vacuum.

From the bonded assemblies, a transverse section was taken and surfaces were prepared using conventional metallographic techniques. The titanium side was etched with an aqueous solution (85 mL) containing HNO_3 (8 mL) and HF (4 mL). The stainless steel substrate was etched with a mixture of HNO_3 (10 mL), HCl (40 mL) and glycerol (50 mL). A solution consisting of glacial acetic acid (50 mL) and concentrate HNO_3 (50 mL) was used for etching pure nickel. The samples were observed in a light microscope (Correct SDME TR5) to reveal the structural changes due to diffusion. Polished surfaces of bonded couples were also examined in a scanning electron microscope (Leica S440) in the back scattered mode (SEM-BSE) to obtain finer structural details in the diffusion zone. The electron probe microanalyser (CAMECA Sx 100) was used to get the elemental concentration profiles across the diffusion interfaces. The k_α lines of Ti, Fe, Ni and Cr are generated at an operating voltage of 15 kV and specimen current of 12×10^{-8} A. The LiF crystal was used to diffract the corresponding characteristic x-ray radiation. The presence of intermetallic phases on fracture surfaces were confirmed by x-ray diffraction (Philips PW 1840) using a copper target. The scanning range of 20–80° with a step size of 0.01^0 $(=2\theta)$ was used in the diffraction study.

The tensile properties of the transition joints were evaluated in a universal testing machine (Instron 4204) at a crosshead speed of 8.33×10^{-4} ms^{-1} at room temperature. Cylindrical tensile specimens were machined as per ASTM specification E8M-96 with gauge diameter and length of 4 mm and 20 mm, respectively. The interlayer was at the centre of the gauge length. The shear strength of the bonded joints was evaluated at room temperature using a screw tensile testing machine set at a crosshead speed of 8.33×10^{-3} ms^{-1}. The shear test specimens were machined to a diameter of 10 mm. Four samples were tested for each process parameter to check the reproducibility of results. Evaluation of the fracture surfaces was performed using the secondary electron imaging mode of the SEM (Leica S440), which was also equipped with an energy dispersive x-ray spectrometer(Oxford 5431) to reveal the nature and location of failure under loading.

Results and discussion

The microstructures of the bonded joints are shown in the light optical micrographs of Fig. 1. Diffusion occurred between the interlayer and two substrates, and this can be observed from the optical micrographs. The stainless steel–nickel (SS–Ni) interface is planar in nature and a thin diffusion layer was revealed for processing temperatures of 800 and 850 °C. The Ti–Ni interface is characterized by the presence of a light shaded reaction zone and a Widmanstatten α-β Ti structure is observed at the same joining temperatures. Nickel is a β-stabilizing element, so migration of nickel atoms in titanium lattice lowers the eutectoid transformation temperature of titanium. The

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
Type 304 SS	0.06	Bal	–	1.38	0.37	0.013	0.03	18.15	8.50	–	0.005	–

Table 2 Mechanical properties of the base metals at room temperature

Alloy	Shear strength (MPa)	0.2% proof stress (MPa)	Ultimate tensile strength (MPa)	Fracture elongation (%)
CP Ti	296.6	205	319	23
Type 304 SS	573.0	740	822.5	42

acicular α-β Ti occurs from the decomposition of β-Ti during cooling [14, 15]. An increase in bonding temperature to 900 °C results in the formation of a dark shaded diffusion zone at both interfaces. The total diffusion zone at the SS–Ni interface is smaller than that at Ni–Ti interface. Nickel and stainless steel have a closed packed face centered cubic (fcc) crystal structure; so, the extent of diffusion is limited. On the other hand, in Ti, a phase transformation in the form of α(hcp) ↔ β(bcc) occurs at 882 °C. Owing to the more open body centered cubic (bcc) crystal structure, nickel atoms can travel a longer distance in titanium matrix with respect to titanium in nickel lattice [2, 15]. Moreover, the intrinsic diffusion co-efficient of Ti ($D_{Ti} = 5.5 \times 10^{-14}$ m^2 s^{-1} at 900 °C and $D_{Ti} = 9 \times 10^{-14}$ m^2 s^{-1} at 800 °C) are greater than α-Fe ($D_{\alpha\text{-Fe}} = 5 \times 10^{-15}$ m^2 s^{-1} at 900 °C), γ-Fe ($D_{\gamma\text{-Fe}} = 3 \times 10^{-17}$ m^2 s^{-1} at 900 °C) and Ni ($D_{Ni} = 3 \times 10^{-17}$ m^2 s^{-1} at 800 °C) [6, 12].

SEM-BSE images and concentration profiles of the elements obtained from EPMA analysis across the diffusion interfaces are presented in Figs. 2 and 3, respectively. At the SS–Ni interface, the composition changes gradually for Fe, Cr and Ni. At joining temperature of 800 and 850 °C, it is observed that the diffusion zone is free from reaction products (Fig. 2a, c), and this observation is in agreement with an earlier investigation [4]. The presence of ~11.8–15.9% Fe and ~3.5–4.1% Cr in the nickel side indicates that substantial diffusion of these two alloying elements occurred at bonding temperatures up to 850 °C. Similarly, Ni also migrates to the stainless steel substrate in a measurable quantity (~29.4–40.9%) for the same temperature range.

For processing temperatures up to 850 °C, three distinct reaction layers have been observed at the Ni–Ti interface (Fig. 2b, d). At the nickel side, the first reaction layer is $TiNi_3$, which contains ~74.7–75.4% Ni and ~24.6–25.3% Ti [12]. Adjacent to the titanium base metal, the darkly shaded area is Ti_2Ni, which contained ~68–68.9% Ti and ~31.1–32% Ni [13]. In between the $TiNi_3$ and Ti_2Ni layers, another distinctly-imaging reaction layer, TiNi, is present with the composition of ~48.4–49.6% Ni and ~50.4–51.6% Ti [12].

At the bonding temperature of 900°C, a significant change was observed in both interfaces. Light optical microscopy revealed the presence of a darkly imaging reaction layer at the SS–Ni interface (on the stainless side),

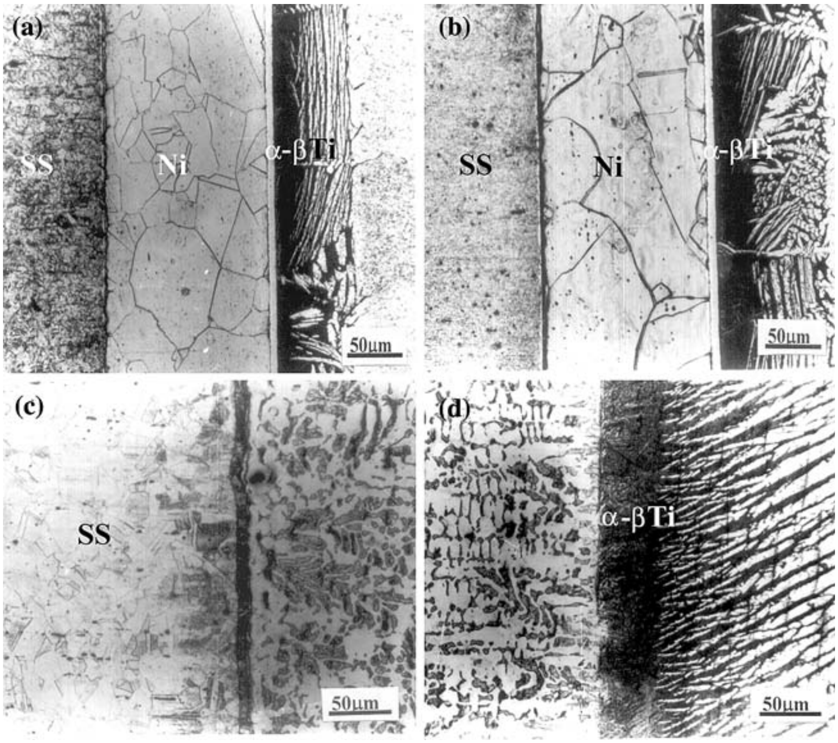
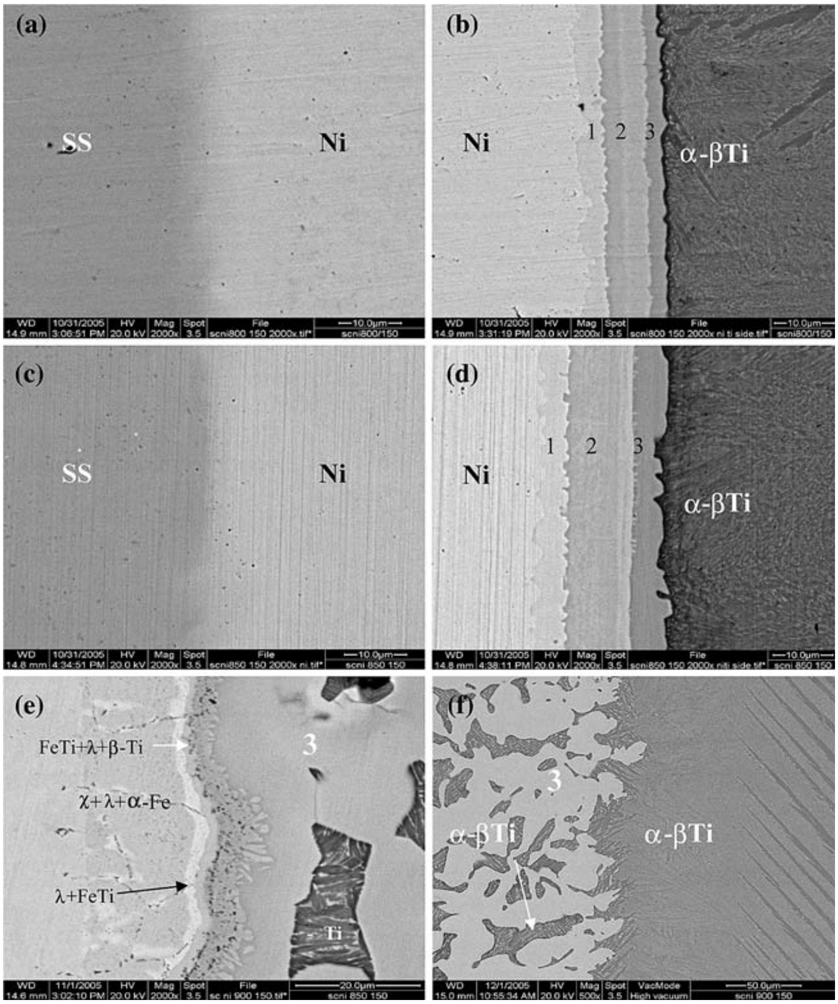


Fig. 1 Light micrographs of the joints diffusion bonded for 9 ks at: (**a**) 800 °C; (**b**) 850 °C; (**c**) 900 °C SS–Ni interface; and (**d**) 900 °C Ni–Ti interface

Fig. 2 SEM-BSE images of the transition joints processed at: (**a**) 800 °C, SS–Ni interface; (**b**) 800 °C, Ni–Ti interface; (**c**) 850 °C, SS–Ni interface; (**d**) 850 °C, Ni–Ti interface; (**e**) 900 C, SS–Ni interface; and (**f**) 900 °C, Ni–Ti interface. 1 → $TiNi_3$, 2 → TiNi, 3 → Ti_2Ni



which contained approximately ~62.9% Fe, ~27.5% Cr, ~5.9% Ti and ~3.7% Ni. This composition is consistent with the α-Fe + λ + χ phase mixture. The χ phase is $Fe_{17}Cr_7Ti_5$. As per the phase diagram the concentration of Fe, Cr and Ti varies as ~49–69 at.%, ~19–34 at.% and ~17 at.% in χ phase with complex cubic structure [16]. The λ phase is a solid solution of $(Fe, Cr)_2Ti$ [6]. The brightly imaging regions observed in the α-Fe + λ + χ phase mixture (Fig. 2e) and adjacent to it, contained ~49.5% Fe, ~33.3% Ti, ~13.2% Cr and ~3.5% Ni; hence these regions perhaps are the phase mixture of λ + FeTi. EPMA analysis of the slightly darker region adjacent to the nickel side of the SS–Ni interface (marked in Fig. 2e) indicated that the composition was ~32.9–33.3% Fe, ~50.1–52.3% Ti, ~5–5.21% Ni and ~10.4–11.9% Cr, which suggests that this region consists of a FeTi + λ + β-Ti phase mixture.

The shaded area has been observed at SS–Ni and Ni–Ti interfaces in nickel side, which consists of ~68.1–68.9% Ti and ~29.1–29.8% Ni with a small amount of ~0.2–0.3% Cr and ~1.1–1.4% Fe. This area is presumably the Ti_2Ni phase. The α-β Ti appears as a combination of bright needles and a dark matrix with the composition of ~92.4–97.1% Ti and 1.7–7.4% Ni with a very low quantity of Fe and Cr. The appearance of optical micrographs of Fig. 1d resembles a solidification structure. These areas appear to be the Ti_2Ni phase with discrete α-β Ti islands. The melting point of Ti_2Ni phase is 987 °C and Ti has melting point above 1600 °C. As in the present study diffusion bonds were processed at 900 °C temperature. The Ti_2Ni intermetallic melting temperature may be lowered due to the presence of Fe and Cr and the intermetallics might have been transformed in to mushy stage, leading to this type of microstructure. A similar type of microstructure in a solid-state diffusion bond between titanium and nickel processed at 850 °C was reported by Hinotani et al. [12].

From the backscattered electron micrographs, it is evident that the increased joining temperature promoted diffusion across the bond lines. The thicknesses of the Ti_2Ni, TiNi and $TiNi_3$ layers were ~2.6, ~6.3 and ~4.2 µm, respectively at 800 °C and increased to ~5.5, ~11.0 and ~5.4 µm, respectively at the 850 °C processing temperature. At the SS–Ni interface, the same trend was also

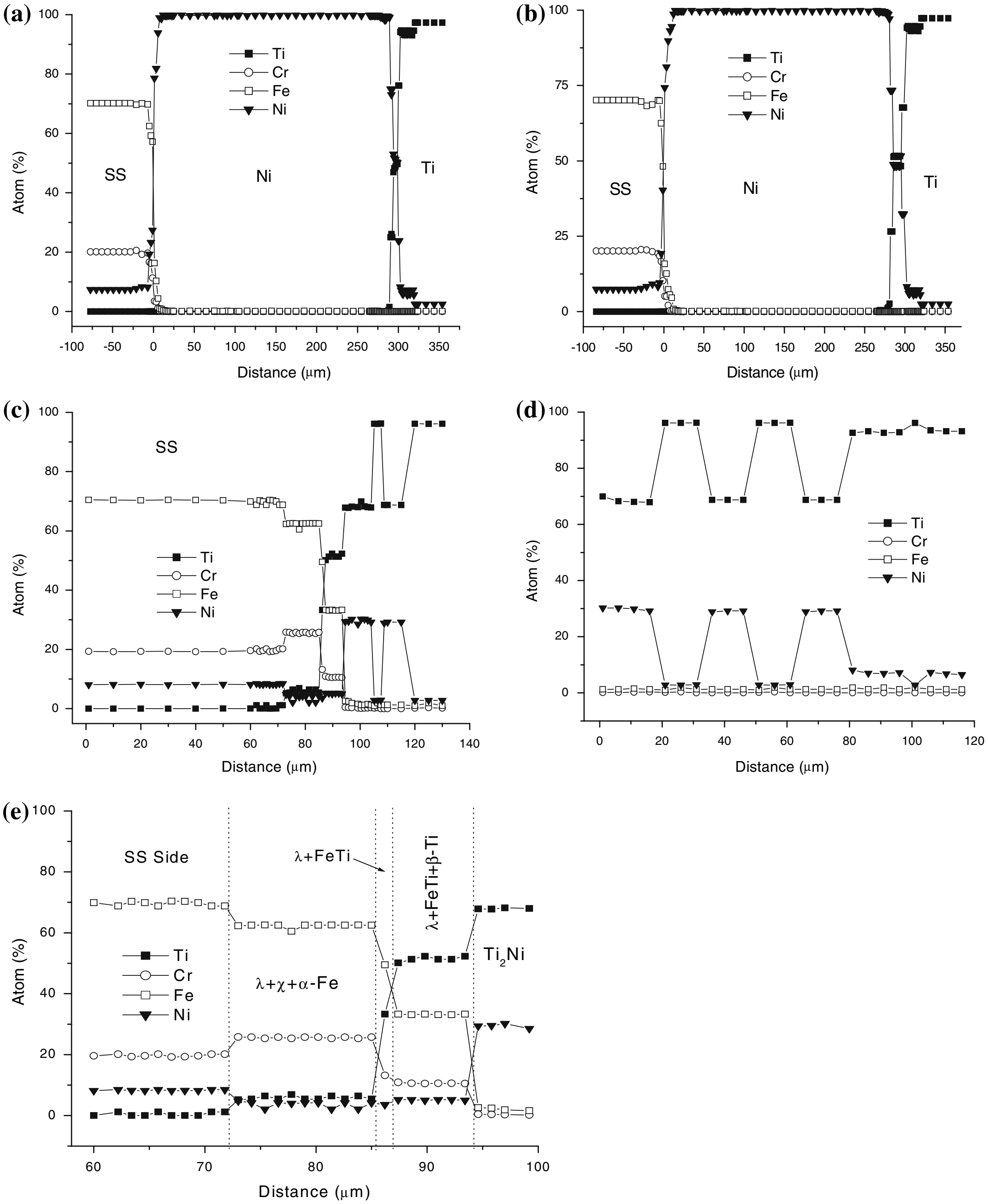


Fig. 3 Concentration profiles from EPMA analysis across the bond interfaces of the specimens bonded at: (**a**) 800 °C; (**b**) 850 °C; (**c**) 900 °C, SS–Ni interface; (**d**) 900 °C, Ni–Ti interface; (**e**) Enlarged view of 900 °C of SS–Ni interface

observed as the presence of Fe and Cr in the Ni matrix and enrichment of nickel in the stainless steel side increased at 850 °C in comparison to that at 800 °C. At the 900 °C bonding temperature, the thickness of the $\lambda + \chi + \alpha$-Fe, λ + FeTi and λ + FeTi + β-Ti phase mixture were ~15.7, ~2.2, and ~6.7 μm, respectively.

Figure 4 shows the x-ray diffraction analyses, which confirmed the presence of different intermetallics in the fracture interface. Up to 850 °C, the x-ray diffraction data confirmed the presence of intermetallics like Ti_2Ni, TiNi, $TiNi_3$, α-Ti and β-Ti phases in the reaction zone. However, at 900 °C, the x-ray diffraction data indicated the formation of reaction products of α-Fe, σ, χ, Fe_2Ti and Cr_2Ti. The absence of σ phase in SEM-BSE micrographs may be due to its small volume fraction and/or fine size. σ phase contains principally Fe and Cr, and is known to be a brittle phase. Ti migration in the stainless steel lattice decreases the activity of Cr [17]. Hence, diffusion occurs down the activity gradient rather than the concentration gradient. Cr enrichment occurs by uphill diffusion of the same and

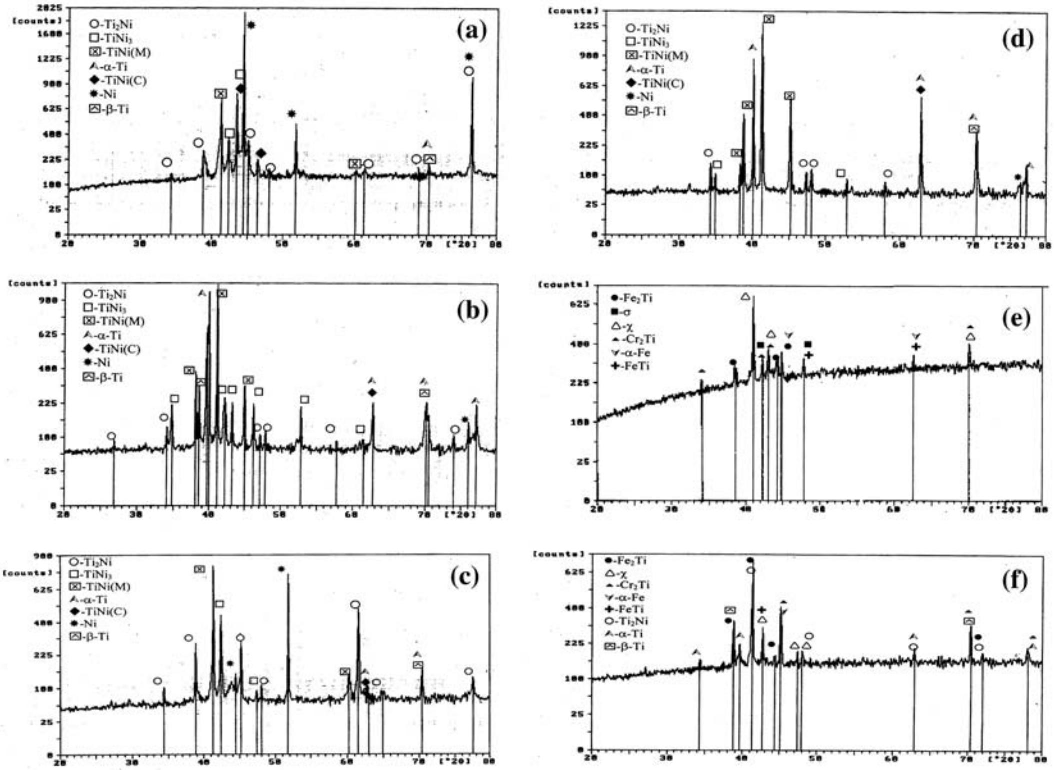


Fig. 4 X-ray diffraction analysis of the fracture surfaces of the couples bonded at: (**a**) and (**b**) 800 °C; (**c**) and (**d**) 850 °C; (**e**) and (**f**) 900 °C

during cooling the chromium enriched region transforms to σ phase [15]. The formation of α-Fe in stainless steel 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 [1].

The effects of bonding temperature on mechanical properties of the transition joints are shown in Table 3. For the 800 °C bonds, both tensile and shear strength of the transition joints are lower due to poor of contact between the mating surfaces. The low processing temperature results in a limited extent of diffusion of alloying elements at both interfaces. As the bonding temperature is increased to 850 °C, both the tensile and shear strength as well as fracture elongation are increased. At this processing temperature, contact between the mating surfaces apparently improves. In addition, the elevated temperature promotes the diffusivity of the solute elements, which, in turn, leads to the increase in the width of the reaction products at the Ni–Ti interface. Though the volume fraction of the Ni–Ti base intermetallics are maximum at 850 °C with respect to that at the 800 °C bonding temperature; however, the plastic collapse of the faying surface asperities may be responsible for increase in tensile properties and shear strength of transition joints. The ultimate tensile strength value reflects a substantial improvement of the bond quality (tensile and shear strength 87% and 70% of that of titanium, respectively) with respect to earlier reported values of directly joined of Ti and stainless steel [2, 8, 15].

A further increase in the bonding temperature to 900 °C sharply decreases both the bond strength and ductility of diffusion-bonded couples. At this bonding temperature, SEM-BSE images reveal that at Ni–Ti interface no layer-wise intermetallic is formed; yet, the SS–Ni interface is characterized by the presence of multiple phases including $\lambda + \chi +$ α-Fe, λ + FeTi and λ + FeTi + β-Ti phase mixtures. The brittle phase mixture degrades the bond quality. It can be inferred from the fracture location that Fe–Ti intermetallics are more detrimental in comparison to Ni–Ti

Table 3 Mechanical properties of the bonded specimens processed for 9 ks

Bonding temperature (°C)	Shear strength (MPa)	Tensile strength (MPa)	Fracture elongation (%)
800	154.3	211.7	4.7
850	209.5	276.5	7.3
900	147.2	204.2	4.3

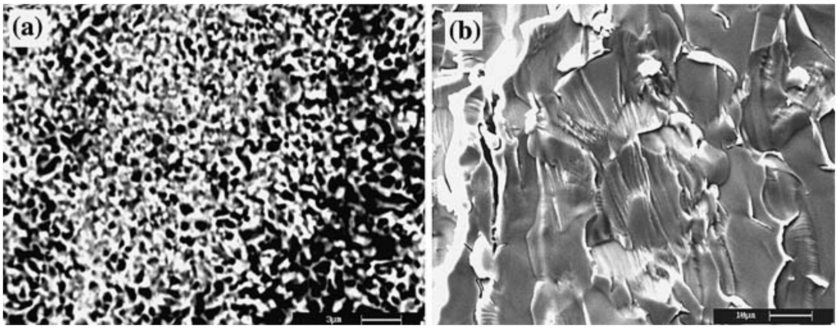


Fig. 5 Fracture surfaces of the bonded assemblies (**a**) SS side, 800 °C; and (**b**) SS side, 900 °C

intermetallics in decreasing bond strength of diffusion-bonded joints.

Fracture surfaces of bonded specimens are shown in Fig. 5. The facture surface of the specimen processed at low temperature (Fig. 5a) is basically featureless. The brightly imaging areas contained ~28.5–30.2% Ni and 69.4–71.5% Ti, suggesting the presence of Ti_2Ni. The dark area indicates the presence of voids. These irregular shaped voids may occur from the incomplete bonding of the mating surfaces, and will promote failure under the load. However, the volume fraction of dark area decreases with increasing the joining temperature due to better bonding of the mating surfaces.

Figure 5b clearly indicates the brittle nature of the transition joint by the presence of cleavage fracture. Some brightly-imaging second phase particles are also visible. Both the matrix (cleavage fracture) and brightly imaging features contain ~29.6–32.1% Fe, ~11.3–13.6% Cr, ~50.6–53.2% Ti and ~2–5% Ni; hence, this area may be a mixture of λ + FeTi + β-Ti.

Summary and conclusions

The solid-state diffusion bonding of commercially pure titanium to Type 304 stainless steel with a 300 μm nickel interlayer has been produced in the temperature range of 800–900 °C for 9 ks under 3 MPa uniaxial load in vacuum. Characterization of the transition joints reveals the following:

(1) The SS–Ni interface is free from reaction products for bonding temperatures up to 850 °C; however, at 900 °C, $\lambda + \chi + \alpha$-Fe, λ + FeTi and λ + FeTi + β-Ti phase mixtures are formed at the same interface.

(2) At the Ni–Ti interface, inter-diffusion between Ni and Ti promotes layer-wise formation of $TiNi_3$, TiNi and Ti_2Ni in the diffusion zone up to joining temperature of 850 °C; however, α-β Ti exists as discrete islands in the matrix of Ti_2Ni at 900 °C.

(3) Increased joining temperatures promote elemental diffusion across the bond lines; the 300 μm Ni interlayer can completely inhibit the diffusion of Ti into stainless steel up to 850 °C joining temperature. However, at 900 °C, titanium atoms can diffuse into the nickel matrix to form Fe–Ti base intermetallics at the stainless steel-nickel interface.

(4) A maximum shear strength of ~209 MPa and tensile strength of ~276 MPa along with 7.3% ductility have been obtained for the transition joint processed at 850 °C due to the improved coalescence of the mating surfaces; failure occurred at the Ni–Ti interface.

(5) At the higher joining temperature of 900 °C, the fracture occurs at the SS–Ni interface due to the formation of brittle Fe–Ti type intermetallics resulting in decrease in the bond strength.

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