1. Introduction

In recent years, there has been a strong interest to produce transition joints between micro-duplex stainless steel and titanium/titanium alloy by diffusion bonding technique for application. Titanium/titanium alloy has excellent corrosion resistance and high specific strength and finds potential application in processing units. On the other hand, micro-duplex stainless steel reveals austenite–ferrite structure with a good combination of strength and toughness, excellent corrosion resistance for medium temperature application and it has super-plastic behaviour at/about 1000°C during processing. Traditional fusion welding or mechanical joining of dissimilar materials promotes the distortion of components, formation of stress concentration sites and development of chemical heterogeneities, which result in crevice corrosion or fatigue failure during service.

The direct bonding between titanium/titanium alloy and stainless steel promotes the formation of various intermetallic compounds due to the limited solid-solubility of Fe, Cr, Ni and Ti in each other. Eroglu et al. reports that the diffusion bonding between micro-duplex stainless steel and Ti alloy was carried out at 900°C for 5–60 min at 23 to 100 K/min heating rate using a 20 μm thick Cu interlayer and maximum shear strength of ~107 MPa was achieved.

In the present study, solid-state direct bonding was carried out between commercially pure titanium and micro-duplex stainless steel and the interlayer was not used to avoid the difficulty of fabrication technique; rather the processing temperature was varied to obtain a good combination of strength and ductility. The present study also envisages the formation of various intermetallics at the bond interface, as a function of processing temperature with a focus on the effect of thickness of intermetallics on the bond strength of the joint.

2. Experimental

The commercially pure titanium (Ti) and micro duplex stainless steel (MDSS) used in the present investigation, were in the form of 35 mm diameter rod in hot rolled condition. The chemical composition of commercially pure titanium is Ti–0.02C–0.10Fe–0.15O–0.02N–0.0011H (wt%) and that of MDSS is Fe–0.05C–0.7Mn–0.37Si–0.005S–0.02P–26.5Cr–5.0Ni–0.05N (wt%). The optical micrographs and X-ray diffraction of the base materials are given in Fig. 1. Commercially pure titanium has α (hcp) structure and the micro-duplex stainless steel has austenite (fcc) along with ferrite (bcc) phase mixture. 30 mm long and 15 mm diameter cylindrical samples were machined from 35 mm diameter rods parent metals. Mating surfaces of the samples were prepared by conventional polishing technique with 1 μm diamond paste, cleaned in acetone and dried in air. The polished surfaces of Ti and MDSS were kept in contact in a fixture and the assembly was inserted in a chamber. The transition joints were prepared in the temperature range of 800 to 1000°C in steps of 50°C for 3.6 ks in (6–8)×10⁻⁴ Pa vacuum under the uniaxial load of 3 MPa. Load was applied along the longitudinal direction of the as-
Assemblies. During processing, heating rate was 0.24°C s\(^{-1}\) and after processing, the samples were cooled in vacuum at a cooling rate of 0.1°C s\(^{-1}\).

From the bonded couples, a transverse section was taken and prepared by usual grinding and polishing techniques. The microstructure in the reaction zone was revealed in a light microscope. The polished samples were also examined in a Scanning Electron Microscope (Leica S440) using backscattered (BSE) mode to exhibit finer structural details in the diffusion zone of the bonded couples. The electron probe microanalyser (CAMECA Sx 100) was used to get the elemental concentration profiles across the diffusion interfaces. The \(K\alpha\) lines of Ti, Fe, Ni and Cr are generated at an operating voltage of 15 kV and specimen current of \(12 \times 10^{-8}\) A. The LiF crystal was used to diffract the corresponding characteristic X-ray radiation. A set of bonded assemblies was fractured under shearing force and the reaction products on both sides of the fracture surfaces were identified by an X-ray diffractometer. A Cu target was used at an operating voltage of 40 kV, with sample current of 20 mA and step height of 0.02° (= 2\(\theta\)) during diffraction study. Tensile properties of the transition joints were evaluated in a universal testing machine (Instron 4204) at a crosshead speed of 8.33\( \times 10^{-3}\) mm s\(^{-1}\) 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 and tensile test was carried out in longitudinal direction of bonding. The interface was at the centre of the gauge length. Shear strength of bonded joint was also evaluated at room temperature in transverse direction using a screw tensile testing machine set at a crosshead speed of 8.33\( \times 10^{-3}\) mm s\(^{-1}\). Shear test specimens were machined to a diameter of 10 mm. The joint position of the specimen was at the centre of the two jaws. The design of the jaws is given in Fig. 2. Four samples were tested at each process parameter to check the reproducibility of results. Fracture surface of the samples were observed in secondary electron mode in SEM using energy dispersive spectroscopy to reveal the nature and location of failure under tensile loading.

Fig. 1. Characteristics of the base metals: (a) optical micrograph of titanium, (b) optical micrograph of MDSS, (c) XRD patterns.

Fig. 2. Schematic diagram of shear jaws.
3. Results and Discussion

The optical micrographs of the bonded joints at varying bonding temperatures are shown in Figs. 3(a) and 3(b). The diffusion zone of the bonded joints is clearly visible without any discontinuity. The extreme left side of the bonded joints indicates austenite with ferrite of the parent microduplex stainless steel. The heavily etched region next to the stainless steel is the combination of different intermetallic layers. Next to the heavily etched region, the unetched region is stabilized β-Ti and the combination of bright and shaded area is α–β Ti. However, at 800°C processing temperature, unetched stabilized β-Ti and α–β Ti have not been observed in optical micrographs. The β-stabilizing elements (Fe, Cr and Ni) migrate in titanium lattice, suppress the transformation temperature of titanium and the acicular nature of α–β Ti occurs from the decomposition into β-Ti during cooling.9,10)

The heavily etched regions of optical micrographs have been resolved in SEM-BSE images and are given in Figs. 3(c)–3(f). The EPMA concentration profiles of the alloying elements across the bond interface are shown in Fig. 4. Composition of the reaction layers by point analysis from EPMA are given in Table 1. The bright reaction layer has been observed in stainless side, which is the phase mixture of α-Fe + λ. Close to the α-Fe + λ phase mixture, a light shaded region is the phase mixture of λ + FeTi + β-Ti. At 800°C bonding temperatures, the λ + FeTi + β-Ti phase mixture has not been observed presumably due to the presence of lower volume fraction. The phase mixture predicted from the EPMA point analysis is obtained by comparing the concentration of alloying elements with the ternary isotherm of Fe–Cr–Ti at 800 to 1 000°C and the effects of Ni and Mn are ignored, as their concentration is low enough to form any intermetallics in combination with Fe, Cr and Ti in the present investigation.11) The wide shaded regions in the titanium side of all bonded assemblies are the stabilized β-Ti. The irregular shaped dark micro-voids are also observed at the diffusion zone of the diffusion bond for 950°C and above processing temperatures (shown by the arrows in Figs. 3(d)–3(f)). Hinotani et al. and Orhan et al. reports that the presence of such voids also occur for the diffusion couples of titanium–nickel and microduplex stainless steel–titanium alloy when processing was done at 700–800°C and 800°C, respectively.12,13) The inter diffusion coefficient of α-Fe ($D_{\alpha-Fe}=5\times10^{-15}\text{m}^2\text{s}^{-1}$) and γ-Fe ($D_{\gamma-Fe}=3\times10^{-17}\text{m}^2\text{s}^{-1}$) are smaller than that of Ti ($D_{Ti}=5.5\times10^{-14}\text{m}^2\text{s}^{-1}$) at 900°C. The presence of voids produced by the kirkendall effect has been reported for diffusion bonded Ti–Ni couple.14) So, diffusion of titanium is
faster than that of iron, which produces imbalance in mass flow across the interface and generates voids.

The X-ray diffraction studies confirmed the presence of different phases in the sheared fracture surfaces and are given in Fig. 5. The diffusion zone contains \( \sigma \) phase, Fe\(_2\)Ti, FeTi, Cr\(_2\)Ti, \( \chi \), \( \alpha \)-Fe, \( \alpha \)-Ti and \( \beta \)-Ti. X-ray diffraction study also exhibits the formation of the \( \sigma \) phase but it could not be observed in SEM images due to its low volume fraction. The \( \sigma \) phase principally contains Fe and Cr. In an earlier investigation of diffusion bonding of a micro-duplex stainless steel to Ti–6Al–4V, Orhan et al. observed that the formation of the \( \sigma \) phase did not occur up to 950°C processing temperature and reported that higher heating rate probably contributes to the retarding effect of nucleation of the \( \sigma \) phase within the bond interface.\(^ {15} \) In the present study slow heating rate may be responsible for the formation of the \( \sigma \) phase.

The width of the different reaction products with the increase in bonding temperature is given in Fig. 6. Increase in the joining temperature drives more number of atoms to migrate across the interface, which is responsible for the widening of the reaction layers. Assuming the growth of individual layer to be parabolic, as it is considered to be diffusion controlled and taking the overall thickness in consideration, the growth can be expressed by the relations of

**Fig. 4.** EPMA concentration profiles across the bond interfaces of the specimens bonded at (a) 900°C, (b) 1000°C.

**Fig. 5.** X-ray diffraction analysis of the fracture surfaces of the specimen bonded at 950°C.

**Fig. 6.** Width of phase and phase mixture formed at bond interface for varies temperatures constant holding time.

<table>
<thead>
<tr>
<th>Reaction Products</th>
<th>Elements (at%)</th>
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<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>( \alpha )-Fe+( \chi )</td>
<td>51.9-54.6</td>
</tr>
<tr>
<td>( \chi )-FeTi+( \beta )-Ti</td>
<td>31.4-34.3</td>
</tr>
<tr>
<td>( \beta )-Ti</td>
<td>10.9-14.4</td>
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**Table 1.** EPMA chemical analysis of the reaction products formed at the joint interfaces.
$X^2 = k t$ and $k = k_0 \exp(-Q/RT)$. Where, $X$ is the thickness of the reaction layer (m), $t$ is time of the bonding (s), $T$ is bonding temperature (Kelvin), $k$ is growth velocity of the reacting layer (m$^2$s$^{-1}$), $k_0$ is growth constant (m$^2$s$^{-1}$), $Q$ is activation energy for layer growth (kJ mol$^{-1}$), $R$ is real gas constant (8.314 J mol$^{-1}$K$^{-1}$). Activation energy ($Q$) of α-Fe + λ, λ+FeTi+β-Ti and β-Ti phase or phase mixture are 76.5, 161.9, 134.1 kJ mol$^{-1}$, respectively and growth constant ($k_0$) values of that phase and phase mixture are $3.1 \times 10^{-5}$, $1.5 \times 10^{-2}$, $9.1 \times 10^{-3}$ m$^2$s$^{-1}$, respectively. The growth rate of λ+FeTi+β-Ti phase mixture is faster than that of the other phase or phase mixture.

The room temperature shear strength and tensile properties of the diffusion bonded joints are given in Fig. 7. At 800°C processing temperature, the shear strength and tensile strength of the bonded joint are 126.6 MPa and 175.8 MPa, respectively. With the increase in bonding temperature both shear strength and tensile strength of the bonded joints are increased and reached a maximum values at 900°C. At lower processing temperature bond strength is minimum due to the lack of contact between the mating surfaces, as the yield stress of the material still remains high. Contact between the mating surfaces of the diffusion bonded joints increases with the increase in bonding temperature. The fracture morphology of the diffusion bonded joints processed at 800°C (Fig. 8(a)) shows that the dark regions indicate the presence of voids. These voids occur due to the lack of coalescence of the mating surfaces and promote the failure under loading. The volume fraction of dark area reduces with the increase in bonding temperature. Dark and bright areas indicate the presence of Ti (~84.2–88.3), Fe (~10.9–14.4) Cr (~3.5–4.3) and Ni (bal.). Hence, the composition is of β-Ti phase. The maximum tensile strength and shear strength of diffusion bonds are 309.1 MPa and 236.3 MPa, respectively. This processing temperature promotes the atomic diffusivity of the chemical species, which is accountable for the increase in width of the reaction products in the diffusion zone. However, with the increase in joining temperature, the amount of mass transfer occurs due to higher thermal excitation which results in stronger atomic bonding and larger plastic collapse of the mating surfaces with respect to lower processing temperature. Effect of void on strength properties of bond is minimum because at that processing temperature generation of void is less.

With a further increase in the bonding temperature to 950°C and above, the contact between the mating surfaces increases with respect to lower bonding temperatures. However, the width of the reaction products increases significantly (Fig. 6) and the embrittlement effect due to the formation of larger volume fraction of brittle intermetallics overcompensates the positive gain obtained from the increase in coalescence of mating surfaces and moreover provides some negative effect. So, the bond strength gradually drops and attains the lowest value at 1000°C processing temperature (tensile and shear strength are 179.3 and 245.1 MPa, respectively). The maximum micro-hardness is obtained at the diffusion interface of transition joints in comparison to base materials and the hardness value increases with the increase in bonding temperature due to the embrittlement effect (Fig. 9). The fracture surfaces at 950°C processing temperature, clearly indicates the brittle

![Fig. 7. Shear strength and tensile properties of the diffusion bonded joints processed for 3.6 ks.](image)

![Fig. 9. Micro-hardness analyses of the diffusion joints processed for 3.6 ks.](image)

![Fig. 8. Fracture surface of the bonded assemblies processed at (a) 800°C SS side, (b) 950°C SS side.](image)
nature of the transition joint by the presence of cleavage planes which are given in Fig. 8(b). The bright and shaded regions are $\lambda+\text{FeTi}+\beta$-Ti with the composition of Fe ($\sim 32.1–35.2$), Ti ($\sim 51.1–52.2$), Cr ($\sim 11.3–14.1$) and Ni (bal.).

4. Summary and Conclusions

Solid-state diffusion bonds of commercially pure titanium and micro-duplex stainless were produced in the temperature range of 800–1000°C under 3 MPa load for 3.6 ks in vacuum. The maximum bond strength (tensile strength of $\sim 309$ MPa and shear strength of $\sim 236$ MPa) along with 6.9% ductility has been obtained at 900°C bonding temperature due to the formation of reaction products of finer width and formation of less micro-void at diffusion zone. The $\alpha$-Fe+$\lambda$, $\lambda$-FeTi$+\beta$-Ti and $\beta$-Ti phases or phase mixtures are formed at the diffusion interface and their width increase with the increase in the joining temperature due to the increase in inter-diffusion of chemical species. The activation energy and rate constant were determined for the growth of reaction layers and the values become maximum for the $\lambda$-FeTi$+\beta$-Ti phase. Fracture surface at low joining temperatures is featureless; however at higher joining temperatures the existence of cleavage pattern indicates the brittle nature of the joints. Failure takes place through $\beta$-Ti phase, when bonding was processed up to 850°C, however, failure takes place through $\lambda$+FeTi+$\beta$-Ti for the diffusion couples processed at 900°C and above bonding temperature.

REFERENCES

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