

# Microstructure and bonding strength of titanium-to-stainless steel joints brazed using a Zr–Ti–Ni–Cu–Be amorphous filler alloy

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Received: 1 September 2010 / Accepted: 13 September 2010 / Published online: 23 September 2010  
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## Introduction

Titanium (Ti) is the material of choice for demanding corrosive environments such as in the power generation and chemical processing industries [1]. With the expanding use of Ti, there is a great demand for joining of Ti to more commonly used stainless steels (STS) [2]. However, fusion welding of Ti to STS readily causes a severe thermal cracking or distortion due to the large difference in their physical properties [3, 4]. So, considerable interest has been given to brazing of Ti to STS in recent years, since brazing eliminates the problems that occur when dissimilar substrates are fused [4–6].

Nevertheless, there are two major problems in Ti–STS dissimilar brazing. First, brittle intermetallic compounds (IMCs) such as  $Ti_xFe_y$ ,  $Ti_xCu_y$ , and  $Ti_xNi_y$  are frequently formed, especially at the interface between the substrates and the filler after brazing [6–8]. Although there have been many studies on a dissimilar brazing of Ti to STS using several Ag-based fillers, most of the joints have revealed poor bonding strengths (usually less than 100 MPa) due to the formation of such brittle IMCs [1–8]. The higher the brazing temperature is, the more intensive reaction occurs among the substrates and the filler, and consequently, thicker intermetallic layers may be formed at the interface,

thereby resulting in a significant deterioration in the bonding strength of the Ti–STS dissimilar joint [6, 7]. Consequently, a low brazing temperature is desirable to minimize the intermetallic formation in Ti–STS dissimilar brazing. Second, the natures of Ti and STS determine important temperature limits of brazing cycles. Heating Ti above its  $\alpha \leftrightarrow \beta$  transformation temperature will induce excessive grain growth of Ti and the mechanical properties of Ti will be impaired [9, 10]. Also, it is crucial for STS to avoid sensitization during brazing. As STS is heated above its sensitization temperature, huge chromium carbides will be precipitated along the grain boundaries and the consumption of the chromium content may result in loss of corrosion resistance of STS [11, 12]. Therefore, it is required that brazing temperature should not exceed both the  $\alpha \leftrightarrow \beta$  transformation temperature of Ti and the sensitization temperature of STS in Ti–STS dissimilar brazing.

In our previous study, a Zr–Ti–Ni–Cu–Be amorphous alloy was successfully applied as a filler for the low temperature brazing of Ti [13]. Since this alloy has a quite low melting temperature of 725 °C, it was able to braze Ti effectively at a considerably low temperature range (below 800 °C). Furthermore, this amorphous alloy can be produced easily in a thin ductile ribbon form with a quite homogeneous composition, resulting in joint properties unattainable for crystalline fillers in powder or clad strip form [14, 15]. The purpose of this investigation is focused on the possible application of the Zr–Ti–Ni–Cu–Be amorphous alloy as a filler for the low temperature brazing between dissimilar Ti and STS. The related microstructure and the bonding strength of the Ti–STS brazed joints with the Zr-based amorphous filler were comprehensively studied with regard to the brazing temperature.

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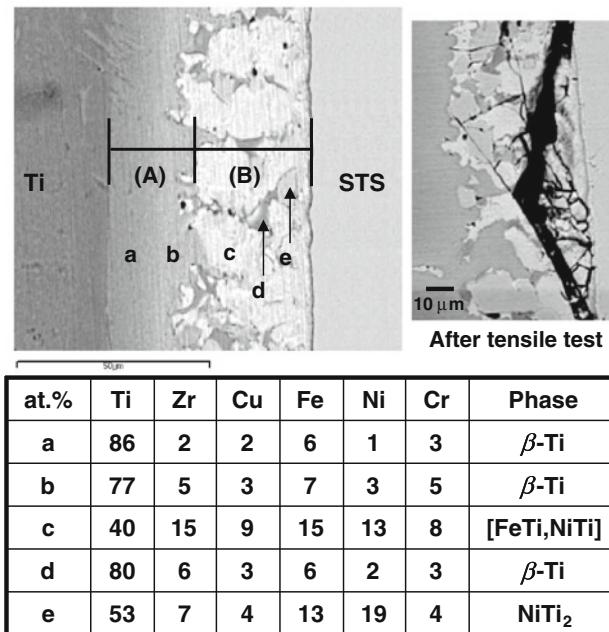
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## Experimental

Square rods of Ti (Gr.2) and STS (UNS S31254) with a size of  $10 \times 10 \times 15$  mm were used as the substrates in this study. UNS S31254 was a super STS containing 20Cr–18Ni–6Mo (wt%). A Zr<sub>41.2</sub>Ti<sub>13.8</sub>Ni<sub>10.0</sub>Cu<sub>12.5</sub>Be<sub>22.5</sub> (at.%) alloy ribbon with the thickness of 50  $\mu\text{m}$ , width of 7 mm and length of 10 mm was used as a filler material. Infrared brazing was performed in a temperature range of 750–900 °C for 10 min. Prior to brazing, the infrared chamber was pre-vacuumed and then a constant (4 L/min) flow of argon was supplied during brazing. The heating and cooling rates were maintained constant at 100 °C/min throughout the experiment. After brazing, the cross-section of the brazed specimens was examined using a scanning electron microscope (SEM) and quantitative chemical analysis was performed using an energy dispersive spectroscope (EDS) in an SEM. In order to evaluate the bonding strength of the Ti–STS dissimilar joint, seven tensile test specimens for each brazing condition were machined with a gauge length of 10 mm, and the room-temperature tensile tests were conducted at a strain rate of  $8.3 \times 10^{-4} \text{ s}^{-1}$ . After the tensile tests, the cross-sectional areas adjacent to the fractured surfaces were investigated using an SEM.

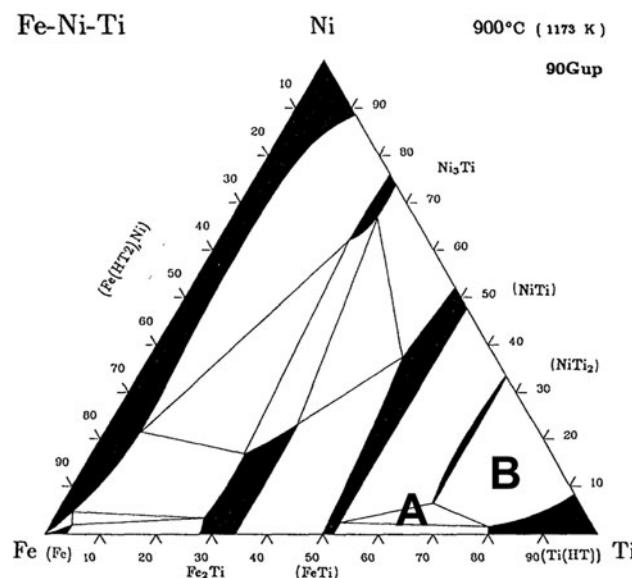
## Results and discussion

Figure 1 shows the SEM back-scattering electron image (BEI) and EDS chemical analysis results of the Ti–STS dissimilar joint brazed at 800 °C for 10 min. The joint consists of two distinctive regions as indicated by (A) and (B) in Fig. 1. (A) is the  $\beta$ -Ti phase region and (B) is composed of  $\beta$ -Ti and NiTi<sub>2</sub> phases dispersed in a [FeTi,NiTi] matrix. From the experimental observation, the dissolution of the Ti substrate was more prominent than that of the STS substrate. At the beginning of brazing, the Ti substrate was dissolved by the molten Zr–Ti–Ni–Cu–Be filler with a dilution of the filler elements. Then, the isothermal solidification was initiated from the Ti substrate because a liquidus of the liquid at the solid/liquid (S/L) interface was increased to the brazing temperature. As the brazing proceeded, the isothermal solidification was continued by the diffusion of the molten filler elements into the Ti substrate. This diffusion phenomenon could be confirmed from the decreasing brightness from the joint center to the Ti substrate in the BEI (a, b in Fig. 1). The primary phase solidified isothermally from the Ti substrate was the  $\beta$ -Ti and this  $\beta$ -Ti layer still remained at room temperature after subsequent cooling ((A) in Fig. 1), since the Ni, Cu, and Fe elements diffused into the Ti substrate are the  $\beta$ -Ti stabilizers. Since the dissolution of the Ti substrate was

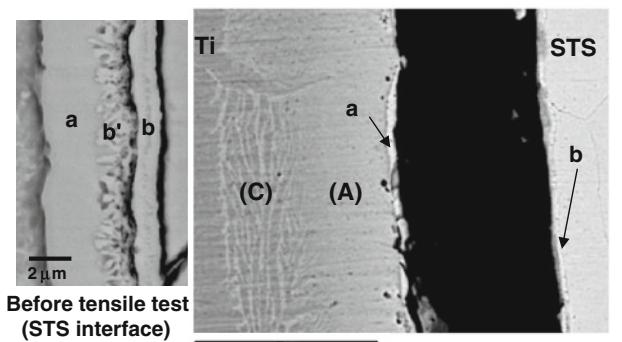


**Fig. 1** SEM BEI and EDS chemical analysis results of the Ti–STS dissimilar joint brazed using a Zr–Ti–Ni–Cu–Be amorphous filler at 800 °C for 10 min

prominent, the remaining region (B) of the joint became rich in Ti during brazing. In the ternary phase diagram of the Ti–Fe–Ni system [16], the equilibrium field comprising three phases of [FeTi,NiTi], NiTi<sub>2</sub>, and  $\beta$ -Ti exists in the Ti-rich corner (A in Fig. 2) and this equilibrium is well coincident with the microstructure of the region (B) in Fig. 1. As the primary [FeTi,NiTi] phase nucleated and started to grow in the region (B) by the reaction of



**Fig. 2** Isothermal section of Fe–Ni–Ti equilibrium ternary phase diagram at 900 °C



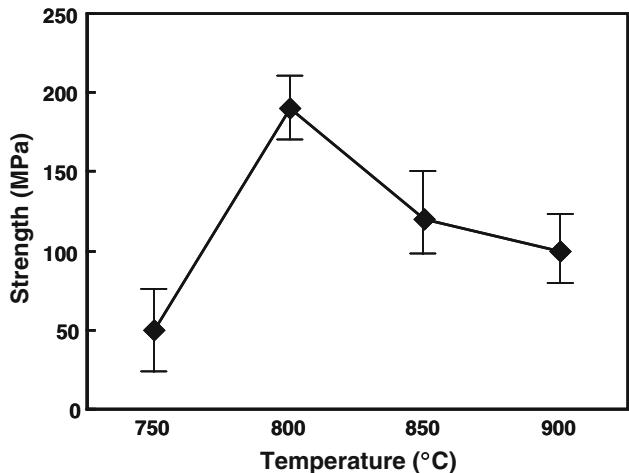
Before tensile test (STS interface)

| at.% | Ti | Zr | Cu | Fe | Ni | Cr | Mo | Phase                |
|------|----|----|----|----|----|----|----|----------------------|
| (C)  | 96 | -  | 1  | -  | 3  | -  | -  | $(\alpha+\beta)$ -Ti |
| (A)  | 82 | 3  | 3  | 6  | 3  | 3  | -  | $\beta$ -Ti          |
| a    | 60 | 8  | 2  | 15 | 12 | 4  | -  | $\text{NiTi}_2$      |
| b    | 13 | -  | -  | 44 | 5  | 34 | 4  | $\sigma$             |
| b'   | 4  | -  | -  | 47 | 7  | 36 | 6  | $\sigma$             |

**Fig. 3** SEM BEI and EDS chemical analysis results of the Ti–STS dissimilar joint brazed using a Zr–Ti–Ni–Cu–Be amorphous filler at 850 °C for 10 min

dissolved Ti and (Fe,Ni) from each substrate, the excessive Ti should be expelled from the [FeTi,NiTi] phase and then the  $\text{NiTi}_2$  and  $\beta$ -Ti phases were formed at the intercellular regions as shown in Fig. 1.

The microstructure of the Ti–STS dissimilar joints brazed with the Zr–Ti–Ni–Cu–Be amorphous filler was significantly changed for the increased brazing temperature. As shown in Fig. 3, the region (B) that had been observed in Fig. 1 disappeared completely when the brazing temperature was increased to 850 °C. As described above, the isothermal solidification of the  $\beta$ -Ti phase took place during brazing by the diffusion of the molten filler elements into the Ti substrate. At the elevated brazing temperature of 850 °C, the isothermal solidification might be accelerated by the enhanced diffusion of Ni, Cu, and Fe elements in the Ti substrate. Consequently, the isothermal solidification could be terminated during brazing when the front of the solidified  $\beta$ -Ti phase encountered the STS substrate at this brazing temperature. At this moment, the region (B) that had been observed in Fig. 1 disappeared completely and the joint only consisted of the isothermally solidified  $\beta$ -Ti phase as shown in Fig. 3. After the initiation of the isothermal solidification of  $\beta$ -Ti phase, a  $(\alpha + \beta)$ -Ti reaction zone ((C) in Fig. 3) was also produced by a solid-state interdiffusion reaction between the  $\beta$ -Ti phase and the Ti substrate at this temperature [17]. At the STS interface, two thin and continuous layers can be observed as indicated by a and b in Fig. 3. When the isothermally solidified  $\beta$ -Ti phase encountered the STS substrate, it can be deduced from the Ti–Fe–Ni ternary diagram (B in Fig. 2)



**Fig. 4** Relation between average tensile strength of the joint and brazing temperature

[16] that the  $\text{NiTi}_2$  phase (a in Fig. 3) was formed by the interfacial reaction between the  $\beta$ -Ti phase and the STS substrate. In addition, the  $\sigma$  phase is formed frequently at the Ti–STS dissimilar interface at high temperatures [18]. When the Ti atoms diffused into the STS substrate, the activity of the Cr element might be decreased in the STS substrate, and then the uphill diffusion of the Cr element occurred toward the interface. As a result, the continuous  $\sigma$  phase layer (b and b' in Fig. 3) was formed along the STS interface by the cooling of such the Cr-enriched region [19].

The variations in tensile strength of the Ti–STS dissimilar joints with the change in brazing temperature are shown in Fig. 4. It is obvious that the average tensile strength of the joints is decreased upon increasing the brazing temperature from 800 to 900 °C. The specimen brazed at 800 °C for 10 min demonstrates the highest tensile strength, up to 190 MPa. However, the average tensile strength of the joint is as low as 100 MPa for the specimen brazed at 900 °C for 10 min.

It is expected that the presence of interfacial IMCs is detrimental to the bonding strength of the joints. Furthermore, the species and morphologies of IMCs in the joint have a strong effect on its bonding strength. As shown in Fig. 3, the feature in the joint brazed at 850 °C was located at the interface between the joint and the STS substrate. The interfacial reaction of the STS substrate was not prominent as compared to that of the Ti substrate, but it greatly deteriorated the bonding strength of the joint. It is deduced that the presence of the  $\text{NiTi}_2$  and  $\sigma$  phases, which was formed continuously along the STS interface, was detrimental to the tensile strength of the joint. On the other hand, the fracture location was shifted to the joint area ((B) in Fig. 1) when the brazing temperature was decreased to

800 °C. At this brazing temperature, no interfacial reaction compound was formed at the STS interface, but the joint was composed of the intercellular  $\beta$ -Ti and NiTi<sub>2</sub> phases dispersed in the [FeTi,NiTi] matrix as shown in Fig. 1. This microstructure of the joint might cause a homogeneous distribution of a stress and a considerable crack deflection during loading, which resulted in a high bonding strength [20]. When the brazing temperature was decreased further to 750 °C, however, the bonding strength of the joint was greatly impaired. It is expected that several defects like pores were formed at the STS interface owing to the insufficient reaction of the STS substrate with the molten filler at 750 °C. And these defects were applied as the initiation sites of a permanent crack at a low stress level, inducing a poor bonding strength of 50 MPa.

## Conclusions

Ti and STS have been brazed at a low temperature of 800 °C using a Zr–Ti–Ni–Cu–Be amorphous filler. At the brazing temperature of 800 °C, the joint was composed of the intercellular  $\beta$ -Ti and NiTi<sub>2</sub> phases dispersed in the [FeTi,NiTi] matrix. This microstructure of the joints resulted in the highest tensile strength of 190 MPa. As the brazing temperature was increased from 800 to 900 °C, however, the interfacial NiTi<sub>2</sub> and  $\sigma$  phases were formed continuously along the STS interface. In this case, the fracture occurred catastrophically along the brittle IMCs and the bonding strength of the joints was as low as 100 MPa.

**Acknowledgements** This research was supported by the Ministry of Knowledge Economy (MKE) and the Ministry of Education, Science and Technology (MEST), Korea.

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