# DIFFUSION BRAZING OF TITANIUM AND ZIRCONIUM ALLOYS USING MULTI-COMPONENT AMORPHOUS FILLER MATERIALS

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### Abstract

In this study, Zr-base amorphous alloy materials with multi-component eutectic composition were introduced as a filler to braze the Ti and Zr alloy. Different types of filler including its particulate, ribbon-shaped, and sputter-coating forms were used to examine the feasibility for practical application to the components. By using the Zr-base amorphous alloy filler, the brazing temperatures could be reduced down to  $800 \sim 900^{\circ}$ C, which is less than the beta transus of Ti and Zr (about  $900^{\circ}$ C). The joints produced by controlling the diffusion brazing conditions were characterized in terms of the structure and mechanical properties.

## 1. Introduction.

Amorphous alloy materials are finding a variety of applications to the structural materials owing to their excellent mechanical, corrosion, and magnetic properties [1]. In spite of their potential advantages and commercial interest, however, their practical applications for structural materials are quite limited owing to their high production cost and lack of ductility.

In search of their practical application, a feasible approach might be the brazing filler metal (BFM), particularly by using their unique properties such as considerably low-melting-point and narrow-melting-range characteristic, excellent compositional homogeneity, and compatibility with the base metals [2]. Moreover, amorphous filler materials for brazing can be readily produced with various forms, i.e. powder, ribbon or foils, coating, etc., by using the conventional rapid solidification techniques (e.g. gas atomization, melt spinning, deposition).

In this study, two different amorphous alloys based on the multi-component eutectic composition, i.e. Zr-Ti-Ni-Cu-Be [3] and Zr-Ti-Ni-Cu [4], which had been developed for the bulk metallic glasses (BMGs), were introduced to braze the Ti and Zr alloy. Three types of the filler, i.e., powder, ribbon, and coating, were used, depending on the shape of the target components. The structure and mechanical properties of the produced joints were investigated.

# 2. Experimental

The base material used in this study was commercially pure Ti (ASTM grade 2; 0.01N-0.01C-0.0001H-0.1O-0.06Fe-bal.Ti, wt.%) and Zircaloy-4 (1.38Sn-0.1Cr-0.2Fe, wt.%). The specimens for brazing were machined into rectangular cubes with dimensions of 10 mm x 10 mm x 15 mm, and their surfaces to be joined were polished and cleaned ultrasonically in ethanol and acetone. Two different compositions of the filler alloys were used as described in Table 1.

Table 1 – Chemical compositions and melting characteristics of the amorphous filler alloys used.

Filler alloy	Elemental composition (at.%)					Melting characteristic	
	Zr	Ti	Ni	Cu	Be	T <sub>s</sub> (°C)	T <sub>1</sub> (°C)
No. 1	41.2	13.8	10.0	12.5	22.5	665	725
No. 2	47.6	19.9	17.4	15.1		785	820

The powders with the spherical diameter of about 50  $\mu$ m were prepared by the gas atomization technique (Fig. 1 (a)). The ribbons with the width of 20 mm and the thickness of 50-60  $\mu$ m were fabricated by the melt spinning technique (Fig. 1 (b)). The coatings with the thickness of 36  $\mu$ m were prepared by sputtering its crystalline bulk target fabricated by the vacuum arc melting (Fig. 1 (c)).

An infrared brazing technique was used to join the Ti and Zircaloy-4 base metals, and the conditions were described elsewhere [5,6]. The as-joined samples were subjected to chemical etching in a solution of 10 mL HF, 45 mL HNO<sub>3</sub>, and 45 mL H<sub>2</sub>O for microscopic analyses. The structure and quantitative chemical compositions of the joints were investigated by SEM and EDS analyses. The mechanical strengths of the joints were evaluated at room temperature by means of a tensile testing machine (INSTRON MODEL 3382) at a strain rate of  $8.3 \times 10^{-4} \text{ sec}^{-1}$ .



Fig. 1 - Three different amorphous filler alloys: (a)  $Zr_{41.2}Ti_{13.8}Ni_{10.0}Cu_{12.5}Be_{22.5}$  powders, (b)  $Zr_{41.2}Ti_{13.8}Ni_{10.0}Cu_{12.5}Be_{22.5}$  ribbons, and (c)  $Zr_{47.6}Ti_{19.9}Ni_{17.4}Cu_{15.1}$  sputter coating.

#### 3. Results and discussion

Both the powdered and ribbon forms of  $Zr_{41.2}Ti_{13.8}Ni_{10.0}Cu_{12.5}Be_{22.5}$  (at.%) bulk metallic glass alloy were applied for the filler of brazing pure Ti Gr.2. The pure Ti was successfully brazed at low-temperatures below 820 °C by employing this amorphous alloy filler. For the joint brazed at 780°C for 10min, the joint formed acicular  $\alpha$ -Ti grains with a continuously segregated region, identified as  $[Ti,(Zr)]_2(Cu,Ni)$  phase, in the central area, while the completely isothermalsolidified joint at 820°C for 10min consisted of only the acicular  $\alpha$ -Ti grains over the joint without segregation (Fig. 2 (a) and (b)). According to the room temperature tensile tests, it was notable that the fracture did not occur in the joint but in the Ti base metal for the joints without the brittle segregation region, indicating that the mechanical strengths of the joints exceeded the bulk strength value (~390MPa) of the Ti Gr. 2 (Fig. (c)).



Fig. 2 - Cross-sectional SEM images for the pure Ti joints brazed at (a) 780°C, 10 min, (b) 820°C, 10 min, and (c) stress-strain curves obtained by a room temperature tensile test.

For the filler of brazing Zircaloy-4, the homogeneous and amorphous-structured Zr-Ti-Cu-Ni coatings were obtained by sputtering an as-casted crystalline  $Zr_{47.6}Ti_{19.9}Ni_{17.4}Cu_{15.1}$  bulk target. Together with the composition nearly consistent with that of the target, the coating was highly uniform in elemental composition distributions for both the surface and cross-section. The DSC analyses revealed almost the same melting characteristic as that of the bulk target, where the solidus and liquidus temperatures were 770 °C and 815 °C, respectively. In the application of amorphous Zr-Ti-Cu-Ni sputter-coatings for a brazing of Zircaloy-4, the joint typically had a segregation in its central region at  $T_B$  below 870 °C due to the solidification from the remaining liquid filler at  $T_B$  (Fig. 3 (a)). The segregation was primarily crystallized into the particular  $Zr_2(Cu,Ni)$  intermetallic compound. On the contrary, the joint produced at  $T_B = 890$  °C (Fig. 3 (b)) was predominantly comprised of coarse  $\alpha$ -Zr grains due to a complete isothermal solidification, which was almost comparable to the base metal structure. The presence of

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 $Zr_2(Cu,Ni)$  at the central joint region induced substantially low joint strengths below 200 MPa, but the joints without such segregation exhibited the strong joints more than the bulk strength (~530MPa) of Zircaloy-4 base metal (Fig. 3 (c)).

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Fig. 3 - Cross-sectional SEM images for the Zircaloy-4 joints brazed at (a) 850°C, 10 min, (b) 890°C, 10 min, and (c) stress-strain curves obtained by a room temperature tensile test.

#### 4. Conclusions

In this study, two different amorphous alloys based on the multi-component eutectic composition, i.e. Zr-Ti-Ni-Cu-Be and Zr-Ti-Ni-Cu were introduced as the fillers to braze the pure Ti Gr. 2 and Zircaloy-4. By using these amorphous alloy fillers, both the Ti and Zircaloy-4 were successfully brazed at low temperatures, e.g.,  $\sim$ 820 °C for the Ti and  $\sim$ 890 °C for Zircaloy-4. Through the control of diffusion brazing, highly reliable joints were obtained with the formation of predominantly grown  $\alpha$ -Ti and  $\alpha$ -Zr grains by the isothermal solidification, which were almost comparable to the base metal structures. Such joints exhibited remarkably high strengths exceeding those of the base metals.

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# PLASMONIC STRUCTURES FOR SURFACE-ENHANCED RAMAN SCATTERING BASED ON SILVERED POROUS SILICON

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The interaction of light with metal nanoarrays at dielectric interface leads to a collective oscillation of electrons known as the surface plasmon resonance (SPR) at specific frequencies. By varying the parameters of plasmonic structure and surrounding media the wavelength of the SPRs can be efficiently tuned giving rise to many successful applications. In particularly, surface-enhanced Raman scattering (SERS) is a plasmonics-based process. SERS takes place for analyte molecules adsorbed on rough metallic surfaces - SERS-active substrates at spatial