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Original Research

A Ti–Zr–Cu–Ni–Co–Fe–Al–Sn amorphous filler metal for improving the strength of Ti–6Al–4V alloy brazing joint

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ABSTRACT

$Ti_{50}Zr_{27}Cu_8Ni_4Co_3Fe_2Al_3Sn_3$ (at%) amorphous filler metal with low Cu and Ni contents in a melt-spun ribbon form was developed for improving mechanical properties of Ti–6Al–4V alloy brazing joint through decreasing brittle intermetallics in the braze zone. Investigation on the crystallization behavior of the multicomponent Ti–Zr–Cu–Ni–Co–Fe–Al–Sn amorphous alloy indicates the high stability of the supercooled liquid against crystallization that favors the formation of amorphous structure. The Ti–6Al–4V joint brazed with this Ti-based amorphous filler metal with low total content of Cu and Ni at 1203 K for 900 s mainly consists of α-Ti, β-Ti, minor Ti–Zr-rich phase and only a small amount of Ti_3Cu intermetallics, leading to the high shear strength of the joint of about 460 MPa. Multicomponent composition design of amorphous alloys is an effective way of tailoring filler metals for improving the joint strength.

1. Introduction

Amorphous brazing filler metals (BFMs), such as Ti- [1–4], Ni- [5,6], Ag- [7], Cu- [8] and Zr-based [9] BFMs, are attractive for the brazing of alloys, ceramics and composites. By melt spinning, amorphous BFMs can be fabricated into continuous flexible ribbons, so that they can be used as a preplaced preform. Especially for the joints with a small clearance, amorphous BFMs can be applied in an accurate and minimal amount. Amorphous BFMs also exhibit other merits including high homogeneity in structure and composition, low melting temperature, narrow melting temperature range, and high purity [1,2,4,6,10]. These advantages of amorphous BFMs lead to outstanding properties of the brazing joints [1,6].

For brazing titanium alloys, Ti–Cu–Ni and Ti–Zr–Cu–Ni system BFMs are commonly considered as the best choice due to the good compatibility with the base material and the resultant high mechanical properties and corrosion resistance of the joints [1,11–13]. A suitable melting temperature range of a BFM is one of critical factors for selecting brazing cycles compatible with α + β titanium alloys. Generally, the brazing should be conducted at a temperature in the range of 38–66 K below the β-transus temperature (T_β) of α + β titanium alloys in order to avoid the property impairment of the base alloys [13]. Cu and Ni in the Ti-based BFMs are important melting point depressant elements, and their total content in commercially available Ti-based BFMs is usually no less than 25 wt% [1,3,11–13]. On the other hand, Cu and Ni are also important constituent elements for glass formation of Ti-based amorphous alloys [10,14–16]. The total content of Cu and Ni in most Ti-based amorphous alloys free from highly toxic beryllium element is no less than 20 wt% [10,14,16]. However, high contents of Cu and Ni in the BFMs lead to the formation of brittle intermetallic compounds in the titanium alloy brazing joints, which deteriorates the mechanical properties of the joints [1,4,13]. Hence, the contents of Cu and Ni in Ti-based amorphous BFMs should be as low as possible in order to achieve a high strength of the titanium alloy joints. Ti–Pd–Zr–Si [17], Ti–Zr–Si(–Ta) [18] and Ti–Fe–Si(–Ge, –Pd, –Zr) [19] amorphous alloys free from elements Cu and Ni have been recently reported. However, for brazing titanium alloys, these Ti-based amorphous alloys may not be suitable due to their high Si contents ranging from 5 at% to 15 at%, which may lead to the formation of brittle titanium silicide in the joints [20]. Therefore, the development of new Ti-based amorphous BFMs with low contents of Cu and Ni and suitable liquidus temperature (T_l) to achieve high joint mechanical properties of titanium alloys is expected.

Multicomponent composition approach is effective in developing amorphous alloys and designing BFMs to meet various composition and property requirements [4,14,21–24]. It has also been reported that the

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coexistence of similar and dissimilar elements favors the glass formation of alloys [25,26]. Besides Cu and Ni, similar elements Co and Fe can be added for obtaining high glass-forming ability of titanium alloys. Zr is miscible with Ti, and may favor the glass formation and the reduction of the liquidus temperature of Ti-based alloys [10,16,27]. Sn is a neutral element, since it has (nearly) no influence on T_β [28]. Meanwhile, it has been reported that the addition of Sn to Ti(–Zr)–Cu–Ni system increased the thermal stability of the supercooled liquid against crystallization, and decreased the melting temperature [29,30]. In our recent study, $Ti_{50}Zr_{27}Cu_8Ni_4Co_3Fe_2Al_3Sn_2Si_1$ (at%) amorphous BFM has been synthesized, and the shear strength of the resultant Ti–6Al–4V (TC4) alloy joint has reached about 413 MPa [4]. It was observed that a Ti – Zr-rich phase containing 6.63 at% Si concentrated in the middle of TC4 joint [4], and the Si content on the fracture surfaces of the joint after shear test was higher than the nominal content of Si in the BFM. Although Si is favorable to the glass formation of Ti–Zr–Cu–Ni alloy system [31], it may lead to the embrittlement of titanium alloys [20]. In order to further improve the mechanical properties of TC4 alloy brazing joint, in the present work, a novel multicomponent Si-free Ti–Zr–Cu–Ni–Co–Fe–Al–Sn amorphous BFM with low total content of Cu and Ni (12 at%) and suitable T_l for brazing TC4 alloy was synthesized by melt spinning. The shear strength of TC4 alloy joint brazed with this amorphous BFM at a relatively low temperature of 1203 K for 900 s was up to 460 ± 7 MPa. The crystallization behavior of the Ti-based amorphous BFM in connection with the mechanism for glass formation was investigated. The origin of high-strength joining of the titanium alloy with the amorphous Ti–Zr–Cu–-Ni–Co–Fe–Al–Sn BFM is also discussed.

2. Material and methods

Alloy ingot with a nominal composition of $Ti_{50}Zr_{27}Cu_8Ni_4Co_3Fe_2Al_3Sn_3$ (at%, denoted as TiZr-I) was prepared by arc melting a mixture of pure Ti (99.995 wt%), Zr (99.7 wt%), Cu (99.95 wt%), Ni (99.95 wt%), Co (99.95 wt%), Fe (99.99 wt%), Al (99.99 wt%) and Sn (99.99 wt%) under an argon atmosphere. From the ingot, alloy ribbon of about 45 µm in thickness and 10 mm in width was fabricated by melt spinning under an argon atmosphere. For comparison, alloy ribbons with nominal compositions of $Ti_{47}Zr_{27}Cu_{10}Ni_5Co_3Fe_2Al_3Sn_2Si_1$ (at%, denoted as TiZr-II) and $Ti_{50}Zr_{27}Cu_8Ni_4Co_3Fe_2Al_3Sn_2Si_1$ (at%, denoted as TiZr-III) were also prepared. X-ray diffraction (XRD, D/MAX-2500) using Cu-Kα radiation was employed to examine the structure of the melt-spun ribbons. Thermal properties of the ribbons were evaluated by differential scanning calorimetry (DSC, NETZSCH DSC 404 C) at a heating rate of 20 K/min under argon flow. The crystallization kinetics of the TiZr-I amorphous ribbon was characterized by isochronal and isothermal annealing in DSC. The applied heating rates for the isochronal experiments were 10 K/min, 20 K/min, 30 K/min and 40 K/min. For isothermal annealing, the samples were heated up to the annealing temperatures at a heating rate of 20 K/min and then held at the annealing temperature for 30 min. Subsequently, the samples were cooled down to room temperature and their structure was examined by XRD.

The base material was TC4 alloy with the T_β of 1268 K [28]. Prior to vacuum brazing, TC4 alloy was machined into plates with a dimension of 25 mm × 10 mm × 2 mm. Then the plates were polished with SiC sandpaper ranging from 60-grit to 1500-grit and ultrasonically cleaned in acetone and alcohol. A single layer amorphous alloy ribbon was placed between the faying surfaces of TC4 plates to form a TC4/BFM/TC4 sandwich configuration for joint microstructure and elementary analyses, and a single-lap joint with the overlapped area of about 10 mm × 2 mm for the joint shear strength evaluation. The assembled samples were heated at a rate of 10 K/min to the brazing temperature of 1203 K under vacuum and held at 1203 K for 900 s, followed by a furnace cooling to room temperature.

After joining, the microstructure, element distribution and the micro-area chemical composition of the joint were studied using an electron probe micro-analyzer (EPMA, JXA-8100) equipped with an energy dispersive spectrometer (EDS). The phases in the braze zone were characterized by XRD and a transmission electron microscopy (TEM, JEM-2100) with selected area electron diffraction (SAED). After polishing the joint samples in the direction paralleling to the faying surfaces of TC4 plates with SiC sandpaper, XRD examination was performed on different layers in the braze zone. The accurate positions of the layers were determined by EPMA observation of the cross-section of the polished joint. The samples for TEM observation were prepared by mechanical polishing followed by ion-beam thinning. To determine the shear strength of the brazed joints, shear tests were performed on 5 single-lap joint samples by using a universal testing machine at a tensile speed of 0.5 mm/min. After the shear test, fracture surfaces of the brazed joints were observed by a scanning electron microscope (SEM, JSM 6010). The chemical analysis was conducted on the fracture surfaces by EDS, and the average composition was determined from 5 measurements. Vickers microhardness across the brazed joints was measured using a micro-hardness tester (FM-800) under a load of 10 gf and dwell time of 15 s at five points.

3. Results and discussion

3.1. Synthesis and thermal properties of Ti–Zr–Cu–Ni–Co–Fe–Al–Sn amorphous alloys

The XRD patterns of the melt-spun TiZr-I and TiZr-II alloy ribbons are shown in Fig. 1. The patterns of the ribbons consist only of a broad halo peak and no any crystalline peaks are observed, indicating the formation of an amorphous phase. The inset of Fig. 1 shows that TiZr-I alloy ribbon exhibits a smooth surface and can be bent through 180 degrees without fracture. The flexible amorphous ribbon can be used as a preplaced preform, which gives an advantage over crystalline BFMs in powder and polymer-bonded strip forms for the joints with small brazement gaps [32]. Fig. 2 presents the DSC curves of the melt-spun TiZr-I and TiZr-II amorphous alloys, where T_x, T_m and T_l correspond to onset temperature of crystallization, melting temperature and liquidus temperature, respectively. Both the curves show two or three exothermic peaks (Fig. 2(a)), which indicate multi-stage crystallization events of the alloys. Each melting curve in Fig. 2(b) exhibits almost one endothermic peak, implying that the alloys could be near-eutectic, which is favorable for the glass formation. The T_l is 1192 K for TiZr-I and 1179 K for TiZr-II, which are 76 K and 89 K lower than the T_β of TC4 alloy, respectively.

It is well known that the amorphous alloys with high glass-forming ability usually consist of more than three elements with significant difference in atomic size and relatively large negative heats of mixing among the main constituent elements [22,23]. In the present

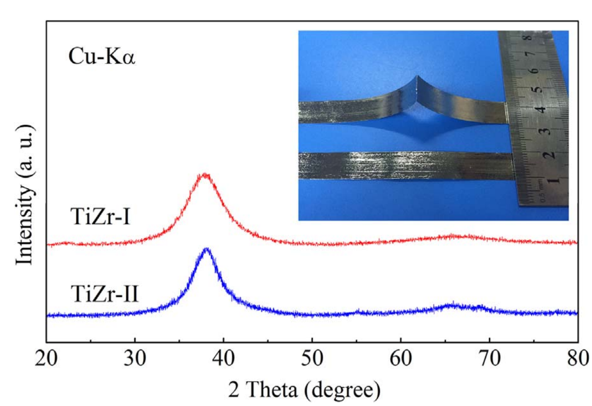

Fig. 1. X-ray diffraction patterns of TiZr-I and TiZr-II amorphous alloy ribbons. The inset shows the photograph of the as-spun TiZr-I ribbon and the ribbon after bending 180°.