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Effect of the volume fraction of the *ex-situ* reinforced Ta additions on the microstructure and properties of laser-welded Zr-based bulk metallic glass composites

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ABSTRACT

To investigate the effect of the volume fraction of the *ex-situ* reinforced Ta additions on the weldability of Zr–Cu–Ag–Al bulk metallic glass composites (BMGCs), in this study, different Ta contents (0–6 vol%) of BMGCs are welded using the Nd:YAG pulsed laser technique with preselected welding parameters. After welding, the microstructure (including the parent material (PM), weld fusion zone (WFZ) and heat-affected zone (HAZ)), mechanical and thermal properties of the test samples are investigated.

The test results show, for all BMGC welds, the micro-sized Ta particles in the PM, WFZ and HAZ to be covered by a crystallized interfacial layer (IL), ZrCu. For both un-welded and laser-welded BMGCs, as the Ta contents increase, the glass transformation temperature (T_g) increases, which in turn reduces the glass formation ability (GFA) indices, ΔT_x, γ and γ_m. However, when compared to that of un-welded BMGC, the GFA index, ΔT_x, of the laser-welded BMGCs is slightly improved. However, the γ, and γ_m of the BMGC welds seem not to be affected.

In addition, due to the characteristics of the rapid thermal cycle of the laser welding process, two smaller sizes of Ta, nano-sized (mainly on the surface of WFZ) and sub micro-sized Ta, are found in the WFZ. These sub-micro-sized Ta particles normally locate near the micro-sized Ta, which tends to slightly reduce the hardness in this area.

Furthermore, an increase in the volume fraction of Ta (0–6 vol%) in the BMGCs does not encourage the formation of the harmful crystalline phase in the amorphous matrix after the laser welding process. It is observed that, other than the IL (ZrCu) on the micro-sized Ta particles, no other type of crystalline is observed in the amorphous matrix of the laser-welded BMGCs.

1. Introduction

Because of their excellent combination of mechanical, chemical and physical properties, BMGs [1,2] are expected to emerge as a new type of industrial or engineering material. To date, a number of new multi-component bulk metallic glass (BMG) alloy systems have been successfully developed for producing amorphous alloys with larger diameters. Among the recently developed BMGs, Zr-based BMGs, especially Zr–Cu–Al–Ag BMG alloy systems [3–8], are considered to have excellent promise due to their greater strength, exceptional glass forming ability (GFA) and extremely wide supercooled liquid region. However, as with all monolithic BMGs, Zr–Cu–Al–Ag BMGs may exhibit inhomogeneous deformation below the glass-transition temperature, (T_g), resulting in low plastic strain under compressive loading, and so severely restricting their applications as structural materials [9–16]. To solve this problem with BMGs, the concept of developing glassy composite microstructures by forming reinforced ductile crystalline phases (e.g., Ta, Nb or Hf) embedded in the glassy matrix through either *in-situ* or *ex-situ* [1,2,17–20] methods has been explored. Both approaches have their advantages and limitations [1,2,13]. *In-situ* composites usually have a good crystal-amorphous matrix interface and a finer crystalline reinforced phase, but this approach can limit the compositional range [13,19]. In contrast, the features of the reinforced phase, such as distribution and volume fraction, of *ex-situ* composites can be easily adjusted. Recently, $(Zr_{48}Cu_{36}Al_8Ag_8)_{99.25}Si_{0.75}$-based BMG composites (BMGCs), *ex-situ* dispersed with various contents of Ta reinforced phase, were fabricated by J. S.

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C. Jang et al. [19]. Although few studies [1,10] have reported that *ex-situ* BMGCs exhibit problematic adhesion of the interface between the reinforced crystalline phase and the glassy matrix, their study found that, for a given Ta particle size, higher volume-fraction particles tended to result in the presenting of greater compression plasticity. Furthermore, they found that, as the reinforced phase, Ta, in the BMGCs increased, the glass forming ability (GFA) index of the BMGCs decreased [21]. Many researchers [1–3] have indicated that BMG alloys with a higher GFA index tend to have a higher glass-forming ability, making it easier to obtain the glass structure at a lower cooling rate for hot work applications, such as hot forging or welding. Thus, the question can be posed as to whether this reduction in the GFA index has a significant effect on the weldability of BMGCs.

As with normal BMGs, a significant challenge for BMGCs is producing them in a size suitable for structural use. To extend the engineering applications of BMGCs, their weldability has to be considered. It was acknowledged in our earlier studies [10,11], that in order to form a composite structure in the weld fusion zone (WFZ) and heat-affected zone (HAZ) after the welding process, BMGC welding is more complex compared to that of normal BMGs. For our recent study [11] we used a Neodymium-doped Yttrium Aluminum Garnet (Nd:YAG) laser welding technique due to its advantages of localized heating and a rapid thermal cycle [22,23], for the laser spot welding of an *in-situ* ($Zr_{48}Cu_{32}Al_8Ag_{8},_{95.25}Si_{0.75}$, Ta_4) BMGC. It was found that, compared to that of the un-welded BMGCs, the pre-selected laser parameters did not significantly affect the magnitude of the GFA indices.

However, for *ex-situ* BMGCs, the effect of the volume fraction of the reinforced Ta additions on the weldability has yet to be systematically studied, particularly the different interface properties between the reinforced crystalline phase and the glassy matrix, as compared to those of *in-situ* BMGCs. Therefore, in this study, different Ta contents (0–6 vol%) of *ex-situ* BMGCs were welded using the Nd:YAG laser technique with preselected welding parameters, after which the microstructures (in the parent material (PM), WFZ and HAZ), mechanical properties and thermal properties of the test samples were investigated.

2. Experimental procedure

The alloy ingots used in this study were designed as *ex-situ* BMG composites. $(Zr_{48}Cu_{36}Al_8Ag_8)Si_{0.75}$ was selected as the base alloy, given its relatively high glass-forming ability and reasonable plasticity in compression [5,6]. The base alloy was prepared from pure elemental Zr, Cu, Al, Ag and Si of 99.9 wt% purity by arc melting under a Ti-gettered argon atmosphere. To form the homogeneous alloy ingots, the base alloy was produced through a two-step arc melting and casting process, as described in the literature [19]. The base alloy ingots were then re-melted with various contents (0, 2, 4 and 6 vol%) of Ta particles (with an average particle size of 20 ± 8 μm) to obtain the target composite compositions. After the melting was completed, the liquid alloy was suction cast into a water-cooled Cu mold cavity to form an alloy cast plate 2.3 mm thick, 2.0 mm wide and 45 mm long. The cast was then machined to a plate 1 mm thick, 20 mm wide and 20 mm long.

All *ex-situ* BMGC sample plates were polished with 4000-grit silicon carbide paper, or up, to remove existing oxides. The composite microstructures of the as-cast plates were characterized using X-ray diffractometry (XRD; Scintag X-400), scanning electron microscopy (SEM; Hitachi S-4700) and differential scanning calorimetry (DSC, Netzsch DSC 404C). The heating rate for each tested DSC sample was 20 K min^{-1}.

The laser pulse shape used in this study was pre-selected in reference to our earlier studies [10,11,23] and based on the empirical approach, with the emphasis on the weld morphology and the possible minimum energy required to penetrate the 1 mm-thick *ex-situ* BMGC plates. The pre-selected parameters for the single-pass laser welding were as follows: laser voltage of 200 V, peak power of 1.9 kW, pulse frequency of 2 Hz, pulse duration of 4.5 ms, laser energy of 8.0 J, welding speed of 60 mm/min and laser spot size of 0.4 mm. During the welding process, the top and bottom surfaces of the test plates were shielded by pure argon (with a gas flow rate of 10 l/min) to prevent surface oxidation. When the welding process was completed, the welded samples were initially observed by means of optical microscopy (OM; Olympus BX51M) and an SEM equipped with an energy dispersive spectrometer (EDS; HORIBA 7200-H). Detailed microstructure observations were performed by means of transmission electron microscopy (TEM; Fei Tecnai G2) employing foils extracted from specific sites using a 5 keV focused ion beam (FIB, SMI 3050). A low ion beam current of 40 pA was used for the final milling. The glass transition and crystallization behaviors of the laser welds (consisting of WFZ and HAZ) were also investigated using DSC (a heating rate of 20 K min^{-1}). The samples for the DSC tests were carefully taken only from the welds. Finally, to reveal the interaction between the matrix and the Ta particles, the Vickers microhardness of the Ta interfacial areas in the PM, HAZ and WFZ was measured using a microhardness tester under a load of 300 g and loading time of 10 s.

3. Results and discussion

3.1. Microstructure and thermal properties of the as-cast ex-situ BMGCs

Prior to the laser welding, the microstructure and thermal properties of the as-cast *ex-situ* BMGC samples were tested. Fig. 1 shows the XRD patterns of the BMGC plates with different Ta contents (including 0, 2, 4 and 6 vol% defined as Samples A, B, C and D, respectively). All samples showed broad halo diffraction patterns in the 2θ range of 30–50°, which indicated the amorphous nature of the alloy matrixes. Except for the crystalline peaks from the BCC-structured Ta particles, no other crystalline peak was apparent. A further detailed metallographic examination of the BMGCs by SEM revealed that Ta particles around 5–20 μm in size could be observed in the amorphous matrix of the samples, as shown in

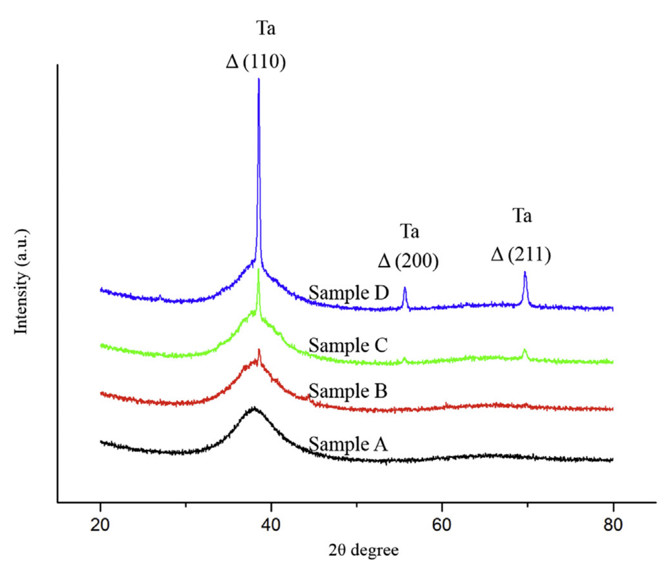

Fig. 1. XRD patterns of BMGC plates with different Ta contents.