Laser welding of annealed Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ bulk metallic glass

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**A B S T R A C T**

Laser welding is one of the promising ways for manufacturing metallic glass products with complicated shape and geometry. In this work we focus on the effect of annealing treatment and welding parameters on laser welding of annealed Zr$_{55}$Cu$_{30}$Ni$_{5}$Al$_{10}$ bulk metallic glass as intended and unintended heat treatment occurs in the process. We find that laser welding can produce well welded specimen plates with no obvious welding defects in the joints and high welding speed may lead to better joints. Although higher annealing temperature or longer annealing time leads crystallization, bulk metallic glass material still remains largely amorphous in the heat affected zone. Compared with the welded joint without annealing, the micro-hardness and bending strength are enhanced due to the presence of the nanocrystals occurred in annealed welding joint. Therefore, appropriate annealing treatment with the annealing temperature near the glass transition temperature and annealing time as long as that in hot embossing of BMG parts may play a beneficial role in laser welding of metallic glasses.

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1. Introduction

Bulk metallic glasses (BMGs) are metastable materials in which the atomic packing is topologically disordered [1]. As compared to crystalline metals, BMGs have many promising properties such as high strength, high toughness, high elastic strain limit, wear-resistance, corrosion-resistance at ambient temperature, etc., [2–4], which make BMGs very desirable in many engineering applications as well as scientific researches [5]. At elevated temperature, or the supercooled liquid region (SCLR) above the glass transition temperature ($T_g$), BMGs exhibit superplasticity-like behavior and behave like Newtonian fluid [6]. This behavior can be used to carry out net shape and produce precision micro parts using hot embossing [7,8]. Among many well-known BMG systems, Zr-based systems have good glass-forming ability, wide SCLR and low critical cooling rates of 1–100 K s$^{-1}$ [9]. Furthermore, the exceptionally high yield stress and high strength to density ratio make Zr-based BMGs quite promising for many mechanical and structural applications [10]. Zhang et al. [11] formed fine spur gears using Zr$_{41.25}$Ti$_{13.75}$Cu$_{10}$Ni$_{10}$Be$_{22.5}$. Schroers et al. [12] prepared several fine BMGs parts using Zr$_{44}$Ti$_{11}$Cu$_{10}$Ni$_{10}$Be$_{25}$. Wang et al. [13] investigated the forming of micro-gear with Zr$_{65}$Cu$_{17.5}$Ni$_{10}$Al$_{7.5}$, Li et al. [14] investigated the thermoplastic forming map of a Zr-based BMG. Although these BMGs parts can be obtained, it becomes increasingly difficult to form complex structures because of the high flow stress in the mold and the increasing capillary effects at small scales. As a result, die casting or hot embossing is limited in net shaping of BMG parts with complex shapes and geometry. In addition, it is difficult to produce metal molds with small and complex structure; and demoulding for such parts is also a problem. Silicon mold is widely used in hot embossing of micro/nano manufacturing because it can be etched into different shapes and dissolved in the KOH solution. However, silicon mold can break easily during the forming process, which limits its application. To date, it is still a challenge for superplastic forming of BMG parts with complex shapes with large aspect ratios and fine scales. On the other hand, laser welding offers a better solution. With high power density, deep penetration, high welding speed, and little deformation, laser welding is used widely to join metals and has been introduced in BMGs material processing gradually. Kawahito et al. [15] welded the Zr$_{55}$Al$_{10}$Ni$_{35}$Cu$_{30}$ BMG using high energy density fiber-optic laser under the welding speed of 72 m min$^{-1}$. Wang et al. [16] used pulsed Nd:YAG laser to weld (Zr$_{53}$Cu$_{30}$Ni$_{17}$Al$_{8}$) Si$_{0.5}$ BMG sheets. Li et al. [17] used laser welding to join the Zr$_{45}$Cu$_{48}$Al$_{7}$ with the welding speed of 8 m min$^{-1}$ and the output power of 1.2 kW. Wang et al. [18] welded Ti$_{40}$Zr$_{25}$Ni$_{3}$Cu$_{12}$Be$_{20}$ with laser welding parameters of 3.5 kW in power and 10 m min$^{-1}$ in speed.
While much attention has been paid to the laser welding of BMGs materials, few investigations focus on the laser welding of BMG parts undergoing hot embossing. As known, besides patterned hot embossing process can also be considered as an annealing treatment. During appropriate annealing treatment, structural relaxation happens and under certain conditions, nano-crystallization may occur that can create another channel to control the mechanical properties of BMGs [19]. Moreover, BMGs have a tendency to crystallize under heating during laser welding due to the metastable nature of the amorphous structure. Therefore, it is important to investigate annealed BMG materials in laser welding and then optimize process parameters for laser welding of complex BMG structure.

In this study, we conduct annealing treatment of $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ firstly and then join the annealed BMG plates using laser beam. The welding bead, microstructure, thermal properties and mechanical properties of welding joints are examined, and the results are discussed. It is found that laser welding can be used to join the annealed BMGs material, and appropriate annealing treatment is helpful to improve welding quality and mechanical property of BMG material by controlling nanocrystallization.

2. Experimental procedures

As-received $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ BMG billets were obtained from the BYD Co. Ltd. The BMGs plates were designed in dimensions of $3 \times 18 \times 1.2$ mm$^3$ for isothermal annealing treatment and laser welding experiment. As shown in Fig. 1, the differential scanning calorimetry (DSC) result indicates the glass transition temperature $T_g$ = 412 $^\circ$C and the crystallization temperature $T_x$ = 489 $^\circ$C (at the heating rate of 10 $^\circ$C min$^{-1}$) respectively. The supercooled liquid region, defined as the difference between the glass transition temperature $T_g$ and the crystallization temperature $T_x$ ($\Delta T_x = T_x - T_g$), is 77 $^\circ$C. There are 10 workpieces used in the experiment. Group I (sample 1–6) has the same annealing treatment conditions but different welding parameters, while Group II (sample 7–9) has different annealing conditions but the same welding parameters. For comparison, the tenth sample was not annealed. The annealing treatment was carried out by the universal material testing machine (Zwick-Z20). Then the workpieces were removed from the furnace and air cooled to the room temperature.

The laser welding experiments of those ten samples were conducted by Ytterbium fiber laser (YLR-4000) in continuous wave mode, where the diameter of focal spot is about 0.4 mm. During the welding process, the welding beads were protected using argon atmosphere to restrain plasma and cool welded samples. The detailed parameters of the annealing treatment and laser welding are shown in Table 1. The oxide layers occurred during annealing treatment were removed from the welded joints by using mechanical lapping. We cut the samples into smaller blocks by CNC precision dicing/cutting machine (Shenyang Kejing Instrument Co., Ltd, EC-400) and embedded the blocks in epoxy for metallographic sample preparation. The prepared samples were then polished using 12 $^\circ$ precision auto lapping/polishing machine (MTI, UNIPOL1202) for evaluating the bonding quality and structural change at the joints.

3. Results and discussion

Before laser welding, the four annealed samples with different annealing conditions (sample 2, 7–9) and the as-received BMG plate were examined using X-ray diffraction (XRD). The results are shown in the inset of Fig. 1. As can be seen there are obvious broad peaks without any detectable crystalline phases in the XRD patterns, indicating the annealed samples still preserving glassy nature. Apparently, the annealing conditions in Table 1 are not sufficient to lead to crystallization.

The macro-planar views of the laser welded samples are shown in Fig. 2. The dark region in the cross section belongs to the heat affected zone (HAZ) where the crystallization is most likely to occur [17,18]. There are many differences among those welded samples, depending on the welding speed and the laser power. Both high welding power and low welding speed lead to large deformation of welding seams and small inclined angle formed by HAZ, a typical feature. As can be seen, the welded samples exhibit sound joints, at least visually, where fully penetrated welded beads are obtained and no porosity is generated. There is no visible defect such as pores or cracks in both the base material zone and the WFZ, indicating that the interfaces are joined successfully. The structure of the whole cross section of the welded joint looks homogeneous.

Table 1

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Annealing Temperature ($^\circ$C)</th>
<th>Laser welding Power (kW)</th>
<th>Speed (m min$^{-1}$)</th>
<th>Argon flow ($\times 10^3$ L min$^{-1}$)</th>
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<td>1.5</td>
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Fig. 1. DSC trace of an as-received $\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{5}\text{Al}_{10}$ BMG and XRD patterns of annealed samples.
The XRD patterns of the seven welded joints are illustrated in Fig. 3(h). It can be seen that these samples have similar patterns with broad diffuse halos rather than sharp diffraction peaks typical for the presence of crystalline phases, confirming that within the detection limit of XRD, no large size crystals occur in the welded joint during laser welding. The angle positions of the amorphous diffraction peaks do not shift practically among these samples, only the height of the peaks increases with annealing treatment, implying that densification caused by relaxation occurs during the annealing treatment [20].

The absorbed energy to melt the materials at interface should be proportional to \( P(d/v) \), where \( P \) and \( d \) stand for laser power, laser spot size and welding speed, respectively. Thein, the spot size of the laser beam is a constant, a result of our laser equipment. The welding power provides energy to melt and penetrates the BMGs. The high welding speed can lead to fast temperature drop of the melt to below crystallization temperature and thus inhibits crystallization [18]. Both of these consequences are closely related to the welding quality and microstructure of the welding joint.

As can be seen in Fig. 2, all BMG plates were fully penetrated. In this case, we will center on the welding speed instead of the welding power. Samples 1–2 and 7–10 were examined using TEM to investigate the microstructural change. As the material in the base material zone has remained in glass state after laser welding, crystallization is most likely to occur in the HAZ [17,18]. Thus, we only focus on the HAZ. Fig. 4 indicates that the microstructure in the HAZ displays a distinct difference. In Fig. 4(a) and (b), different welding speeds obviously affect the glassy structure of the samples under the same annealing parameters and welding power. For sample 1 with 8 m min\(^{-1}\) welding speed, the high-resolution TEM (HRTEM) image (see Fig. 4(a)) displays orderly periodic arrangement of atoms, indicating that crystallization indeed occurs in the HAZ. The magnified image in the inset for the marked area A shows that only very little amorphous phase is embedded in the crystalline substrate. Moreover, the selected area electron diffraction (SAED) pattern shows the matrix with inconspicuous diffraction rings, further revealing that crystallization occurs after the laser welding. The inset of the bright field image (BFI) also shows the feather-like shape of crystals. These are consistent with the HRTEM result. Fig. 4(b) shows the microstructure of sample 2 with the welding speed of 10 m min\(^{-1}\). The HRTEM image shows that atoms in most areas still remain disordered except in the marked area B. The SAED pattern shows a typical amorphous diffraction ring together with several bright specks. The BFI gives the typical morphology of these particles during crystal nucleation with flower-like shape and the size about 50 nm. According to the description mentioned above, the BMGs maintain amorphous structure plus a very few crystals present in BMG substrate, confirming the high welding speed is apparently useful to obtain desired microstructure. For samples 2 and 7–9 that have the same welding parameters and different annealing parameters, the microstructures are different, as shown in Fig. 4(b)–(e). The results suggest that the annealing temperature and time affect the welding quality. Both sample 7 (Fig. 4(c)) and sample 9 (Fig. 4(e)) have crystallized more seriously as compared with sample 8 (Fig. 4(d)). The HRTEM graphs show more ordered atomic packing and the corresponding SAED patterns show less obvious amorphous diffraction ring with regular specks. The observations confirm that pretreatment with higher annealing temperature or longer annealing time facilitate crystallization during welding process. Even so, part of BMG material in the HAZ retains amorphous structure, as marked in B, C, D and E.

The microstructure of the welded sample 10 (without annealing) under the welding speed of 10 m min\(^{-1}\) is shown in Fig. 4(f). In the HAZ, the BMG has completely crystallized, and the average size of the crystals is larger than 100 nm. The white and black phases coexisting in WFZ are eutectic structures. The HRTEM image of the HAZ is quite different from those annealed welding samples. Firstly, the amorphous phase exists in all annealed welding samples rather than complete crystallization in sample 10 without annealing. Secondly, the crystalline phase and geometrical shape is visibly different, e.g., the crystals are “polygon-like” in sample 10 but “flower-like” in sample 2. Thirdly, the grain size of the crystals in sample 10, mostly about 100–200 nm, is much bigger than that in...
Quite a few nanoparticles appear after annealing and laser welding in sample 2. This is because the annealing treatment induces structure relaxation and rearrangement of atoms, and then the BMG after annealing and laser welding can be transformed into a glass-matrix composite containing nanoparticles.

To evaluate the mechanical property of the welded samples, the Vickers hardness of the welded samples 1, 2, 10 and the as-received BMG billet were measured using a micro-hardness tester (Wilson Hardness 432SVD) under the force of 1 kgf and Dwell time of 15 s. There are 8 points in the welded cross section being randomly selected, including 4 points in the welding zone and 4 points in the base material zone. As can be seen in Fig. 5(a), the hardness in the base material zone of welded samples 1, 2 and 10 basically equals to the as-received BMG material. Nevertheless, the hardness values of these samples in the welding zone have changed obviously after annealing and laser welding. The hardness values of sample 2 are larger than others. By comparing the results of sample 1 and sample 2, we find that the higher welding speed for
sample 2 results in a quickly drop of temperature during laser welding. There is not enough time for the crystals to grow up, and the heat effect of annealing increases the nucleation rate and nanocrystallization. The nanocrystal can improve the material properties, including hardness, strength, plasticity, etc [21,22]. Thus, the hardness of sample 2 is enhanced. However, the large grain size with 100–200 nm leads to a slightly decrease of hardness in sample 10.

Fig. 4. TEM images of the welding joints under different processing conditions. (a)–(f) the HRTEM image, SAED pattern, BFI results in the HAZ corresponding to samples 1–2 and 7–10, respectively.
4. Conclusions

The annealing treatment and laser butt welding for Zr55Cu30-Ni5Al10 BMG plates were conducted. The welded joints were inspected by Keyence photos, SEM, XRD, TEM, Vickers hardness, three-point bend test, respectively. There is no incomplete penetration or visible defect observed, demonstrating that the BMG plates are joined together successfully. Different welding speed and annealing treatment conditions can lead to sub-micron scale crystals and nano-scale particles in the HAZ and also different crystals phases.

For complete penetration, we found that the high welding speed can lead to a quick temperature drop, which is beneficial to obtain a better joint, including small nanoparticle formation and better mechanical property at the joints. Under the same welding conditions, however, annealing affects both the microstructure and welding quality significantly. We found that part of material in the HAZ with annealing treatment still maintains amorphous structure. Especially, the welding sample with the annealing temperature of 415 °C and the annealing time of 10 min before laser process retains almost full amorphous structure with very few nanoparticles with the average size of 50 nm. Due to the existence of nanocrystalline phase, the welded joint with appropriate annealing treatment exhibits larger micro-hardness and bending strength than the un-annealed samples and the BMG billets. However, too higher annealing temperature and longer annealing time is not beneficial for BMGs.

Therefore, we conclude that if the penetration bead is obtained in the laser welding process, higher speed need to be selected. Besides, appropriate isothermal annealing can suppress crystal growth and hence leads to nanocrystallization, which improves the welding quality and mechanical property of the welded joints. Sample comparison for Zr55Cu30Ni5Al10 BMG plates, appropriate annealing temperature should be near the glass transition temperature and the annealing time can be selected as long as that in hot embossing of BMG parts. This work shows that the laser welding of annealed BMG material is a promising technology for the welding of BMG materials and the manufacturing of the complex BMG structure.

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