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Influence of powder size on the crystallization behavior during laser solid forming $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy

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The $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glasses (BMGs) were prepared using laser solid forming (LSF) process from the plasma rotating electrode process (PREP) powder. The effect of the powder size on the crystallization behavior of the remelted zone (RZ) and heat affected zone (HAZ) was investigated. It was found that the as-prepared powders were composed of the amorphous phase and $Al_5Ni_3Zr_2$-type phase. The RZ mainly kept the amorphous state after LSF. The residual $Al_5Ni_3Zr_2$-type phase could be observed in RZ only if the powder size was larger than 106 μm. Meanwhile, the $NiZr_2$-type nanocrystals at the boundary of RZ primarily formed from the solidification of remelted liquid. With the increase of the powder size, the lower overheating temperature and shorter existing time of the molten pool enhanced the heredity of $Al_5Ni_3Zr_2$ clusters and other intermetallic clusters in remelted alloy melt, which decreased the thermal stability of the already-deposited layer. The volume fraction of crystallization in the deposit increased with the increase in powder size. There was no crystallization occurred in the HAZ between the adjacent tracks and layers for the deposit prepared by the powder with the size range of 53−75 μm. However, the wide crystalline band with $Al_5Ni_3Zr_2$-type faceted phase, CuZr-type dendrite, $CuZr_2$-type spherulite and $NiZr_2$-type nanocrystal were observed in the entire HAZ for the deposit prepared by the powder with the size range of 106−150 μm. The finer powder was benefit to prepare the BMGs by LSF.

1. Introduction

Bulk metallic glasses (BMGs) have attracted tremendous attentions as the potential structural materials due to their superior tensile strength, hardness, toughness and extraordinary tearing and corrosion resistance in recent years [1–5]. However, the critical cooling rate required to produce an amorphous structure limits the dimensions of as-cast BMG components and therefore restricts their widespread application [6].

Recently, Kawahito [7] and Chen [8] used laser welding to successfully join the $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous alloy owing to the rapid heating and cooling characteristics during laser radiation. However, the thickness of the welded amorphous plates was only about 1 mm. Many researchers had attempted to manufacture 3D BMGs by laser solid forming (LSF) and selective laser melting (SLM) technique, which can realize the additive manufacturing process with point-by-point deposition characteristics and the high cooling rate during the solidification process of the remelted alloy melt [9]. H. Sun et al. [10] deposited one layer Zr-based amorphous alloy on both amorphous and crystalline substrates, and investigated the morphology of HAZ in different underlying substrates. Gan et al. [11] prepared Zr-based BMGs (1.7 mm in thickness) by LSF. It is found that the increasing of crystallization degree from the top surface of the deposit to the substrate was mainly attributed to the composition dilution from the remelted substrate. We also deposited the multilayer $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous alloy on the pure Zr substrates by LSF [12]. Since the composition dilution occurred in the transition zone between the deposit and substrate, the crystallization degree did not increase remarkably as the number of deposited layers increased. Yang et al. [13] compared the crystallization behavior of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMGs during laser remelting and LSF process. They found that the HAZ in the substrate could keep the amorphous state, when the HAZ only experienced a certain number of heat shock and the thickness of HAZ was smaller than that of single deposited layer during LSF of BMGs. Zheng et al. [14] used a LSF system to build multi-layer Fe-based BMGs components. However, the volume fraction of crystalline phase

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increased with the increase of deposited layer because of the heat accumulation during multi-track and multi-layer laser deposition. For reducing the crystallization degree during LSF of Fe-based BMGs, Ye et al. [15] added a 5-s interval between the adjacent deposited layers to keep the lower temperatures in the already-deposited layers. Finally, the BMGs composite with a large volume fraction of amorphous phase was accomplished. Li et al. [16] fabricated the marginal $Al_{86}Ni_6Y_{4.5}Co_2La_{1.5}$ metallic glass by the selective laser melting (SLM) with different laser powers. They found that the thermal fluctuation at the higher laser power led to an inhomogeneous chemical distribution in the deposit, which induced the severe crystallization in the deposited metallic glass. Pauly et al. [17] eventually employed the SLM technique to fabricate the large-scale $Fe_{75}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ amorphous alloy with little crystallization. Based on the mentioned above, the crystallization in the deposit was usually influenced by the composition dilution from the substrate, laser processing parameter, heat accumulation during multi-layer deposition and the reheating treatment in the already-deposited layers by the subsequent deposition. In addition, according to the structure heredity during the solidification process, the glass forming ability and the thermal stability of the deposit could also be affected by the initial crystalline phases in the powder. Balla et al. [18] used the fine and coarse mixed powders to fabricate the Fe-based BMGs components (10 mm in diameter and 15 mm in height) by LSF and inserted a short time delay between the successive laser scans. The crystalline phase that arised from the feedstock coarse powder could be found in the deposit. They thought that only finer amorphous powder could be used for preparing BMGs. Up to now, the relevant work has not reach the satisfaction, especially the influence of crystalline state of the powder on the thermal stability and crystallization behavior of the BMGs deposit during LSF is still not clear enough.

Considering the variation of the cooling rate with powder size during the plasma rotating electrode process (PREP) [19], the crystallization state of the powders with different sizes should be different. In present work, the $Zr_{55}Cu_{30}Al_{10}Ni_5$ (Zr55) powders with the different sizes were used as the deposition materials to perform the LSF of the bulk amorphous alloy. The effect of the powder size on the crystallization behavior of the remelted zone (RZ) and heat affected zone (HAZ) in the deposits was revealed by analyzing the crystallization characteristics of the deposits. The microhardness distribution in the deposit was further characterized.

2. Experimental procedures

The $Zr_{55}Cu_{30}Al_{10}Ni_5$ (atomic percent) alloy powders were produced by the plasma rotating electrode processing (PREP). The powders were sieved to obtain three different nominal size ranges (powder 1: 53–75 μm (200–270 mesh), powder 2: 75–106 μm (150–200 mesh) and powder 3: 106–150 μm (100–150 mesh)). The oxygen contents of the powders were measured using a LECO TC600 oxygen-nitrogen analyzer and determined to be 0.17 wt%, 0.16 wt% and 0.18 wt% for the powder 1, powder 2 and powder 3. The pure zirconium plates with the dimensions of $30 \times 10 \times 3$ mm^3 were used as substrates. The LSF experiments were performed by pre-laid powder method with the LSF-IIIB laser solid forming system [12]. The experiments were carried out in a glove box under argon gas environment. The oxygen content in the glove box was kept to be 15–35 ppm during laser processing. Firstly, the powder layer with a thickness of 0.3 mm was laid on the substrate or pre-deposited layer. Subsequently, this powder layer was remelted along the pre-set trajectory by laser beam and resolidified to form a solid deposited layer, which was bonded metallurgically with the substrate or pre-deposited layer. Finally, the 3-D BMGs were performed by repeating this deposition process layer by layer. The detailed parameters of the laser solid forming are shown in Table 1. In order to investigate the effect of powder size on the crystallization of deposited layers, samples 1–3 were deposited by powders 1–3 with the same processing parameters, respectively. The sample 4 was deposited by powder 1 with five layers for investigating the change of the crystallization extent with the deposited layer. In addition, the $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous plate with the dimensions of $120 \times 10 \times 2.1$ mm^3 was prepared by water copper mold casting [6] for comparative study.

The crystallization state of the powder and deposits was investigated by the X-ray diffraction (X′ Pert MPD PRO, XRD). Powders and samples were polished and etched in a solution comprising of 90 vol% HNO_3 and 10 vol% HF for metallographic observation. Microstructural examination of the powders and deposits was performed using an optical microscope (Olympas-PMG3, OM), a scanning electron microscope (Tescan VEGAII LMH, SEM) with secondary electron (SE) imaging and back-scattered electron (BSE) imaging. Detailed microstructure analysis was performed on the transmission electron microscopy (Philip Tecnai G2 F30, TEM). TEM thin plates extracted from the deposits were prepared by grinding to a thickness of 60 μm followed by ion beam etching. Differential scanning calorimetry (DSC) analysis of the powders, deposits and as-cast amorphous alloy was performed using Netzsch STA 449C thermal analyzer at a heating rate of 10 K/min under a continuous flow of high purity argon. Vickers microhardness measurements were performed on Struers Duramin-A300 microhardness tester using a 200 g load and a holding time of 15 s.

3. Results

The BSE images of PREPed $Zr_{55}Cu_{30}Al_{10}Ni_5$ powders are shown in Fig. 1a–c. The microstructures of powders all consist of the dark gray faceted phase with an average size of 15 μm in a light gray featureless matrix. The EDS analysis shows that the faceted phase contains a lower proportion of Zr, Cu and Ni as well as being enriched in Al compared to the amorphous matrix (see Table 2). Through the analysis of XRD patterns, the result shows the dark gray faceted phase and light gray matrix correspond respectively to the $Al_5Ni_3Zr_2$ phase and amorphous phase (Fig. 1d). Despite the high cooling rate in the PREP process, the $Al_5Ni_3Zr_2$ phase is still formed in the amorphous substrate of the powder because of the $Al_5Ni_3Zr_2$ clusters in the Zr–Cu–Al–Ni alloy melt system [20]. The $Al_5Ni_3Zr_2$ crystalline phase is like $NiZr_2$–type and $Cu_{10}Zr_7$–type phases, which also contain the other elements as solutes in their crystal structure [12]. Thus, it can also be expressed as $Al_5Ni_3Zr_2$-type phase. This type of substitutional intermetallic structure is commonly observed in Zr–Cu–Al–Ni alloy [12]. The DSC curves of the PREPed powders and as-cast amorphous sample are shown in Fig. 1e. The as-cast sample is identified as the complete amorphous phase by XRD analysis (The lowest curve in Fig. 1d). According to the measurement of the crystallization enthalpy from the powders and as-cast sample, the volume fractions of the $Al_5Ni_3Zr_2$-type crystalline phase in the powder 1 (53–75 μm), powder 2 (75–106 μm) and powder 3 (106–150 μm) are 4.2%, 7.4% and 15.8%, respectively. Since the smaller particles usually present the higher cooling rate during PREP process [19], the volume fraction of the $Al_5Ni_3Zr_2$-type faceted phase in the large powder is higher than that in the small powder.

The morphologies of the LSFed $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMGs deposits fabricated with different powder sizes are shown in Fig. 2. It mainly consists of the featureless microstructure for the deposit with powder 1. However, the gray crystalline band occurs between the laser tracks and layers. And the black crystalline band takes place in the overlapping zone between the adjacent deposited tracks and