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Microstructural analysis of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glasses by laser surface remelting and laser solid forming

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ABSTRACT

The crystallization behavior of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy during laser solid forming (LSF) was analyzed. Since laser surface remelting (LSM) is a key process for the LSF, the crystallization behavior of as-cast $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glasses (BMGs) during LSM was also investigated. It was found that the amorphous state of the as-cast BMGs was maintained when they were repeatedly remelted four times in a single-trace LSM, and as for the LSF of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy, the crystallization primarily occurred in the HAZ between the adjacent traces and layers after the two layers were deposited. The as-deposited microstructure exhibited a series of phase evolutions from the molten pool to the HAZ as follows: the amorphous → $NiZr_2$–type nanocrystal + amorphous → $NiZr_2$–type equiaxed dendrite + amorphous → $Cu_{10}Zr_7$–type dendrite + $NiZr_2$–type nanocrystal. Among these microstructural patterns, the $NiZr_2$–type nanocrystals and equiaxed dendrites primarily formed from the rapid solidification of the remelted liquid in the laser processing process, and the $Cu_{10}Zr_7$–type dendrites in the HAZ primarily formed by the crystallization of pre-existed nuclei in the already-deposited amorphous substrate.

1. Introduction

Bulk metallic glasses (BMGs) have attracted much attention due to their unique properties, such as high electrical resistivity, superior hardness and strength, large elastic limit, excellent tearing and corrosion resistance, and low magnetic energy loss [1–3]. This alloy has been suggested as a suitable material for various applications including golf clubs, optical parts, microgeared motors, and pressure sensors [2]. However, the BMGs are typically produced using the copper mold casting method, and the critical size limitation of the as-cast BMGs (the critical diameter of most of the BMGs is typically lower than 20 mm) restricts their further widespread application [4]. If larger BMGs can be prepared, they can be used more widely in aerospace vehicles, aero engines, electron devices, and biomedical implants [5].

In recent years, laser additive manufacturing of bulk near-net-shape metallic components using the laser remelting and additive manufacturing route is a viable and promising method for preparing BMGs without size limitations, which is primarily due to the laser additive manufacturing possessing point-by-point forming characteristics with a high cooling rate of 10^5–10^8 K/s in the laser molten pool [6]. Zheng et al. [7] prepared Fe-based BMGs that were 10 mm × 10 mm × 10 mm by laser solid forming (LSF) using the powder blown method and found that serious crystallization occurred in the deposit due to thermal accumulation during the multi-trace and multi-layer laser deposition. Balla et al. [8] also deposited bulk cylindrical samples using LSF with Fe–Cr–Mo–W–Mn–C–Si–B fine and coarse powders, and the incomplete melting of the coarse powder during laser deposition restricted the formation of a fully amorphous structure. Yang et al. [9] investigated the crystallization behavior of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMGs prepared by LSF with the pre-laid powder method and proposed a physical model to describe the LSF of BMGs. Recently, Ye et al. [10] determined that there was a large fraction of amorphous structure in the Fe–Cr–Mo–W–C–Mn–Si–B BMGs cylinder, which was 10 mm in diameter and prepared by LSF using the powder blown method, when a 5-s interval was added to allow the already-deposited layers to cool prior to depositing subsequent tracks and layers. Pauly et al. [11] also fabricated large-scale $Fe_{74}Mo_4P_{10}C_{7.5}B_{2.5}Si_2$ amorphous alloys with much lower crystallization using selective laser melting (SLM) and the powder bed method. Our understanding of the crystallization behavior in the

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laser additive manufacturing of BMGs remains unsatisfactory, and some crystallization still occurs in the deposits due to the repeated remelting and reheating process. Therefore, the process should be controlled more carefully to prepare large scale BMGs based on a deeper understanding of the crystallization behavior and microstructure during the laser additive manufacturing of BMGs.

Many recent studies have suggested that the amorphous matrix with a certain volume fraction of crystalline phases (referred as BMG composite) may improve the ductility of amorphous metallic alloys and result in a better integrated mechanical performance [12–15]. Wu et al. determined that the $Cu_{46.5}Zr_{47.5}Al_5Co_1$ BMG composites obtained by laser surface treatment exhibited better compressive mechanical properties than the as-cast CuZr-based amorphous alloy [13]. Calin et al. demonstrated that $Cu_{47}Ti_{33}Zr_{11}Ni_8Si_1$ BMG composites with in situ formed nanoscale particles in the amorphous matrix exhibited a distinct plastic strain [14]. In general, the mechanical properties of the BMG composites depend on various characteristics (i.e., morphology, size and volume fraction) of the crystallization phases.

It is important to note that LSF can construct a large-scale component with a higher deposition rate compared to other laser additive manufacturing methods. In the current study, the crystallization behavior of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy during LSF was investigated. Because laser surface remelting (LSM) is a key process for the LSF, the crystallization behavior of $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMGs during LSM was also investigated. The hardness distribution in the BMGs deposit prepared by LSF was further characterized.

2. Experimental procedures

The LSM and LSF experiments were performed with a LSF-IIIB laser solid forming system equipped with a 4 kW continuous wave CO_2 laser with a wavelength of 10.6 μm, a four-axis numerical control working table and a controlled-atmosphere glove box. The experiments were carried out in a glove box under argon gas to avoid oxidation during laser processing. (1) For LSM of BMGs, the $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous plates, which were prepared by the copper mold casting method and $30 \times 10 \times 2$ mm^3, were used as substrates. The oxygen content of the substrates was measured using a LECO TC600 oxygen–nitrogen analyzer and determined to be 0.02 wt. %. The processing parameters for LSM were chosen as follows: laser beam diameter 1 mm, laser power 700 W and the scanning velocity 200 mm/s. Using single-track LSM, the substrates were remelted four, seven, twelve and twenty-four times. (2) For LSF of BMGs, pure zirconium plates were used as substrates because it is difficult to obtain a large-scale $Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous plate, and the composition dilution is typically low during LSF. The pre-laid powder method was carried out using the gas atomized $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy powder that was 5–150 μm in size with an oxygen content of 0.2 wt. %. First, the powder layer, which had a thickness of 0.3 mm, was laid on the substrate or pre-deposited layer. Then, this powder layer was remelted along the pre-set trajectory by the laser beam and resolidified to form a solid deposited layer, which was bonded metallurgically with the substrate or pre-deposited layer. Therefore, the three dimensional BMGs were produced layer by layer using this repeated laser deposition process. The LSF processing parameters were as follows: laser beam diameter 1 mm, laser power 700 W, scanning velocity 200 mm/s, and the overlap rate 50%. The rectangular samples were deposited with one, two, three and five layers. The dimension of the deposit with five layers was $30 \times 10 \times 1.2$ mm^3.

The crystallization state of the samples was examined using X-ray diffraction (X′ Pert MPD PRO, XRD). The Micro-XRD was performed with Cu Kα radiation at 40 kV and a relatively high tube current of 35 mA, and the diameter of the analysis area was limited to approximately 100 μm by the collimator. The samples were polished and etched with an etchant consisting of 90 vol. % HNO_3 and 10 vol. % HF for metallographic observation. The microstructural characterizations were conducting using an optical microscope (Olympas-PMG3, OM), scanning electron microscopy (Tescan VEGAII LMH, SEM) equipped with energy dispersive X-ray (EDS) analysis and transmission electron microscopy (Philip Tecnai F 30G2, TEM). For the TEM observation, thin plates extracted from the deposits were first mechanically ground to foils with a thickness of ~60 μm. The foils were further ionically thinned using a 30 keV focused ion beam (FIB). The composition distribution in the deposit was examined using electron probe microanalysis (EPMA). The variations in the microhardness of the deposits as a function of the laser heat input (the ratio of laser power to scanning velocity) were measured with a Vickers microhardness tester under a normal load of 0.2 N. The Comsol Multiphysics software was used to simulate the thermal field during LSF using the heat transfer model. During the simulation, the dimension of the substrate was set to $30 \times 10 \times 3$ mm^3 according to the LSF experiment. A transient heat analysis was performed by moving a heat source along the center line in the top layer of the surface with a certain laser power and scanning velocity [16], and the intensity of the beam exhibits a Gaussian distribution. The specific heat and thermal conductivity of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy were obtained from the literature [17,18].

3. Results

The LSMed microstructures in the as-cast $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMGs are shown in Fig. 1. No crystallization occur in the as-cast BMGs when it was remelted four times (Fig. 1a). After remelting seven times, a featureless white remelted zone (RZ) is observed, which is surrounded by some tiny grains in the heat affected zones (HAZ) (Fig. 1b). After consecutively remelting twelve times, numerous needle-like dendrite colonies appear in the HAZ (Fig. 1c). These dendrites grew and collide with each other to ultimately form a distinct broad crystalline band with many clusters of spherulites after remelting twenty-four times (Figs. 1d and 1f). As shown in the TEM image in Fig. 1f, no nanocrystals are observed in the HAZ. In general, the number and size of the dendrite colonies in the HAZ increases with the number of remelting. However, the RZ remains featureless during the LSM process.

Fig. 2 shows the micro-focused XRD patterns of the substrate, RZ and HAZ in the LSMed $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMGs. The XRD patterns of both the substrate and the featureless white RZ exhibit a broad amorphous peak. A few weak sharp crystalline peaks are observed in the XRD patterns of HAZ. These XRD patterns indicate that the RZ and the substrate maintain an amorphous state, and crystallization occurs in the HAZ during LSM. The crystallization phases in the HAZ correspond to the orthogonal $Cu_{10}Zr_7$–type phase.

Fig. 3 shows the morphologies of the LSFed $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk amorphous alloy deposits with one, two, three, and five layers. For the one-layer deposit, the microstructure has a completely white featureless pattern. From the enlarged image with the EDS line scan pattern in Fig. 3a, only a thin transition zone with a maximum width of 15 μm between the deposited layer and the substrate is observed, which indicates a good metallurgical bonding. The epitaxial dendrites in this transition zone grow from the pure Zr substrate due to the dilution of Zr from the substrate. For the two-layer deposit, most of the deposited zone is white and featureless, and only a small amount of crystallizations occur between laser tracks, as shown in Fig. 3b. In addition, some crystallization phases are trapped in the white featureless zone. For the three- and five-layer deposit, obvious crystalline bands are observed between the adjacent deposited layers and tracks (Figs. 3c and 3d), and the