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Spherulitic crystallization mechanism of a Zr-based bulk metallic glass during laser processing

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ABSTRACT

Laser deposition of a Zr–Cu–Ni–Al–Nb metallic glass has been studied in an effort to understand and evaluate the challenges of fabricating metallic glass components via additive manufacturing techniques. The parent amorphous alloy crystallizes into micro-scale spherulites at heating rates up to 10^4 K/s during laser processing. Detailed microstructural and compositional examinations of the spherulites reveals that rapid heating suppresses phase separation and nucleation at the initial stage of crystallization, resulting in a growth-dominated crystallization behavior. The activation energy of spherulitic crystallization is estimated to be 124 kJ/mol, significantly lower than that of multiphase nanocrystallization reported elsewhere. The low activation energy of spherulitic crystallization is consistent with observations of the short-range redistribution of constituent elements at the amorphous–crystalline interfaces during growth of the spherulites.

1. Introduction

The advent of bulk metallic glasses, metallic alloys which maintain a disordered atomic structure when cooled from the melt at rates on the order of 10 K/s or less, has opened the door for the use of these very high strength, highly formable alloys in a number of interesting applications. Crystallization of metallic glasses is strongly thermal history dependent due to the significant difference in the temperatures at which the maximum crystal nucleation and growth rates are achieved [1]. This phenomenon, in addition to the presence of quenched-in nuclei, leads to a pronounced asymmetry in the critical cooling and heating rates required to prevent crystallization [2,3]. Our previous research observed crystallization of the glass at heating rates on the order of 10^3 K/s during laser deposition even though the critical cooling rate of the alloy was on the order of 10 K/s [4,5]. Furthermore, the crystallization products formed at high heating rates differ from those found from low heating rate or isothermal annealing conditions. Micro-scale spherical crystals or spherulites have been observed as the crystallization products in metallic glasses upon rapid heating [5–9], in contrast to the nanocrystalline phases produced at low heating rates or at low annealing temperatures. After uniform rapid heating, the spherulites are found distributed homogeneously throughout the amorphous matrix, with a characteristic appearance indicating radial growth from the nucleation sites. These observations motivate the present work, which examines crystallization at the even higher heating rates found during laser processing in order to more fully describe the crystallization kinetics of the spherulites.

In this work we present a detailed experimental investigation and theoretical analysis on the formation of spherulites during laser deposition of a Zr-based metallic glass ($Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$, nominal at.%). The microstructure evolution in both the melt zone and the heat affected zone (HAZ) is discussed. Based on numerical simulations calibrated by direct measurements obtained with a thermal imaging camera, we find that the spherulites form in the HAZ at heating rates on the order of 10^3–10^4 K/s, and that the activation energy required for spherulite formation is approximately half that previously reported for nanocrystallization [9].

2. Experimental methods

Pre-alloyed $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (nominal at.%) ingots were prepared by vacuum arc melting. Oxide layers were carefully removed from the surfaces of the high purity elemental constituents before melting. A mixture of pure Zr (99.9%), Cu (99.99%), Ni (99.95%), Al (99.9%) and Nb (99.95%) were melted by the arc discharge controlled by a tungsten rod cathode in an argon environment, and then homogenized at least four times in the melting

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chamber. The Zr-based alloy ingots were then cast into a copper mold under high purity argon to produce amorphous plates with a thickness of 3 mm. It should be noted that the stated alloy composition is based on the fractions of pure constituents prior to melting. Prior spot checks of the chemical composition of homogenized ingots and cast plates indicate that the nominal composition is typically correct to within less than 10% of each atomic fraction. The as-cast 3 mm thick plates were cut into multiple sections to act as substrates during laser deposition process. The as-cast substrate surfaces were ground with 600 grit SiC papers and thoroughly cleaned in ethanol prior to laser processing. Powder of the same composition alloy and with an average size of 31 μm was produced via gas atomization of some of the arc-melted ingots at Ames Laboratory in Ames, Iowa.

All of the laser deposition experiments in the present study were performed on a Laser Engineered Net Shaping (LENS™) 750 system housed in the Department of Materials Science and Engineering at the Ohio State University. A 750 W Nd:YAG laser with a wavelength of 1.064 μm was used for the deposition experiments. All experiments were performed in a glove box maintained at less than 15 ppm oxygen. Argon was used as the shielding gas. The laser beam was focused on the substrate surface to a spot of approximately 1 mm in diameter. The laser power was varied from 100 W to 350 W, and the travel speed of the laser beam relative to the substrate surface was varied from 10 in/min (4.2 mm/s) to 50 in/min (21.2 mm/s). The powder was delivered into the laser molten pool with the rate fixed at 1.5 g/min.

Microstructural characterization was carried out via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM imaging was performed on a Philips XL-30 environmental SEM using back-scattered electrons (BSE). More detailed microstructural and compositional analysis were conducted using a FEI Tecnai TF-20 TEM in bright field (BF) condition and scanning TEM (STEM) mode with a high angle annular dark field (HAADF) detector and nano-beam energy dispersive X-ray spectroscopy (EDS). TEM foils were prepared from sites of interest using a focused ion beam (FIB) operating at 30 kV. A low ion beam current of 93 pA was used for the final milling step to reduce damage to the structure during FIB processing. The milled foils were then extracted by ex situ lift-out and placed on carbon-coated copper TEM grids. It should be noted that the Cu fractions given by TEM EDS measurements may be high due to the effect of the Cu grids used to support the FIB-milled TEM foils. A Scintag PAD-V X-ray diffraction (XRD) system and a Mettler-Toledo differential scanning calorimetry (DSC) system were used to investigate the amorphous and crystalline natures of the processed materials.

3. Results

Single-layer deposition of Zr-based metallic glass powder on the as-cast substrate at laser travel speeds of 30 in/min (12.7 mm/s) and 35 in/min (14.8 mm/s) with a fixed laser power of 150 W results in the microstructures shown in Fig. 1. In both cases the HAZs are composed of roughly equiaxed spherical crystals, which are identified as spherulites, resulting from central nucleation and rapid radial growth. At the slower travel speed, corresponding to a higher heat input, the HAZ is made up of close-packed spherulites, with a distinct transition from the featureless melt zone to crystalline HAZ. At the higher travel speed (lower heat input) both the transitions from the melt zone to the HAZ and the HAZ to the underlying substrate are rougher and less well defined, as shown in Fig. 1(b). Spherulites formed with lower heat input are the same morphology but smaller in size than those formed at higher heat input. They are observed throughout the HAZ and are occasionally surrounded by amorphous substrate material. Note that in both cases the melt zones remain featureless.

Fig. 2(a) shows the XRD patterns of a featureless melt zone and crystalline HAZ, which were processed at a laser power of 150 W and a travel speed of 30 in/min (12.7 mm/s), compared with that of the as-cast substrate. As expected, the melt zone exhibits the same broad amorphous peaks as the as-cast substrate, which is consistent with the featureless regions observed via SEM. On the other hand, the HAZ is completely crystalline, as indicated by the multiple sharp Bragg diffraction peaks. Although phase identification is difficult due to the complexity of the five component alloy system, it has been demonstrated that the spherulites produced by different processing conditions have similar crystalline structures [9].

The glass transition and crystallization behaviors of the melt zones were investigated using DSC and compared with the as-cast glass. Care was taken to remove the DSC specimens from only the deposit and not the underlying substrate materials. DSC scans performed at a heating rate of 10 K/min are presented in Fig. 2(b). The melt zone and the as-cast amorphous substrate both exhibit second-order endothermic events characteristic of the glass transition followed by the exothermic peaks associated with crystallization. Both specimens exhibit similar crystallization behaviors with the same peak crystallization temperature $T_x = 763$ K. The glass transition temperature, T_g, of the melt zone ($T_{gm} = 676$ K) is slightly higher than the value for the as-cast material ($T_{g0} = 668$ K). This increase is consistent with higher cooling rates being achieved in the melt zone during laser deposition than during the casting process, in which the melt was poured into a copper mold with a cooling rate of about 100 K/s.

Microstructural investigation was carried out by TEM and EDS. The FIB TEM foils were prepared from different positions of the HAZ

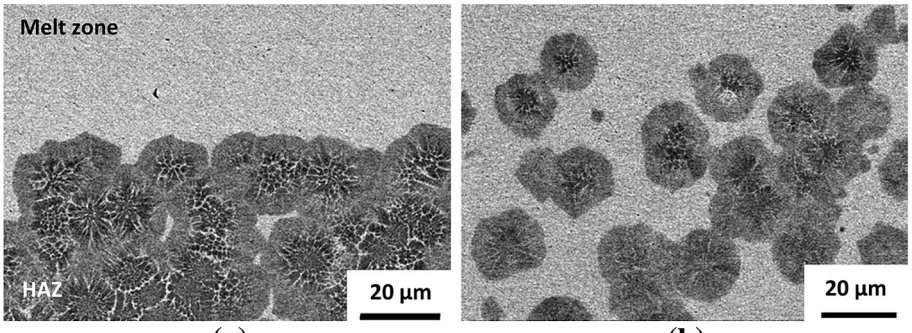

Fig. 1. Morphologies of the HAZs processed at a laser power of 150 W and a travel speed of (a) 30 in/min and (b) 35 in/min. In both cases the HAZs are composed of polycrystalline spherulites and unconsumed amorphous base material.