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3D printing of crack-free high strength Zr-based bulk metallic glass composite by selective laser melting

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A B S T R A C T

3D printing of crack-free bulk metallic glasses remains challenge due to the generation of huge thermal stress during the selective laser melting and their intrinsic brittleness. Herein, $Zr_{55}Cu_{30}Ni_5Al_{10}$ system was selected and 3D printed by selective laser melting technique. The results indicated that bulk metallic glassy composite comprises a large fraction (about 83%) of amorphous phase and minor fraction of intermetallic compounds with free of cracks were successfully fabricated. The 3D printed metallic glassy composite exhibited high strength over 1500 MPa. Experiment combined with finite-element-method simulation not only revealed the mechanism of crystallization at heat affected zones, but demonstrated that low thermal stress reduce the risk of micro-cracks generation and fracture toughness plays a crucial role in suppression the crack propagation during selective laser melting process.

1. Introduction

Efforts have been devoted to manufacturing of bulk metallic glasses (BMGs) in the past decade due to their processing limitation at ambient temperature. Though copper mold casting method has been used to fabricate simple components, but the complexity and dimension are intrinsically restrained owing to the requirement of high cooling rate [1,2]. Thermoplastic forming (TPF) that benefits from the superplasticity of supercooled BMGs, have been widely employed to fabricate precise and versatile geometries on length scales ranging from 10 nm to several centimeters [3–12], exhibiting potential applications in the miniaturization of modern industry. Whereas the fabrication of complicated 3D structures still remains challenge due to high viscosity of the supercooled liquids of BMGs and conspicuous interfacial effect between materials and mold [3,13]. By comparison with copper mold casting and TPF, selective laser melting (SLM) is a promising additive manufacture technique with advantages of direct fabrication of 3D parts with complex geometries. During SLM, components are manufactured by selective melting and consolidation of thin layers of powders using a scanning laser beam according to CAD designed data of the components [14]. Since only small volumes of material are molten and cooled as the laser beam scans across the powder bed during SLM [15], the cooling rates reach up to 10^4–10^6K/s [16–18] that is higher than the critical cooling rate required for most of BMG systems (10^2–10^4 K/s) [19–21].

In 2013, Pauly et al. [22] first reported the 3D printed scaffold structure by selective laser melting of Fe-based amorphous powders, and found that the amorphous structure could be retained under appropriate conditions [23]. The 3D printing of BMGs was then patented by Apple Ico., for seeking applications in the key components of consumer electronics [24]. Recently, Li et al. [25,26] revealed that the inhomogeneous energy density during SLM induces heterogeneous distribution of microstructure and mechanical properties. Notable that the rapid heating/cooling during SLM usually generate a steep temperature gradient, inducing a huge thermal stress and causing micro-cracks in the 3D printed parts [27]. To alleviate the micro-crack phenomenon, a re-scanning strategy was applied in an Al-based bulk metallic glass composite (BMGC) during SLM [26]. Li et al. [28] also found that the micro-crack can avoided in a Zr-based BMG fabricated by SLM. The question then arises as what are the decisive parameters to hinder micro-cracking of BMGs prepared by SLM, this is crucial to the properties and applications of 3D printed BMGs compounds. It is well accepted that the materials with high fracture toughness essentially performs a good ability of preventing crack propagation, due to the plastic deformation that dissipates fracture energy, moderates stress concentration in front of crack tip and shield the crack propagation. Previous work [15,29,30] has also revealed that micro-cracks usually happened in alloys with low fracture toughness. Accordingly, we

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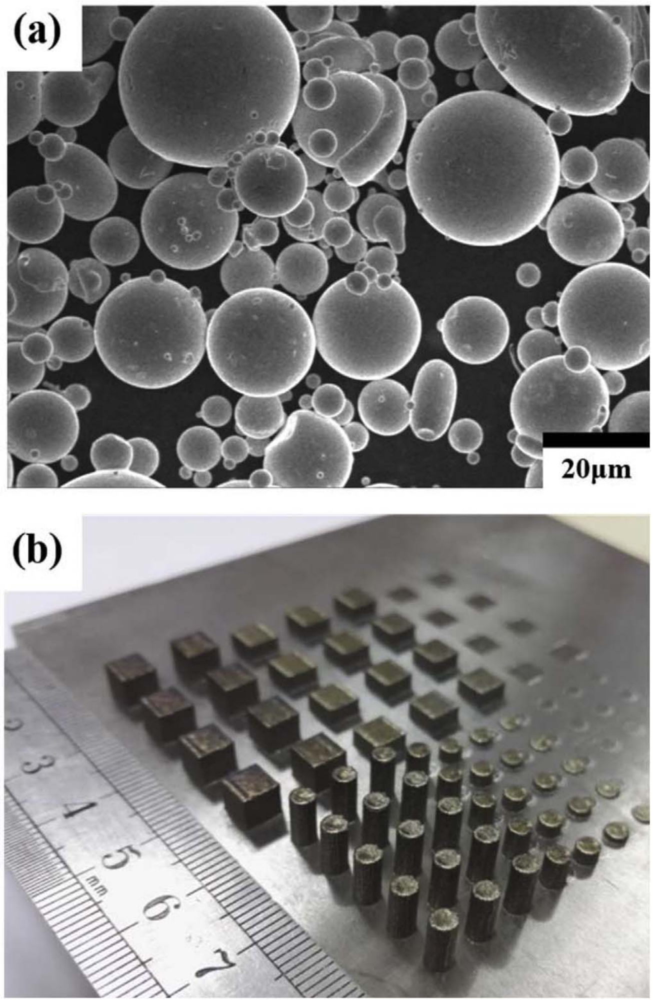

Fig. 1. (a) SEM micrographs of gas-atomized Zr-based amorphous alloy powder, (b) 3D printed Zr-based BMG samples.

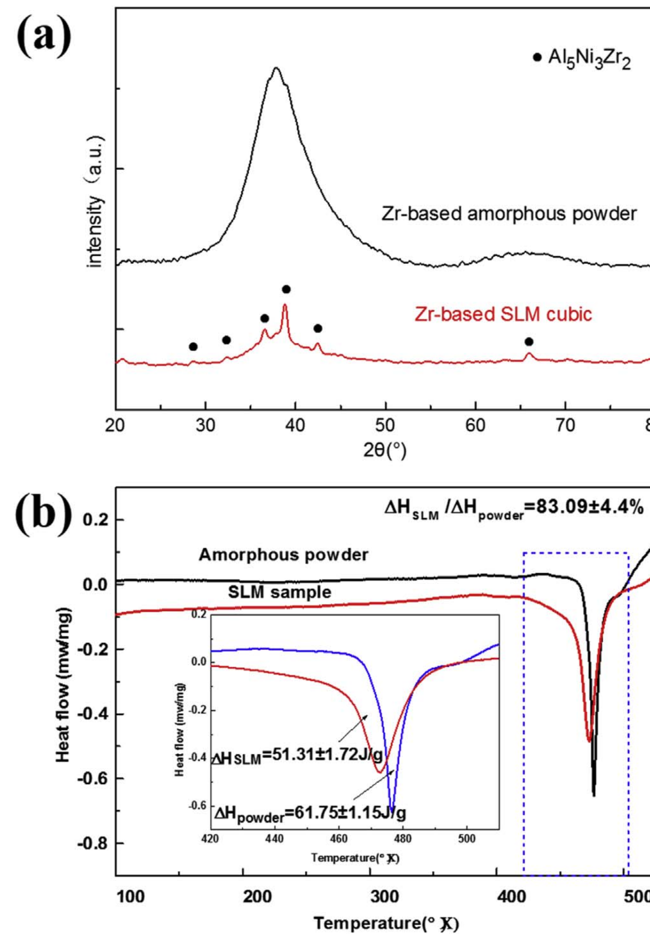

Fig. 2. (a) and (b) exhibit the corresponding X-ray patterns and DSC curves, respectively, as compared with the original powder.

selected $Zr_{55}Cu_{30}Ni_5Al_{10}$ metallic glass alloy with fracture toughness of 70 MPa $m^{1/2}$ [31] in this research, and 3D printed by selective laser melting. The results reveal that a crack-free Zr-based bulk metallic glassy composite with high strength could be fabricated. The physical origin of the above scenario can be fundamentally understood on the basis of low thermal stress that reduce the risk of micro-cracks generation, and high fracture toughness plays a crucial role in suppression the crack propagation during selective laser melting process.

2. Materials and methods

The $Zr_{55}Cu_{30}Ni_5Al_{10}$ (in at.%) amorphous powders were produced through high-pressure inert gas atomization, the particles used for SLM have smooth surface and size ranges from 2 μm to 33 μm, as illustrated in Fig. 1(a). The SLM experiment was performed by commercial SLM machine (FORWEDO LM-120, Forwedo), equipped with a Nd:YAG fiber laser (maximum power, $P_{\max} = 500$ W, wavelength $\lambda = 1060$ nm, focus diameter $d = 80$ μm) and an F-theta lens systems. The forming chamber was vacuumed and protected by argon gas with the oxygen content below 100 ppm. Here, $P = 240$ W, scanning speed $V = 1200$ mm/s, powder bed layer thickness $h = 60$ μm, scan line hatch spacing $t = 100$ μm, and scanning direction of 90° alternately among layers were adopted in this work based on experienced experiments. The cylindrical specimens with diameter of 3 mm and height of 7.2 mm were 3D-printed, as shown in Fig. 1(b). For comparison, rods with a diameter of 3 mm and a length of 90 mm, were fabricated by arc-melting amorphous powder under a Ti-gettered argon atmosphere, followed by suck casting into copper molds.

To detect the laser induced microstructural evolution, the 3D printed rod samples were analyzed by X-ray diffraction (XRD, 7000SX, Shimadzu) and differential scanning calorimetry (DSC, NETZSCH STA 449F3). The microstructure around the molten pool was characterized through transmission electron microscopy (TEM, FEI Tecnai G20, 200 kV). The TEM thin foil was prepared by focused ion beam (FIB, Quanta 3D FEG). The mechanical properties of the 3D printed Zr-based alloy rods were tested under quasi-static uniaxial compression (strain rate of 1×10^{-4} s^{-1}) using a Zwick machine (Zwick/Roell 020) at room temperature. The micrographs of the samples' cross section were observed through an optical microscopy (Leica DFC450) after being polished and etched with a corrosive agent (mixture of 15 ml H_2O, 15 ml HNO_3 and 1.5 ml HF). The fractural surfaces were characterized by scanning electron microscopy (SEM, QUANTA FEG450). To probe the fraction and distribution of porosity formed during SLM, the printed specimen with diameter of 3 mm and height of 7.2 mm was tested by lab-based high resolution X-ray tomography (XRT) [32,33]. Wherein X-rays are transmitted through sample and are detected using a scintillator screen, the raw tomographic data were then imported to tomographic reconstruction software, using inverse Fourier transforms to create three-dimensional image, the XRT investigations were performed with a voxel size of (1.36 μm^3).