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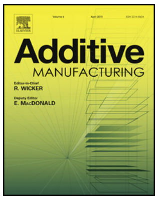

Full length article

Enhanced mechanical properties of additively manufactured bulk metallic glasses produced through laser foil printing from continuous sheetmetal feedstock

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ABSTRACT

Metal additive manufacturing (AM) is a rapidly growing field aimed to produce high-performance net-shaped parts. Therefore, bulk metallic glasses (BMGs), known for their superlative mechanical properties, are of remarkable interest for integration with AM technology. In this study, we pioneer the utilization of commercially available BMG sheetmetal as feedstock for AM, using laser foil printing (LFP) technology. LFP and traditional casting were used to produce samples for four-point bending and Vickers hardness measurements to rigorously compare the mechanical performance of samples resulting from these two fabrication techniques. Through LFP, fully amorphous BMG samples with dimensions larger than the critical casting thickness of the same master alloy were successfully made, while exhibiting high yield strength and toughness in bending. This work exemplifies a potential method to fabricate high-value BMG commercial parts, like gears or mechanisms, where the parts are conventionally machined after printing, and greatly benefit from utilizing novel materials.

1. Introduction

The development of novel metal parts for demanding applications requires high-performance structural materials. Conventional crystalline metals, such as steel, aluminum and titanium, offer a wide range of mechanical properties that are attractive for metal parts but have inherent limitations due to their dislocation-based plasticity. Bulk metallic glasses (BMGs) are a class of metal alloys described by their non-crystalline, or amorphous, microstructures and have been widely researched for the past three decades due to their unique combinations of mechanical properties and processing potential. BMGs are typically multicomponent metal alloys designed near deep eutectics which can be cooled from above their melting point to below their glass transition temperature at slow enough cooling rates that they can be formed into parts greater than a few millimeters in thickness without crystallization [1–4]. Commonly researched BMGs that have potential for structural applications include Zr-Ti-Cu-Ni-Be [5,6] and Zr-Cu-Ni-Al [7–11]. These alloy systems can be cast into components more than one centimeter in thickness and still form a glass; i.e. they possess a high "glass forming ability (GFA)." BMGs, by virtue of being designed near deep eutectics, have low enough melting temperatures that they could be die-cast repeatedly into steel molds without damaging to the mold. Die-cast BMG parts were created with complex geometries coupled with high strength, high hardness, and high elasticity [12–14]. The focus of the majority of the emerging BMG industry utilized this manufacturing potential to die-cast or injection mold parts for use in consumer products such as golf clubs, electronic cases, and watches [15–17].

As desired parts increase in complexity, producing net-shaped samples with sufficiently high cooling rates required to fully vitrify the BMG becomes increasingly challenging. Thermoplastic forming (TPF) is a method used to shape BMGs into intricate shapes by decoupling the cooling rate requirement from the forming mechanism [16]. However, TPF requires that the BMG possesses a sufficiently high GFA, such that crystallization doesn't occur during the TPF process [16,18], which will dramatically deteriorate the BMG's mechanical properties [19,20]. This drastically limits the number of alloys that can be potentially used for TPF [21].

Metal additive manufacturing (AM) is another method to fabricate complicated parts with high cooling rates [22–24]. Metal AM has recently seen a rapid and widespread growth in both commercial applications and research due to its unique ability to process difficult-to-manufacture metals into exceptionally com-

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plex net-shapes [25–29]. While metal AM technologies emerged in the 1990's [30], little effort was focused on the development of AM technologies for BMGs. Metal AM technology was especially attractive for hard-to-machine metals, such as titanium and steel, but was initially not competitive with easily castable metals, such as aluminum, magnesium, and BMGs. However, as the metal AM technology has matured, part complexity, cost, volume and alloy selection have all improved, allowing many parts to be manufactured into net-shapes that simply could not be manufactured in other ways. Recently, this progress in AM has been extended to BMGs to take advantage of some of the deficiencies in casting.

A number of research groups have therefore starting using commercially available AM machines to fabricate BMG parts. Although many metal AM technologies exist, the vast majority rely on metal feedstock in the form of powder. Manufacturing is then accomplished either through sintering the powder in a bed, called selective laser melting (SLM) or direct metal laser sintering (DMLS), or through depositing the powder into a laser or electron beam melt pool, called direct energy deposition (DED). The availability of BMG powder and equipment for AM makes the technology widely accessible. Laser processing of BMGs has been widely studied [31] and shown to be an effective way to heat the BMG powder to above its liquidus and then rapidly solidify to below the glass transition temperature at cooling rates in the order of 10^3–10^4 K/s [22,24]. The AM technology can be thought of as rapid solidification manufacturing, which is ideally suited for quenching weak glass-forming BMG alloys into amorphous layers. Some groups in the literature have manufactured BMG parts using AM technology from large GFA Zr-based BMGs [32,33] while others have demonstrated weak GFA Fe-based BMGs [23,34]. The imposed cooling rates of AM therefore also broaden the potential alloys that can be manufactured into bulk parts. AM equipment have also been used as a means to scientifically study BMG crystallization [35,36] and for combinatorial evaluation of GFA of BMGs [37,38].

These powder-based systems make up a majority of the metal AM research, however there are a wide assortment of technologies that utilize non-powder-based feedstock, including wire, molten liquid, ribbon, shot, deposition, and metal powder infused with polymeric binders. These feedstock geometries are readily available for BMGs. Fig. 1 demonstrates an assortment of BMG feedstock material that could potentially be used for AM, and Table 1 describes advantages and disadvantages of each. The different BMG feedstock materials listed in Fig. 1 are drawn wire, shot, rods >1 mm, powder, cast plates, wire <1 mm, liquid (an ingot is shown), thin melt-spun ribbon <50 μm thick, and sheetmetal 100–250 μm in thickness. Although not shown here, each BMG feedstock material can be used in one or more specific AM technologies. For example, the Fe-based BMG powder shown in Fig. 1d is suitable for use in commonly available powder-bed AM machines and also for thermal spray AM while the Zr-based ingot in Fig. 1g can be melted in a crucible and then deposited as a liquid stream. The Zr-based BMG shot in Fig. 1b is suitable for metal injection molding (MIM) technology but could also be combined with a polymer binder to do fused deposition modelling (FDM). Ni and Fe-based ribbons in Fig. 1h can fabricated into laminates or fabricated using ultrasonic additive manufacturing (UAM). Rods and wires, like the Zr-based alloys in Fig. 1a,c,f, can be melted and sprayed or deposited as a liquid stream to do AM. Lastly, plates and sheetmetal of BMG, like the Zr-based alloy shown in Fig. 1e,i can be thermoplastically consolidated or laser welded to form net shapes.

To overcome the limitations imposed by powder-based AM technologies, we utilize sheetmetal as a continuous feedstock for AM using laser foil printing (LFP) technology, previously demonstrated in [22,39]. Using LFP and traditional casting, we fabricate samples for measurements of mechanical properties through four-point bending and Vickers hardness, and draw direct comparisons between sample geometry and fabrication method.

2. Experimental

In this study, $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ amorphous sheetmetal, with a nominal thickness of 150 μm that was manufactured through slow melt spinning using master alloys fabricated from industrial-grade purity constituent elements (produced by Eco FM Co. Ltd., South Korea), was used as feedstock material. The sheetmetal therefore contains nominally 600 ppm of oxygen by weight and 0.25 at.% Hf from the Zr precursor. All LFP experiments were conducted in an Ar-shielded chamber (>99%) using an IPG YLR-1000 CW (continuous wave) fiber laser with a wavelength of 1070 nm and a maximum output power of 1000 W. Prior to the LFP process, the feedstock sheetmetal's surfaces were slightly polished with 800 grit SiC paper followed by ethanol cleaning in order to remove potential surface oxidization. The sheetmetal was pre-fixed on the substrate (and/or previous layer) by laser spots before welding the whole surface to prevent potential sheetmetal deformation. Further details of LFP can be found in our previous publication [22].

For the LFP process, laser power, laser pulse duration, and spot interspacing are the three most important parameters. For successful welding in between layers, the laser power must be sufficiently high such that the weld depth is larger than the sheet thickness. However, above a certain power threshold, the welding mechanism produces a "keyhole" and pores will be generated [40]. Therefore, the laser power must be maintained between the aforementioned limits. The laser pulse duration must be short to avoid crystallization of the amorphous sheetmetal. The size of the fusion zone defines the upper limit of the spot interspacing. If the interspacing is too small, the material may experience multiple reheating and crystallize. If the interspacing is too large, the welding will be discontinuous. Optimizing the laser parameters, samples were fabricated using 300 W laser power in pulse mode, 1 ms laser pulse duration, 430 μm spot size, and 100 μm spot interspacing. Therefore, the resultant pulse energy is 0.3 J/pulse and the power density is 2×10^5 W/cm^2.

LFP samples are fully amorphous, as verified by X-ray diffraction (XRD), and 99.9% dense, measured using the Archimedes principle (Fig. 2). It should be noted that the roughness of laser welded surface was measured as $R_a = 2.43$ μm. This level of roughness will not affect the laser welding of the next layer. Thus, there is no need to remove the surface irregularities for continuous welding. However, in the presented work, we did polish the welded surface with 800 grit SiC paper followed by ethanol cleaning right before the laser welding, the same protocol as the feedstock sheetmetal, to maintain consistency. Rectangular beams were then printed by LFP on a pure Zr substrate. The beams could then be cut from the substrate using wire electrical discharge machining (EDM). Optical microscopy (OM) was performed on the top and cross sectional views of the sample. The images show evidence of high laser pulse overlap and complete melting in between layers with no contrast produced by crystallinity. Pores are also observed due to "keyholes," which were minimized but could not be avoided due to the thickness and thermal stability of the BMG sheetmetal.

For a comparison of the mechanical properties of samples produced by LFP, sheetmetal from the same batch utilized as feedstock for LFP was carefully remelted, by arc melting, to preserve the composition. The resulting ingots were then suction casted, using the arc melter, into beams that are at least 50 mm long and with 2.5 mm, 3.5 mm, and 4.5 mm square cross sections. XRD was then performed to evaluate GFA of the cast samples.

Oxygen content has been known to deteriorate the GFA and embrittle BMGs of same or similar chemistry to $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$