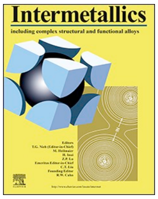
Intermetallics 103 (2018) 67–71

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet



# Graded structure of laser direct manufacturing bulk metallic glass

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ARTICLE INFO

*Keywords:*
Laser direct manufacturing
Bulk metallic glass
Amorphous materials
Functionally graded materials
Laser deposition

ABSTRACT

Extending the applications of metallic glasses for use as functionally graded materials could mitigate their intrinsic problems such as limited dimensions. Laser direct manufacturing (LDM) technology is an outstanding and reliable technique to fabricate structural-graded materials. Here, a $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ (Zr50) alloy was chosen as the model material to fabricate metallic glass by the LDM. By optimizing the LDM process through the finite-element simulation, a nearly fully amorphous Zr50 alloy with the thickness of larger than 10 mm was fabricated. The structural gradients, induced by gradual variation of crystallinity, were found in the deposited Zr50 metallic glass.

## 1. Introduction

Metallic glasses have received considerable scientific and technological attentions due to their extraordinary mechanical and chemical properties [1–3]. However, the small dimensions of metallic glasses largely hinder their wide applications as structural materials [4,5]. Extending the use of metallic glasses as functional materials could mitigate this problem [6,7]. As a special class of functional materials, functionally graded materials, possess a number of advantages including an improved residual stress distribution, enhanced thermal properties, higher fracture toughness, and reduced stress intensity factors [8]. These advantages make them attractive in technological applications. Herein, a question arises: can we fabricate high performance structural-graded metallic glasses to overcome their “bottleneck” problems?

Consolidation of the amorphous powders into bulk materials, using the methods such as hot pressing [9], spark plasma sintering [10], injection [11], etc., is an effective way to fabricate metallic glass components. Among these methods, laser direct manufacturing (LDM) technology, which is a powder-based layer-by-layer shaping and consolidation process, allows us to finely tailor microstructure, porosity, shape and size of deposited materials [12–14]. The flexibility of structural design associated with the LDM makes it a reliable technique to fabricate structural-graded materials [15]. Moreover, comparing with the above mentioned powder metallurgy methods, LDM technology can produce metals having low levels of voids and porosity. At present, extensive works have been conducted on the LDM of metallic glasses [16–19]. The cooling rates achieved by the LDM method can generally reach up to $10^3$–$10^4$ K/s, significantly higher than the critical cooling rate required to produce an amorphous structure for most glass-forming alloy systems. This provides an opportunity to fabricate metallic glasses, even those with poor glass-forming ability, to overcome their size limitation. Moreover, the metallic glasses fabricated by the LDM method may essentially possess graded structures, which would be induced by the thermal history gradient along the building direction during the LDM process. In the previous works, however, most attention has been paid to the degree, characteristics and behaviors of the crystallization in the metallic glasses fabricated by LDM [20–22]. The graded structures, which would generate tremendous effects on the physical, chemical and mechanical properties of the LDM produced metallic glasses, have been ignored.

In the present work, a $Zr_{50}Ti_5Cu_{27}Ni_{10}Al_8$ (Zr50) alloy was chosen as the model material to fabricate large-size metallic glass by the LDM technology. The structural gradients, induced by the gradual variation of crystallinity, across the thin crystalline bands and along the building direction were found in the deposited Zr50 metallic glass. The

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https://doi.org/10.1016/j.intermet.2018.10.005
Received 21 May 2018; Received in revised form 7 October 2018; Accepted 7 October 2018

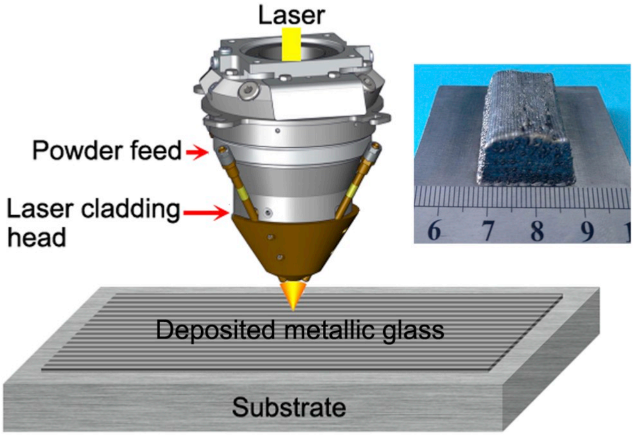

**Fig. 1.** Schematic of the LDM process. The inset shows the outer appearance of a multi-layer 10-mm-thick Zr50 alloy sample fabricated by the LDM.

microstructure and mechanical properties of the graded components were carefully studied. The formation mechanism of the graded structures was illustrated from the frame of thermal history. The gradient mechanical properties induced by the gradual crystallinity were also investigated in details.

## 2. Materials and methods

LDM of Zr50 metallic glass was performed using a coaxial powder feeding LDM system. The laser source used in the experiments was IPG YLS 6000W SM CW ytterbium fiber laser with wavelength of 1070 nm. The schematic of the LDM process is shown in Fig. 1. The inset of Fig. 1 shows the outer appearance of a multi-layer 10-mm-thick Zr50 alloy sample fabricated by the LDM. The diameter, power and travel speed of the laser beam was 2 mm, 200 W and 800 mm/min, respectively. LDM experiments were conducted inside a working chamber, which is filled with argon gas to keep the oxygen level lower than 10 ppm. Argon atomized Zr50 powders in a size range of 20–50 μm were used for LDM process. Owing to the rapid solidification conditions, the majority of the particles produced by gas atomization in an argon atmosphere are spherical or near-spherical in shape. 45 carbon steel was selected as substrate materials due to its high yield strength and a relatively high thermal conductivity. Parallel tracks were partially overlapped with an overlap fraction of 30%. The layer thickness in $z$ direction during multi-layer deposition was set as 0.6 mm. The microstructure of deposited metallic glass samples was characterized using high energy synchrotron X-ray diffraction (HEXRD) and scanning electron microscope (SEM). The HEXRD experiments were carried out at beamline I15 of the Diamond Light Source, UK, using high energy, monochromatic X-rays with a photon energy of 76 keV. The X-ray beam was focused down to 70 μm in diameter and cleaned up with the pinhole directly in front of the sample. 2-Dimensional XRD images were recorded using a Perkin-Elmer XRD1621 flat-panel detector positioned ~1 m from the sample. The scattering intensity $I(Q)$ versus scattering vector were extracted by integrating the obtained 2-D diffraction patterns along the radius of the diffraction circles in $Q$-space using Data Analysis WorkbeNch (DAWN) software. The nanoindentation experiments were performed on the alloys at room temperature by an MTS Nanoindenter-XP, where the displacement and load resolution were lower than 0.1 nm and 50 nN. A professional finite-element simulation software, SYSWELD, is applied to calculate the thermal cycle curves in the present LDM processing. In the present study, the laser beam is modeled as a Gaussian distribution of heat flux from a moving heat source with a conical shape. The surface heat flux was assumed to be uniform during the process and produce a melt zone depth consistent with that experimentally observed. This heat flux corresponds to a laser power of 200 W and beam diameter of 2 mm. All the specific heat and thermal conductivity values used in the finite-element simulation are temperature-dependent, as described in our previous literature [23].

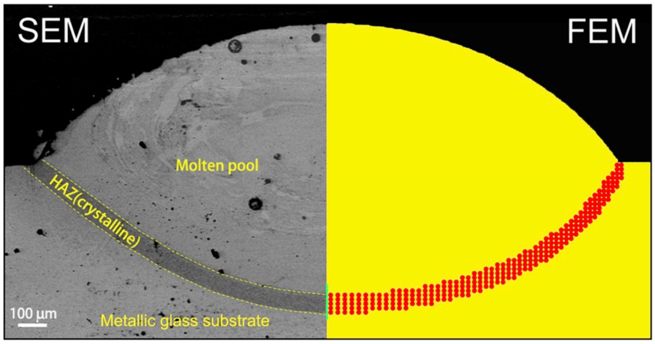

**Fig. 2.** The left part is a SEM image showing the microstructure in the cross section of the single-track deposited Zr50 alloy sample, the right part is the spatial distribution of crystallization obtained from the FEM analysis.

## 3. Results and discussion

The resulting microstructure of deposited samples is directly determined by the local thermal conditions, which are controlled by two key processing parameters in the LDM process, i.e., the laser power and the travel speed [24]. In order to obtain an ideal laser deposited Zr50 sample with fully or nearly fully amorphous microstructure, the processing parameters are optimized by using the finite-element method (FEM) analysis and the time-temperature-transformation (TTT) diagrams of the Zr50 alloy. The TTT-diagram estimation and FEM simulation in details were prescribed in our recent published paper [23]. To optimize the LDM processing parameters, single-track Zr50 alloy were printed on a Zr50 metallic glass substrate. The cross-sectional microstructure of the single-track deposited Zr50 alloy sample is shown in the left part of Fig. 2. The laser travel direction is perpendicular to the plane of the images. Three different regions can be easily distinguished, namely the molten pool in the upper part, the crystalline heat-affected zone (HAZ (crystalline)) in the middle part, and the metallic glass substrate in the lower part. For comparison, we analyze the crystallization of all the nodes of finite element mesh in the cross section of the FEM-simulated single-track Zr50 alloy. The crystalline positions are indicated by red dots. The spatial distribution of crystallization obtained from the FEM analysis is shown in the right part of Fig. 2. Clearly, the distributions of crystallization calculated by our method agree well with the experimental observations, confirming the validity of our method to predict the crystallization in the LDM of Zr50 metallic glass. Then, the ratios of the crystalline area to the total area shown in right part of Fig. 2 are calculated to evaluate the crystallinity of the deposited Zr50 metallic glass. A combination of laser power of 200 W and travel speed of 800 mm/min is found to present the lowest crystalline fraction. Thus, the laser power of 200 W and travel speed of 800 mm/min are chosen as the optimum LDM parameters to fabricate large-sized Zr50 alloy samples.

A typical microstructure of a deposited 10-mm-thick Zr50 alloy perpendicular to the laser travel direction is shown in Fig. 3(a). Featureless light gray regions, corresponding to amorphous zones, are observed surrounded by thin dark gray crystalline bands. From Fig. 3(a) we can note that the thin gray bands take lower than 5% of the total cross area, indicating the deposited Zr50 alloy with the thickness of larger than 10 mm contains lower than 5 vol% crystalline phases. More inspiringly, the widths of dark gray crystalline bands remain almost unchanged with increasing the deposited layers, indicating that the deposited Zr-based alloy does not crystallize more seriously as the sample becomes thicker. Therefore, using the present processing parameters can produce Zr50 metallic glass without dimensional limitation.