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High-throughput discovery and characterization of multicomponent bulk metallic glass alloys

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ABSTRACT

This work describes a high-throughput experimental method to characterize compositional trends in the glass forming ability and mechanical behavior of a ternary metallic alloy system. Continuously-graded composition libraries of Cu-Zr-Ti ternary alloys were produced by laser deposition, and continuous regions of glass-forming compositions were rapidly identified through an optical microscopy technique. By varying the laser processing parameters and thereby the cooling rate of the melt within each library, the composition with the greatest glass-forming ability within the range studied was determined to be $Cu_{51.7}Zr_{36.7}Ti_{11.6}$. An alternative deposition scheme was applied to fabricate libraries containing a large array of discrete compositions. Instrumented nanoindentation was performed on the discrete libraries to establish compositional trends in the measured properties. The indentation modulus was observed to be strongly correlated with the Ti-content over the entire region of study, while the hardness was more sensitive to Cu for high Zr-contents and to Ti at lower Zr-contents. These trends could inform the design of new metallic glass alloys possessing an optimized balance of both ductility and glass forming ability.

1. Introduction

Over the past century, engineering alloys have become increasingly sophisticated in order to meet challenging performance specifications required by cutting-edge technology. The most advanced structural alloys of today are multicomponent, typically comprising a dominant solvent species and at least two or more minor constituents. For example, typical Ni-based superalloys used widely in the aerospace industry could contain more than ten alloying components to achieve complex microstructures that retain the alloys' mechanical integrity at high operating temperatures [1,2]. A promising class of multicomponent alloys, and the subject of the present study, is bulk metallic glasses (BMGs). BMGs are characterized by an amorphous atomic structure devoid of long-range translational symmetry, resulting in a rare combination of properties that are unattainable in even the most advanced crystalline alloys. These include near-theoretical strengths, large elastic strain limits, and the unique ability among metallic materials to undergo thermoplastic processing [3,4]. The salient commonality among these example classes of advanced engineering alloys is the vast composition space they occupy, motivating the development of combinatorial synthesis methods that could facilitate the high-throughput discovery of new alloys with optimized properties [5–9]. In this paper, we describe a novel strategy for correlating glass forming ability and other properties with composition in multicomponent BMGs.

Since the discovery of BMGs, intense focus has been directed towards understanding the origins of glass forming ability (GFA) and the necessary criteria for identifying alloy compositions with high GFA. As a result, a number of empirical rules, temperature-based metrics, and structural models have been developed for predicting optimum glass-forming compositions [10–18]. Despite the value that various guidelines and predictive parameters have contributed to the present understanding of GFA, none have demonstrated consistent reliability as standalone predictors of GFA *a priori*[19–21]. Johnson et al. recently showed that only two parameters, the reduced glass transition temperature (T_{rg}) and the dynamic fragility of the supercooled liquid, are necessary for quantifying GFA accurately [22]. However, these parameters are acquired from experimental measurements performed on the glass

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itself and consequently do not enable true predictive capability. Without a robust means of prediction, the exploration of glass formation in an alloy system still relies heavily on experimental trial and error methods.

Conventional approaches for investigating the compositional landscape of GFA in multicomponent systems typically follow a serial, one-at-a-time experimental paradigm, where discrete compositions are synthesized and their amorphous structure verified by various diffraction techniques. Despite the success of serial methods in discovering many notable BMG alloys, the sensitivity of GFA to chemical composition [23,24] necessitates fabrication of an impractically large quantity of individual specimens in order to systematically probe the vast composition space occupied by multicomponent alloys. As a result, many alloy systems containing potential glass formers remain either only partially investigated or entirely unexplored.

In recent years, vapor deposition techniques have emerged as a combinatorial method to explore glass formation in complex metallic systems more efficiently [25–32]. Most notably, Ding et al. reported using magnetron co-sputtering to deposit ternary Au-Cu-Si and Mg-Cu-Y composition libraries [30,31]. By applying a thermoplastic blow molding technique to an amorphous thin-film library, the authors were able to map out the compositional landscape of thermoplastic formability and successfully identify the compositions with optimized processability. However, it is important to note that the mechanism of vitrification from the vapor phase may produce structures and glass properties that are different from glasses synthesized by liquid quenching [33,34]. The influence of the substrate in thin-film libraries may also preclude accurate determination of mechanical properties during instrumented indentation experiments.

Alternatively, we have developed a novel experimental methodology using laser additive manufacturing as a high throughput synthesis tool to accelerate the discovery of new BMGs. In our previous studies, compositionally graded specimens of the binary Cu-Zr alloys were fabricated and the optimum glass formers within the binary system were accurately identified [35,36]. In the present work, we demonstrate the ability to systematically investigate GFA across the substantially larger composition space of a ternary system. Alongside this effort, we demonstrate a fabrication scheme that, when combined with instrumented nanoindentation, enables high-throughput characterization of mechanical properties across large regions in composition space.

2. Experimental

2.1. Continuously-graded libraries for GFA optimization

All composition libraries reported in this paper were fabricated with an Optomec MR-7 LENS™ system. The substrates were grade 702 zirconium ground with 320 grit SiC paper and then cleaned with methanol to remove surface contaminants. The elemental powders used in the experiments had minimum purities of 99.9, 99.2, and 99.2 at. % for Cu, Zr, and Ti respectively.

Three 25.4 mm × 25.4 mm compositional libraries were constructed using a three layer sequential fabrication scheme with intermediate re-melting steps to fully incorporate the deposited powders. To preserve the as-deposited surface topography, the fabricated libraries were not polished following fabrication. Fig. 1 provides a schematic illustration of the overall experimental concept. Each elemental powder layer was deposited using a constant laser power and powder delivery rate, while the travel speed of the substrate relative to the laser and powder source was varied continuously across the specimen (8.47–29.63 mm/s) to achieve the desired composition gradient. For each library, the Zr was deposited first using a 250 W laser with the travel speed decreasing in the +x direction (in the coordinate frame of the substrate), resulting in an increasing amount of powder deposited in the +x direction. The Cu was deposited in the second layer using a 250 W laser with the travel speed decreasing in the -x direction, in the

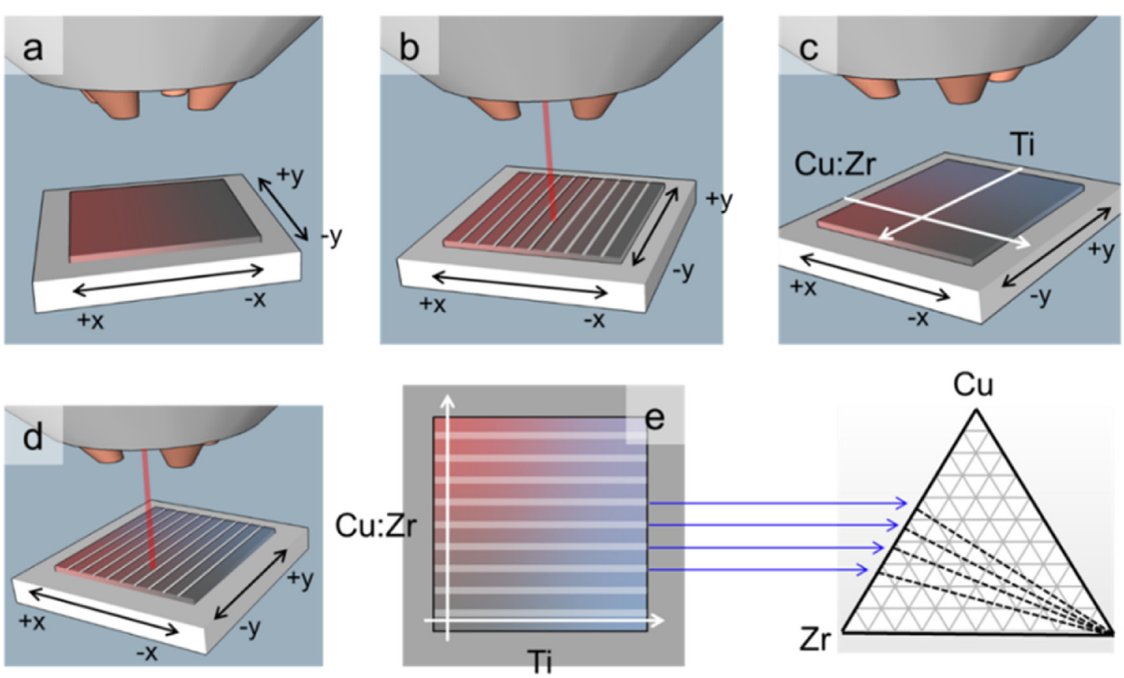

Fig. 1. Experimental concept for fabricating a Cu-Zr-Ti composition library via laser additive manufacturing. a, Initial deposition of two successive layers of Cu and Zr to produce a graded Cu-Zr composition profile. **b**, Creation of evenly-spaced re-melted lines perpendicular to the direction of the composition gradient to promote thorough mixing of the two components. **c**, Deposition of Ti gradient in a direction perpendicular to the initial gradient. **d**, Final glazing of the re-melted lines with a fast laser to promote vitrification. **e**, The alloyed lines in the completed library correspond to ternary tie lines featuring a fixed Cu:Zr ratio.