High-throughput Discovery and Characterization of Multicomponent Bulk Metallic Glass Alloys

Peter Tsai^a & Katharine M. Flores^{a,b}

- a. Washington University in St Louis, Institute of Materials Science & Engineering
One Brookings Drive
St Louis, MO 63130
- b. Washington University in St Louis, Department of Mechanical Engineering & Materials Science
One Brookings Drive
Campus Box 1185
St Louis, MO 63130

Primary Author: Peter Tsai^a

Email address: ptsai23@wustl.edu

Corresponding Author: Katharine M. Flores^{a,b}

Email address: floresk@wustl.edu

Phone: (314) 935-3184

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 $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$. 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.

1.0 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

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4 aerospace industry could contain more than ten alloying components to achieve
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6 complex microstructures that retain the alloys' mechanical integrity at high operating
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8 temperatures [1,2]. A promising class of multicomponent alloys, and the subject of the
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10 present study, is bulk metallic glasses (BMGs). BMGs are characterized by an
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12 amorphous atomic structure devoid of long-range translational symmetry, resulting in a
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14 rare combination of properties that are unattainable in even the most advanced
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16 crystalline alloys. These include near-theoretical strengths, large elastic strain limits,
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18 and the unique ability among metallic materials to undergo thermoplastic processing
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20 [3,4]. The salient commonality among these example classes of advanced engineering
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22 alloys is the vast composition space they occupy, motivating the development of
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24 combinatorial synthesis methods that could facilitate the high-throughput discovery of
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26 new alloys with optimized properties [5–9]. In this paper, we describe a novel strategy
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28 for correlating glass forming ability and other properties with composition in
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30 multicomponent BMGs.
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38 Since the discovery of BMGs, intense focus has been directed towards
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40 understanding the origins of glass forming ability (GFA) and the necessary criteria for
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42 identifying alloy compositions with high GFA. As a result, a number of empirical rules,
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44 temperature-based metrics, and structural models have been developed for predicting
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46 optimum glass-forming compositions [10–18]. Despite the value that various guidelines
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48 and predictive parameters have contributed to the present understanding of GFA, none
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50 have demonstrated consistent reliability as standalone predictors of GFA *a priori* [19–
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52 21]. Johnson et al. recently showed that only two parameters, the reduced glass
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54 transition temperature (T_{rg}) and the dynamic fragility of the supercooled liquid, are
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4 necessary for quantifying GFA accurately [22]. However, these parameters are
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6 acquired from experimental measurements performed on the glass itself and
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8 consequently do not enable true predictive capability. Without a robust means of
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10 prediction, the exploration of glass formation in an alloy system still relies heavily on
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12 experimental trial and error methods.
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16 Conventional approaches for investigating the compositional landscape of GFA
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18 in multicomponent systems typically follow a serial, one-at-a-time experimental
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20 paradigm, where discrete compositions are synthesized and their amorphous structure
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22 verified by various diffraction techniques. Despite the success of serial methods in
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24 discovering many notable BMG alloys, the sensitivity of GFA to chemical composition
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26 [23,24] necessitates fabrication of an impractically large quantity of individual specimens
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28 in order to systematically probe the vast composition space occupied by
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30 multicomponent alloys. As a result, many alloy systems containing potential glass
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32 formers remain either only partially investigated or entirely unexplored.
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39 In recent years, vapor deposition techniques have emerged as a combinatorial
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41 method to explore glass formation in complex metallic systems more efficiently [25–32].
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43 Most notably, Ding *et al.* reported using magnetron co-sputtering to deposit ternary Au-
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45 Cu-Si and Mg-Cu-Y composition libraries [30,31]. By applying a thermoplastic blow
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47 molding technique to an amorphous thin-film library, the authors were able to map out
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49 the compositional landscape of thermoplastic formability and successfully identify the
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51 compositions with optimized processability. However, it is important to note that the
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53 mechanism of vitrification from the vapor phase may produce structures and glass
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55 properties that are different from glasses synthesized by liquid quenching [33,34]. The
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4 influence of the substrate in thin-film libraries may also preclude accurate determination
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6 of mechanical properties during instrumented indentation experiments.
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9 Alternatively, we have developed a novel experimental methodology using laser
10 additive manufacturing as a high throughput synthesis tool to accelerate the discovery
11 of new BMGs. In our previous studies, compositionally graded specimens of the binary
12 Cu-Zr alloys were fabricated and the optimum glass formers within the binary system
13 were accurately identified [35,36]. In the present work, we demonstrate the ability to
14 systematically investigate GFA across the substantially larger composition space of a
15 ternary system. Alongside this effort, we demonstrate a fabrication scheme that, when
16 combined with instrumented nanoindentation, enables high-throughput characterization
17 of mechanical properties across large regions in composition space.
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30 31 **2.0 Experimental**

32 33 **2.1 Continuously-graded libraries for GFA optimization**

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35 All composition libraries reported in this paper were fabricated with an Optomec
36 MR-7 LENSTM system. The substrates were grade 702 zirconium ground with 320 grit
37 SiC paper and then cleaned with methanol to remove surface contaminants. The
38 elemental powders used in the experiments had minimum purities of 99.9, 99.2, and
39 99.2 at. % for Cu, Zr, and Ti respectively.
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48 Three 25.4 mm x 25.4 mm compositional libraries were constructed using a three
49 layer sequential fabrication scheme with intermediate re-melting steps to fully
50 incorporate the deposited powders. To preserve the as-deposited surface topography,
51 the fabricated libraries were not polished following fabrication. Figure 1 provides a
52 schematic illustration of the overall experimental concept. Each elemental powder layer
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4 was deposited using a constant laser power and powder delivery rate, while the travel
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6 speed of the substrate relative to the laser and powder source was varied continuously
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8 across the specimen (8.47-29.63 mm/s) to achieve the desired composition gradient.
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10 For each library, the Zr was deposited first using a 250 W laser with the travel speed
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12 decreasing in the +x direction (in the coordinate frame of the substrate), resulting in an
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14 increasing amount of powder deposited in the +x direction. The Cu was deposited in the
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16 second layer using a 250 W laser with the travel speed decreasing in the -x direction, in
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18 the direction opposite to the Zr gradient. To facilitate thorough alloying of the Cu and Zr,
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20 a series of parallel, evenly spaced lines oriented in the y direction were then re-melted
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22 with a 200 W laser at a travel speed of 12.7 mm/s, such that each re-melted line had a
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24 fixed Cu:Zr ratio. Ti was then deposited in the third layer, using a 150 W laser with the
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26 travel speed decreasing in the +y direction, resulting in a Ti gradient perpendicular to
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28 the Cu-Zr gradient. The re-melted lines were melted again to thoroughly incorporate the
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30 Ti. Thus, the Cu:Zr molar ratio nominally remained fixed within a re-melted line while
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32 the Ti content increased along the length of the line, producing a collection of tie lines in
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34 the ternary composition map. To investigate the effect of processing conditions on the
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36 compositional extent of glass formation, the final re-melting step was performed at
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38 different laser powers (200, 240, and 280 W) for the three libraries. An individual library
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40 required no more than 20 minutes to complete, including the three deposited layers and
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42 intermediate re-melting steps. The processing parameters used to create the
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44 specimens are summarized in Table 1.
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55 A built-in two-wavelength pyrometer was used to obtain cooling rates at the
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57 surface of the laser melted zones corresponding to the 200 W, 240 W, and 280 W laser
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4 power settings. In-situ acquisition of accurate temperature profiles during fabrication of
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6 the libraries was challenging due to the varying emissivity across the libraries requiring
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8 different camera exposure times. Because Zr constitutes the bulk of the thermal mass
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10 in the composition libraries, it was assumed that cooling rates are dominated by the
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12 thermal transport properties of the underlying substrate. Therefore, temperature profiles
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14 were collected from laser line scans performed separately on a bare Zr substrate to
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16 estimate the cooling rates involved during fabrication of the libraries.
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21 In previous work, we have demonstrated the ability to rapidly identify glassy
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23 regions of laser-deposited composition libraries using an optical microscopy-based
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25 differential interference contrast (DIC) imaging method [35,36]. We applied this high-
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27 throughput screening method to the ternary libraries prepared in this work. As was
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29 demonstrated in our prior work, smooth, liquid-like segments were assumed to be
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31 indicative of vitrified material, in contrast to the rough surface topography of crystalline
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33 material. The correlation between the smooth surface topography and a glassy structure
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35 was later confirmed by TEM. To define a compositional range of glass formation,
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37 composition measurements were collected via energy dispersive spectroscopy (EDS) at
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39 the endpoints of each topographically-smooth segment within a library.
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45 Following the fabrication of the continuously-graded libraries, three different alloy
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47 compositions possessing high GFA in the Cu-Zr-Ti ternary system were prepared by
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49 copper mold suction casting. Two of these alloys, $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ and $(\text{Cu}_{0.64}\text{Zr}_{0.36})_{90}\text{Ti}_{10}$,
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51 were identified in the literature as having large critical casting dimensions [21,37]. The
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53 third alloy, $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$, was identified in the present work as potentially having a
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55 greater GFA than these literature compositions. The cast specimens were prepared
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from elemental feedstock metal with minimum purities of 99.8 at. %. Differential scanning calorimetry (DSC) was performed for the three alloys to obtain T_g and onset temperature of crystallization T_x . Differential thermal analysis (DTA) was used to obtain the liquidus temperature T_l . The heating rates for the DSC and DTA traces were 20 K min⁻¹ and 5 K min⁻¹, respectively.

2.2 Discrete composition library for mechanical properties evaluation

An alternative deposition scheme was used to create a 12 x 12 square array of discrete composition “dot” specimens, with each dot spaced 2 mm from its nearest neighbors (Figure 2). Cu and Zr powders were simultaneously deposited row by row with a 250 W laser. In this deposition scheme, the powders were again continuously delivered to the substrate, but the laser shutter was open for a duration of 120 milliseconds only at the positions defined in the array. The delivery rates of the two elemental powders were maintained fixed during the deposition of a row of dots to achieve a constant Cu:Zr molar ratio within each row. After completion of a row, the powder delivery rates were adjusted incrementally to increase the molar ratio in the next row of dots. This was repeated sequentially until completion of the array, resulting in a discretized Cu-Zr composition gradient along each column. Following the initial deposit, a layer of Ti powder was deposited over the entire array of binary dots using a 150 W laser and the travel speed increasing in the -x direction from 8.47-29.63 mm/s. Each dot was re-melted with a 200 W laser and a pulse time of 200 milliseconds to facilitate thorough mixing of the three components. In the final step, the array was re-melted again with a 180 W laser and reduced pulse time of 60 milliseconds. Following fabrication, EDS was used for compositional characterization of the library.

The DIC microscopy screening method was also applied to identify vitrified dots in the discrete library. Due to the exceptionally smooth surface of the vitrified material, no further polishing was necessary to prepare the discrete dot library for instrumented nanoindentation measurements. All indentation experiments were performed with a Hysitron TI 950 Triboindenter equipped with a diamond Berkovich indenter tip. Using a maximum load of 25 mN and loading rate of 3.1 mN/s, four indents, spaced 10 μm apart, were performed in the central region of each vitrified dot in the array to obtain average hardness (H) and indentation modulus (E_r) values.

3.0 Results

3.1 Continuously-graded libraries

A number of distinct surface topographies were observed in the as-deposited specimens, representing a wide spectrum of possible microstructures, from fully amorphous (featureless and smooth) to fully crystalline (rough with distinct asperities) (Figure 3). The surface roughness of smooth regions was quantitatively evaluated with scanning probe microscopy. The resulting probe images yielded sub-nanometer roughness values, an order of magnitude lower than the surface roughness of metallic samples that have been polished to a mirror finish with colloidal media.

Using the smooth surface topography as an indicator of a predominantly glassy structure, the compositional range of glass formation was identified in each of the three as-deposited libraries (Figure 4). The compositional range of the glass region was observed to diminish with increasing laser power (or laser heat input, defined below), consistent with our previous findings in the Cu-Zr binary system [35,36]. A master plot containing the experimentally-obtained glass region of each library is shown on the

ternary composition map in Figure 5. For comparison, two compositions [21,37] reported in literature to possess high GFA are also shown on the plot.

Average surface cooling rates estimated from laser melting a Zr substrate are listed in Table 1, calculated directly from the measured thermal profiles by the product of the temperature gradient with laser travel speed, averaged from 1600 to 2200 °C. (While the cooling rate through the glass transition temperature is of greatest interest, lower temperatures were not accessible by the two wavelength pyrometer employed in this study.) The estimated rates decrease with increasing laser power, in agreement with the diminishing compositional range of vitrified regions in the three continuously-graded libraries. The magnitude of the estimated surface cooling rates are also consistent with prior finite element analyses of cooling rates achieved with the LENSTM process [38,39].

3.2 Discrete dot composition library

Figure 6 shows a cross-sectional view of a dot screened as amorphous in the discrete composition library. Heat affected zones corresponding to each re-melting step are clearly visible, surrounding a featureless melt zone that is presumably amorphous. The featureless melt zone has a depth of approximately 200 µm, sufficiently thick to avoid substrate effects during nanoindentation. The apex of the dots provided a flat, planar surface for nanoindentation, eliminating the usual requirement of post-fabrication polishing. Assuming a radius of curvature of at least 1 mm, and indentations with lateral dimensions of 2 µm, the variation in surface height across the width of an indent would not exceed 10 nm for the indents performed in this study, meeting the acceptable surface condition required for nanoindentation.

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4 Of the 144 discrete dots in the discrete composition library, 92 of them were
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6 screened as amorphous via differential interference contrast imaging. Figure 7 shows
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8 property-composition contour plots for the measured E_r and H values. Each data point
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10 used to construct the plots represents the average value of interest from the four
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12 indents performed on every vitrified dot in the array (see *Experimental*). The average
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14 standard deviation was 0.85 GPa and 0.03 GPa for E_r and H , respectively.
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19 It should be noted that the discrete and continuously graded composition libraries
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21 did not overlap completely; the continuous libraries extended to larger Ti contents than
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23 the 12 x 12 array of discrete dots. Thus, while the property maps of Figure 7 do not
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25 include all of the glass forming compositions delineated in Figure 5, this is because the
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27 complete 12 x 12 array did not include any dots in that composition range. In fact, the
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29 glass forming range of the discrete dots extends to lower Ti and Cu contents than was
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31 observed in any of the continuously-graded libraries.
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36 **4.0 Discussion**

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38 A central goal of this work was to demonstrate a high-throughput method for
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40 evaluating glass forming ability as a function of composition in multicomponent alloys.
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42 This was facilitated by the use of differential interference contrast (DIC) optical
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44 microscopy, which is highly sensitive to surface topography, to screen the as-deposited
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46 libraries and eliminate the obviously crystalline compositions from further consideration.
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48 When the free surface of a liquid solidifies, crystal nucleation and growth produces a
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50 rough surface that is easily visible using DIC [40]. In contrast, if the liquid vitrifies on
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52 cooling, no surface asperities are apparent using DIC, suggesting a lack of crystallites
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54 larger than the resolution of the measurement, on the order of 100 nm. Further scanning
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4 probe microscopy observations of the smooth regions identified by DIC confirmed sub-
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6 nanometer RMS surface roughness values, consistent with the lack of even smaller
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8 crystallites. Using this screening as a first step, the amorphous structure can then be
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10 confirmed by x-ray or electron diffraction methods. In our previous studies of the binary
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12 Cu-Zr system [35,36], TEM foils extracted from the smooth areas identified by DIC were
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14 repeatedly verified as amorphous by electron diffraction, lending support for DIC
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16 microscopy as a reliable screening tool. For the remainder of this work, we assume that
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18 the regions of the composition libraries screened as “smooth” by DIC are primarily
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20 amorphous.
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26 In order to evaluate the glass-forming ability of a given alloy composition, it is
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28 necessary to experimentally access a wide range of cooling rates. In the conventional
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30 serial casting approach, this is accomplished primarily by casting wedge shaped
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32 specimens or several individual specimens of different cross-sectional thicknesses, in
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34 order to determine the critical casting thickness that avoids crystallization. Notably, the
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36 measured critical thicknesses are highly sensitive to other processing parameters, such
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38 as the initial temperature of the melt or dwell time in the liquid phase prior to casting.
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40 Differences in the details of the processing often lead to different critical casting
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42 dimensions [24] as measured by different laboratories, complicating cross-lab
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44 comparisons. In the present work, the full range of compositions in a given library are
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46 prepared under consistent processing conditions, facilitating the GFA comparison.
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53 In laser processing, cooling rates within the localized melt pool depend largely on
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55 the laser heat input, defined as $\lambda = P/(\nu D)$, where P , ν , and D denote laser power, travel
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57 speed, and beam diameter, respectively. It is well-known from studies involving
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4 crystalline alloys that high laser powers or low travel speeds produce coarser grain
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6 microstructures, signaling an inverse scaling of cooling rate with λ [41–43]. Thus, an
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8 alloy's minimum or critical cooling rate should correspond to an upper limit of λ . Indeed,
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10 Chen *et al.* performed laser surface melting experiments on $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ substrates and
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12 reported a threshold laser power above which crystallization became unavoidable [44].
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14 Similarly, Sun and Flores conducted laser deposition experiments with a Zr-based BMG
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16 powder on amorphous substrates of the same composition [45]. By fixing P and
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18 increasing v above a threshold value, the authors were able to nearly eliminate
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20 crystalline features from the heat affected zone. Taking advantage of the empirical
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22 relationship between GFA and laser heat input, we demonstrated in our prior studies of
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24 compositionally-graded binary specimens that increasing the applied λ has the general
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26 effect of narrowing the compositional range of glass formation towards the best glass-
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28 former in the system.
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36 It follows that the reduction in the extent of the smooth region within the ternary
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38 composition libraries with increasing laser power, or equivalently, increasing λ (Figure
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40 5), was a direct consequence of subjecting the ternary libraries to successively lower
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42 cooling rates. Our pyrometer measurements of surface temperature profiles indicated
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44 that increasing the laser power from 200 W to 280 W reduces the average cooling rate
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46 by nearly 30%. As cooling rates decreased with increasing laser power, fewer
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48 compositions remained that could vitrify, resulting in the gradual convergence of the
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50 glass region towards the composition with the highest GFA. Based on this trend in GFA
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52 with λ and a qualitative assessment of the overlapping regions in Figure 5, GFA
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54 appears to be much more sensitive to the Ti content than to Cu or Zr; the glass forming
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regions narrow much more rapidly with changes in Ti content than with Cu or Zr. This is consistent with the extensive glass forming range of the Cu-Zr binary system.

It is important to note that the average surface cooling rates (on the order of 10^4 K/s) measured with the pyrometer are not the *critical* cooling rates required for glass formation in the vitrified regions within the libraries. The critical cooling rate for glass formation is derived from averaging the instantaneous cooling rate in the temperature range between T_g and T_l , approximately 430 – 900 °C for near-eutectic Cu-Zr-Ti compositions, well below the range of the pyrometer employed in the present study. However, the measured surface cooling rates are consistent with the results of previous finite element models of laser surface melting in similar metallic glass systems [38,39]. These models demonstrated that the instantaneous cooling rate decreases rapidly with time and temperature after the surface heating event. Approaching the glass transition temperature, the cooling rates measured by the models were an order of magnitude lower than those measured at high temperatures. Both the peak temperature and the cooling rates also decrease rapidly away from the surface. While the high temperature surface cooling rates measured here represent an extreme, the pyrometry results remain useful in providing quantitative verification of the inverse relationship between laser heat input and average cooling rate, as well as the relative change in the necessary critical cooling rate for extending the compositional region of glass formation.

Based on the observed GFA trend with composition, we predicted $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$ as the optimum glass former in the region of the ternary system covered by our composition libraries. Within this ternary system, Inoue *et al.* had previously identified $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ as a notable glass former [21], while Wang *et al.*

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4 further explored glass formation along a series of compositional tie lines and reported
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6 $(\text{Cu}_{0.64}\text{Zr}_{0.36})_{90}\text{Ti}_{10}$ as the best glass former in the alloy system [37]. (Note the similarity
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8 in the Ti content among these three “optimal” compositions, which again highlights the
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10 strong sensitivity of GFA to Ti in this system.) Both studies reported a critical rod
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12 diameter of 4 mm for their respective compositions. It is significant that while these two
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14 compositions occupied the vitrified region of the 200 W library, they were excluded from
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16 the glass regions in the 240 and 280 W libraries, implying that our predicted
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18 composition should exhibit higher GFA. In addition, although the same reported critical
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20 casting diameter of the Inoue and Wang compositions would suggest equivalence of
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22 GFA, our results indicated that $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$, positioned near the periphery of the vitrified
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24 region in the 200 W library, should have poorer glass forming ability than both Wang’s
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26 alloy and our predicted composition.
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33 To validate our method for optimizing GFA, wedge samples of $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$,
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35 $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$, and $(\text{Cu}_{0.64}\text{Zr}_{0.36})_{90}\text{Ti}_{10}$ were prepared by copper mold suction casting.
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37 Care was taken to maintain consistent processing conditions for all three alloys. The
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39 wedge critical casting thickness was determined to be 1.50, 1.35, and 1.20 mm (± 0.05
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41 mm), respectively for $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$, $(\text{Cu}_{0.64}\text{Zr}_{0.36})_{90}\text{Ti}_{10}$, and $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$. While these
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43 differences are small, they are consistent with the expected ranking of GFA among the
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45 three alloys based on the results from the laser-deposited libraries. The apparent
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47 discrepancy between the critical casting dimensions measured here and those
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49 measured by the Inoue and Wang studies again highlights the difficulty of comparing
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51 critical casting dimensions across multiple laboratories and processing methods to
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53 evaluate GFA.
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Figure 8 provides the DSC heating traces for the three suction cast samples. The glass transition temperature T_g , crystallization temperature T_x , and liquidus temperature T_l (obtained from DTA measurements) for each alloy are listed in Table 2. Also listed are $T_{rg} = T_g/T_l$ and $\Delta T = (T_x - T_g)$, two of the most prevalent indicators of GFA and glass stability in the literature. According to the ranking of ΔT , $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$ has the lowest thermal stability, defined here as the temperature range over which the supercooled liquid resists crystallization. On the other hand, the similar T_{rg} values show no correlation with the respective glass forming ability of the three alloys, as measured by either their critical casting thicknesses or their assumed critical laser heat inputs based on the present work. This demonstrates that, although temperature-based predictors reflect certain crucial aspects of glass formation, they neglect other important determining factors of GFA, such as the structural motifs that comprise the overall glass as well as kinetic properties (e.g. viscosity, dynamic fragility) of the supercooled liquid.

A second major objective of this work was to identify correlations between glass composition and mechanical behavior, taking advantage of the extensive compositional range that can be rapidly produced by the laser deposition technique. The contour plot (Figure 7a) of the measured indentation modulus values from the discrete library shows a strong inverse relationship between E_r and the titanium content and less sensitivity of E_r to changes in the Cu:Zr molar ratio. It is as yet unclear if and how the sensitivity of GFA to the Ti content (and relative insensitivity to Cu and Zr) is related to the dependence of E_r on Ti, although the elastic modulus depends on atomic bonding characteristics and hence the degree of local ordering, which should in turn influence

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4 glass formation. It is apparent that glass formation does not directly correlate with the
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6 elastic modulus.
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9 For alloys with Zr contents less than ~37 at. %, the hardness also exhibits an
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11 inverse relationship with the Ti content (Figure 7b). However, for alloys with greater than
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13 37 at % Zr, H instead scales with the Cu content. Again, there is no clear correlation
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15 between the hardness and GFA. However, it is interesting that the optimal glass forming
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17 composition identified in this work, $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$ (marked with a red X in Figure 7b),
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19 is on the boundary between the region where H scales with Cu and where it scales with
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21 Ti. Like the elastic modulus, the hardness (or resistance to plastic deformation) should
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23 depend on the underlying atomic structure, in particular the ease with which atomic
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25 rearrangements occur. That our optimal composition occurs along the intersection of
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27 two competing compositional trends in hardness suggests that it may correspond to a
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29 composition where two structural motifs are competing for dominance. Further study is
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31 required to describe the glass structure as a function of composition in this region of the
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33 ternary system.
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41 The disparate compositional trends of H and E_r over the majority of the
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43 investigated compositions contrasts with a previous study investigating the correlation
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45 between Vickers hardness and shear modulus for a wide variety of BMGs belonging to
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47 different compositional families [46]. In that work, the hardness was observed to scale
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49 linearly with shear modulus. Figure 7c shows a master plot of H versus E_r from data
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51 obtained in the present study. The data exhibits a large amount of scatter; a linear fit to
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53 the data yielded a relatively low R^2 value of 0.42. However, within narrow bands of
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55 Cu:Zr ratios (highlighted by the color-coded scale provided), a stronger linear trend
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4 does seem to persist, with higher Cu:Zr ratios yielding larger intercept values for the
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6 trend lines (not shown). Although these results suggest a weak correlation between
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8 hardness and modulus over the entire composition range, it is important to recognize
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10 that our measurements were limited to only ternary Cu-Zr-Ti alloys and covered a
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12 relatively narrow range of hardness values. From a global perspective that includes all
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14 BMG alloys, a strong linear relationship between hardness and modulus may still apply,
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16 but here we show that deviation from the rule is possible when studying a specific family
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18 of alloys.
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24 As shown in Figure 7c, for a given value of indentation modulus, hardness
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26 increases with increasing Cu content. Indentation hardness measures the resistance of
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28 a material to permanent deformation under a constrained state of stress determined by
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30 the indenter shape, the applied load, and the material's elastic properties. For two
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32 compositions possessing identical E_r but different H values, the elastic contribution to
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34 the total tip displacement is the same for both alloys, but the plastic contribution is larger
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36 for the alloy with the lower hardness. That is, the alloy with the lower H value would be
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38 intrinsically less resistant against plastic flow under identical loading conditions. The
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40 direct implication of the trend in hardness with Cu:Zr ratio for a fixed E_r value is that
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42 reducing the overall Cu content in the ternary alloys may enhance plasticity.
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49 Recent molecular dynamics studies of the binary Cu-Zr system carried out by Ma
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51 *et al.* have linked elastically soft regions within the heterogeneous structure of the model
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53 glasses to a propensity to undergo localized, non-affine shear transformations [47,48].
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55 Moreover, the soft regions strongly corresponded with the most unstable atomic cluster
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57 species, termed by the authors as geometrically unstable motifs (GUMs). It was
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observed that the population of GUMs increased with increasing Zr content (decreasing Cu) in the binary alloys, providing a fundamental design rationale for the discovery of $\text{Zr}_{61}\text{Cu}_{25}\text{Al}_{12}\text{Ti}_2$, which to date exhibits the highest reported fracture toughness among known monolithic BMG alloys [49]. Our experimental finding that decreasing the Cu content promotes plastic deformation in Cu-Zr-Ti ternary alloys is in agreement with the results of these previous studies, suggesting structural changes of the glass with varying composition as the underlying reason for the measured trends in H and E_r .

The present work introduces a high-throughput method for rapidly evaluating the relative ductility or toughness of glass forming alloys. It should be noted that the state of stress in nanoindentation experiments is very different from the stress distribution immediately ahead of crack tip in fracture toughness tests, and one could argue that pronounced plasticity observed in indentation does not necessarily translate to higher fracture toughness or ductility. However, if we assume that plastic flow is ultimately dictated by the availability of structurally soft regions that are more susceptible to shear transformation, alloys with a denser population of soft spots should display a greater intrinsic capacity for accommodating plastic strain regardless of the manner in which stress is applied. Although further experimental validation is needed, we propose that the high-throughput mechanical testing method described in this paper, in conjunction with computational modeling, offers a promising pathway for designing new monolithic alloys with optimal combinations of toughness and GFA.

5.0 Conclusions

We have demonstrated a novel high-throughput methodology to systematically examine glass formation in complex, multicomponent alloy systems. Continuously

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4 graded Cu-Zr-Ti libraries covering a composition range of several tens of atomic percent
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6 were rapidly fabricated by a laser additive manufacturing technique. Smooth, liquid-like
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8 surface topographies in the as-deposited libraries were indicative of vitrified material,
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10 enabling rapid screening via optical microscopy to define continuous regions of glass
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12 forming within a library. Multiple libraries were synthesized with varying laser heat input
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14 in the final re-melting step. With increasing laser heat input, the regions of glass
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16 formation were observed to gradually diminish towards the glass-forming composition(s)
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18 with the lowest critical cooling rate(s). $\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$ was estimated as the optimum
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20 glass former in the ternary system and subsequent casting results verified the new
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22 alloy's superior GFA in comparison with previously identified bulk glass formers.
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28 Nanoindentation measurements performed on the discrete composition library
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30 revealed that indentation modulus was primarily sensitive to the Ti content, while
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32 hardness was sensitive to Ti for low Zr contents and to Cu for high Zr contents. The
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34 cross-over in the trend for hardness with composition, which corresponded to the
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36 composition of the optimal glass former identified in this work, suggested a change in
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38 the underlying structural motifs controlling both glass forming ability and plastic
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40 deformation. Comparison of the hardness and modulus trends further suggested that
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42 reducing the Cu content promotes ductility.
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48 Although the procedural strategy described in this study is most suitable for
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50 exploring ternary composition space, it could be adapted to interrogate higher order
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52 systems through the use of elemental powder blends and pre-alloyed powders. An
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54 alternative application of our methodology is the optimization of existing multicomponent
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56 BMGs that possess notably high GFA. It is unclear whether such BMGs, originally
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identified through conventional serial casting methods, truly represent the global GFA maxima in their respective composition space. However, it is likely that the global maximum lies in the compositional neighborhood of these alloys [24]. By using the method described in this paper to probe the neighboring space surrounding known glass formers, new BMGs with optimized GFA could be quickly identified.

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Figure 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.

Figure 2 **a**, Photograph of discrete dot Cu-Zr-Ti composition library. **b**, Schematic illustrating the deposition scheme for incorporating the desired composition gradients in

the discrete dot libraries. Black arrows indicate direction of increasing Cu:Zr molar ratio (vertical) and Ti content (horizontal).

Figure 3 Differential interference contrast (DIC) optical micrographs showing the surface topography of various microstructures in the as-deposited libraries. **a**, Fully amorphous. **b**, Semi-crystalline. **c**, Crystalline.

Figure 4 DIC image of the composition library processed with a 200 W laser. The boxed segments collectively represents the glass-forming region identified by observing the smooth, liquid-like topography of amorphous material. White arrows indicate directions of increasing Ti and Cu:Zr molar ratio. Inset is a photograph of a complete as-deposited library.

Figure 5 Vitrified regions of three composition libraries processed with different final-glazing laser powers (200, 240, and 280 W), plotted on a ternary composition map. The black dot within the glass region of the 280 W library is the predicted best glass former. The other two black dots are notable glass formers previously reported in other studies (Ref. 21, 36). The gray region approximates the overall extent of the ternary composition space contained within the three libraries.

Figure 6 DIC image of a cross section through one of the dots screened as amorphous in the discrete composition library. Heat affected zones produced by the re-melting steps are visible surrounding a featureless melt zone.

Figure 7 **a**, Reduced modulus and **b**, hardness contour plots, constructed from nanoindentation measurements performed on 92 glassy alloys within the ternary Cu-Zr-Ti system. Our predicted best glass-former is indicated by a red X. **c**, Hardness plotted against the reduced modulus for all 92 alloys. The color of each data point indicates its corresponding Cu:Zr molar ratio.

Figure 8 Differential scanning calorimetry heating traces of three suction-cast Cu-Zr-Ti metallic glass alloys. The scans were performed at a heating rate of 20 K/min.

Table 1 Processing parameters for the Cu-Zr-Ti composition libraries.

Library	Powder delivery rate (g/min)			Laser travel speed (mm/s)	Final re-melt laser power (W)	Average surface cooling rate, 1600 - 2200 °C
	Cu	Zr	Ti			(K/s)
Continuous 1	4.12	2.83	0.93	8.47 - 29.63	200	1.68×10^4
Continuous 2	4.12	2.83	1.3	8.47 - 29.63	240	1.43×10^4
Continuous 3	4.12	2.83	1.51	8.47 - 29.63	280	1.19×10^4
Discrete Array	0.56 - 8.80	2.51 - 0.77	0.56	8.47 - 29.63 (Ti)	180	--

Table 2 Characteristic temperatures, temperature-based predictive parameters, and wedge critical casting thickness (d_c) of three Cu-Zr-Ti metallic glass alloys.

Alloy Composition	T_g (K)	T_x (K)	T_l (K)	T_{rg}	ΔT (K)	d_c (mm)
$\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$	708	751	1146	0.62	43	1.20
$(\text{Cu}_{0.64}\text{Zr}_{0.36})_{90}\text{Ti}_{10}$	693	740	1167	0.59	47	1.35
$\text{Cu}_{51.7}\text{Zr}_{36.7}\text{Ti}_{11.6}$	682	715	1146	0.60	33	1.50