Cu–Zr–Ti ternary bulk metallic glasses correlated with 
(L → Cu₈Zr₃ + Cu₁₀Zr₇) univariant eutectic reaction

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Starting from Cu₆₀Zr₃₀Ti₁₀, the compositional dependence of bulk metallic glass (BMG) formation was revisited in the Cu–Zr–Ti ternary system. It was revealed that the optimal BMG-forming composition is located at Cu₆₀Zr₃₃Ti₇, for which a monolithic BMG rod 4 mm in diameter can be fabricated using copper mold casting. This composition is along, although slightly off, the univariant eutectic groove for the reaction (L → Cu₈Zr₃ + Cu₁₀Zr₇). With respect to the corresponding Cu–Zr binary alloys, Ti has a significant effect on further stabilizing the liquid, thus increasing the glass-forming ability. For the Cu₆₀Zr₄₀₋ₚTiₚ₄₋ₚ₃ series BMGs, the glass transition temperature Tₓ decreased with increasing Ti content, at a rate of about 2.8 K/at.%. Among these BMGs, significant compositional dependence of compressive plasticity is not observed, irrespective of the Tₓ change. Cu₆₀Zr₃₃Ti₇ glass exhibits maximum fracture strength around 2160 MPa.

I. INTRODUCTION

Among the family of bulk metallic glasses (BMGs), Cu-based alloys are particularly interesting for practical application as new structural materials due to their significant advantages, including low-cost, high fracture strength around 2 GPa often coexisting with visible ductility, and feasibility for forming BMG-based composites.¹⁻¹¹ So far, Cu-based BMGs with a critical size (Dₓ) on the centimeter scale have been discovered in several alloy systems, such as the quaternary Cu₄₆Zr₄₂Al₇Y₅,⁷ Cu₄₃Zr₄₃Al₇Be₇,⁸ Cu₄₄.₂₅Ag₁₄.₇₅Zr₃₆T₁₅,⁹ and Cu₄₆.₂₅Zr₄₄.₂₅Al₇.₅Zr₂,¹⁰ and even ternary Cu₄₉Hf₄₅Al₉.¹¹ In fact, the majority of the currently developed Cu-based BMGs are derived from binary Cu–Zr¹²⁻¹⁴ or Cu–Hf¹⁴,¹⁵ as the base system, such as Cu–Zr–Ti,¹,² Cu–Zr–Al,⁴,⁷,¹⁶ Cu–Zr–Ag,¹⁷ Cu–Hf–Ti,² and Cu–Hf–Al.¹¹,¹⁸ In the Cu–Zr binary system, it has been found that BMG with a Dₓ of 2 mm can be formed at Cu₆₄Zr₃₆, which is located near a deep eutectic, L → Cu₆₄Zr₃₆ + Cu₁₀Zr₇.¹²,¹³ Also, it was noticed that the glass-forming ability (GFA) exhibits a strong compositional dependence, sensitive to changes as small as 0.5 at.%.¹² Furthermore, in the Cu–Zr–Ti ternary, Inoue and his collaborators discovered a BMG-forming composition at Cu₆₀Zr₁₀Ti₁₀,² even though residual crystallites remained in the 4-mm-diameter as-cast rod.¹⁹ However, their work did not explain whether the BMG formation is related to a particular type of eutectic reaction. The phase diagram of Cu–Zr–Ti ternary system currently available was contributed by Woychik and Massalski.²⁰ Unfortunately, the eutectic reaction around the Cu₆₀Zr₃₀Ti₁₀ composition remains ambiguous due to complexity. Thus, in terms of metallurgical insight, the origin of BMG formation remains unclear.

On the other hand, it has become highly interesting recently that the ductility and elastic constants of BMGs have been found to be composition-dependent in a given alloy system.²¹–²⁴ Duan et al.²⁴ showed that the glass transition temperature Tₓ, shear modulus G, and Poisson’s ratio ν for the Cu–Zr–Be BMGs are very sensitive to change in compositions. For this system, as the (Zr + Ti) content increase, Tₓ and G decrease, while ν exhibits the opposite trend. The BMG with lower G and higher ν is expected to be more ductile than other compositions since the shear flow barrier for an unstressed shear cooperative zone is relatively small.²⁵

The purpose of this paper is threefold. First, the compositional dependence of BMG formation was revisited in the vicinity of the previous Cu₆₀Zr₃₀Ti₁₀ composition (denoted as Inoue’s alloy) to locate the optimal BMG-forming composition in the Cu–Zr–Ti ternary system. Second, the BMG-forming composition zone is correlated with the eutectic reaction the alloy melt undergoes during solidification by determining the phase selection
in the sample solidified at a cooling rate slightly lower than the critical cooling rate for BMG formation. Third, the effect of Ti on the \( T_g \) and compressive properties for the \( \text{Cu}_{60}\text{Zr}_{30-y}\text{Ti}_y \) \((3 \leq y \leq 10)\) series BMGs was studied to examine the compositional dependence in this system.

II. EXPERIMENTAL

Elemental pieces with purity better than 99.9\% were used as starting materials. The master alloy ingots of 20 g in weight with the nominal composition (in atomic percentage) were prepared by arc melting under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The alloy ingots were melted several times to ensure compositional homogeneity. The weight change of the master alloys before and after arc-melting was less than 0.1 wt\%. For the bulk samples with a diameter between 2 and 4 mm, the master alloy was remelted in a quartz tube using induction melting and injected in a purified inert atmosphere into the copper mold that has internal rod-shaped cavities of about 50 mm in length. Bulk samples of 1 mm in diameter are fabricated using suction casting in a mini-arc melter for compression tests.

The arc-melted ingots and as-cast rods were sectioned transversely and polished for scanning electron microscopy (SEM) observation and x-ray diffraction (XRD) analysis. SEM observation of the samples was carried out in a LEO Supra 35 scanning electron microscope (Heidenheim, Germany). The local compositions were semiquantitatively determined using an electron probe microanalyzer (EPMA; EPMA-1610, Shimadzu, Kyoto, Japan). XRD analysis was performed using a Rigaku D/max 2400 diffractometer (Tokyo, Japan) with monochromated Cu K\(_\alpha\) radiation. Samples for conventional transmission electron microscopy (TEM) observations in a JEM-2010 (JEOL, Tokyo, Japan) were prepared by twin-jet electropolishing with a solution of 9 vol\% nitric acid in a mixture of methanol and butoxyethanol (2:1).

The glass transition and crystallization behavior of the as-cast glassy rods were investigated in a differential scanning calorimeter (DSC-diamond, Perkin-Elmer, Shelton, CT) with alumina container under flowing purified argon at a heating rate of 0.67 K s\(^{-1}\). A second run under identical conditions was used to determine the baseline after each run. To confirm the reproducibility of the experimental results, at least three samples were measured for each composition. All the measurements of the \( T_g \) and onset temperature of crystallization events (\( T_{x1} \)) were reproducible within the error of \( \pm 1 \) K. The heat of crystallization \( \Delta H_c \) for the glassy phase was determined by integrating the area under the DSC curve. The melting behavior of the alloys was measured in a Netzsch 404 DSC (NETZSCH-Geratebau GmbH, Bayern, Germany) with alumina container, using the heating and cooling rates of 0.33 K s\(^{-1}\).

Compression test samples 2 mm in height were cut from the as-cast rods 1 mm in diameter. The loading surfaces were polished to be parallel to an accuracy of less than 10 \( \mu \)m. Room-temperature compression tests (Instron 8871, Canton, MA) were carried out using a strain rate of 1 \( \times 10^{-4} \) s\(^{-1}\). At least eight samples were measured to ensure reproducible results. The strain was determined from the platen displacement after correction for machine compliance.

III. RESULTS

A. Composition dependence of BMG formation around \( \text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10} \)

Figure 1 displays the BMG-forming composition map in the vicinity of the previous Inoue’s alloy. The selected triangular region involves only four compounds, \( \text{Cu}_{51}\text{Zr}_{24}, \text{Cu}_{8}\text{Zr}_{3}, \text{Cu}_{10}\text{Zr}_{7}, \) and \( \text{Cu}_{2}\text{ZrTi}. \)

The assumed tie-lines between the compounds are drawn as the solid or dashed lines. \( D_c \) of each composition was presented with different symbols. It was found that the best BMG former is located at \( \text{Cu}_{60}\text{Zr}_{33}\text{Ti}_{10} \), for which fully glassy rod of 4 mm in diameter can be fabricated. Its GFA is better than the previous Inoue’s alloy\(^2\), even though there was only a 3 at.\% change in Zr or Ti content.

Figure 2(a) displays the XRD patterns taken from the cross-sectional surfaces of as-cast rods (with diameters equal to \( D_c \) of the respective composition) for three representative BMGs, \( \text{Cu}_{60}\text{Zr}_{31}\text{Ti}_{9}, \text{Cu}_{60}\text{Zr}_{33}\text{Ti}_{7}, \) and \( \text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10} \). The typical diffusive maxima between 2\( \theta \) = 30\(^\circ\) and 50\(^\circ\) reflecting the amorphous nature, without detectable crystalline peaks within the XRD resolution, prove the complete glass formation at their respective sizes. The

![Figure 1](image-url) Composition map of BMG formation for as-cast rods around \( \text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10} \) composition. \( D_c \) of each composition was presented with different symbols. The assumed tie-lines between the compounds are drawn as the dashed lines.
corresponding DSC traces for these glassy rods are given in Fig. 2(b). In all cases, a pronounced endothermic signal resulting from glass transition and at least two-step crystallization events are observed. The thermal properties measured from DSC curves for the three alloys are summarized in Table I, including the \( T_g \), \( T_{x1} \), width of the supercooled liquid region \( \Delta T_x \) (\( \Delta T_x = T_{x1} - T_g \)), and \( \Delta H_x \). The \( \Delta T_x \) of the best glass former \( \text{Cu}_{60}\text{Zr}_{33}\text{Ti}_7 \) is about 47 K. It is not the largest one among the investigated glasses. Figure 3 shows \( T_g \) and \( T_{x1} \) as a function of Ti content for the \( \text{Cu}_{60}\text{Zr}_{40-y}\text{Ti}_y \) \( (3 \leq y \leq 10) \) series BMGs. Both temperatures decreased with increasing Ti substitution for Zr. The rate of decrease in \( T_g \) is about 2.8 K/at.% as the Ti content is increased.

Figures 4(a) and 4(b) display the DSC curves for the \( \text{Cu}_{93-x}\text{Zr}_x\text{Ti}_7 \) \( (3 \leq x \leq 36) \) and the \( \text{Cu}_{60}\text{Zr}_{40-y}\text{Ti}_y \) \( (3 \leq y \leq 10) \) series alloys, respectively, near and above their melting temperature during heating. The \( T_m \) and \( T_L \) are marked with arrows on each curve in the figures. The two series of alloys investigated, for which the Ti and Cu content is fixed at 7 and 60 at.%, respectively, are marked using dashed lines (lines I and II) in Fig. 1. Using these data, the \( T_m \) and \( T_L \) values as a function of Zr and Ti content are plotted in Figs. 5(a) and 5(b), respectively. Although the \( T_L \) values obtained from such continuous heating are usually about 10–30 K higher than real \( T_L \) in the equilibrium state, current data of the \( T_L \) can be treated as an approximation to reflect a same trend of the liquidus variation. As shown in Fig. 5(a), the \( T_m \) of these alloys remains nearly constant at 1140 K within experimental error, when the Ti content is fixed at 7 at.%. With respect to the binary invariant eutectic temperature of \( (L \rightarrow \text{Cu}_8\text{Zr}_3 + \text{Cu}_{10}\text{Zr}_7) \) (denoted as \( e_2 \) hereafter, \( T_{eut}=1158 \) K, see phase diagram[26]), the \( T_m \) value dropped by about 18 K. Nevertheless, it is of interest to note that the \( T_L \) variation shows a U-shaped dependence on the Cu/Zr fraction. The lowest \( T_L \) temperature (1176 K) is located at \( \text{Cu}_{59}\text{Zr}_{34}\text{Ti}_7 \) [see Fig. 5(a)], which is believed to be located at the univariant eutectic groove, as marked using an arrow in Fig. 5(a). The optimal BMG-forming composition is slightly off the eutectic groove and skews

![Figure 2](image1.png)

**TABLE I.** Thermal properties of \( \text{Cu}_{60}\text{Zr}_{40-y}\text{Ti}_y \) \( (3 \leq y \leq 10) \) BMGs fabricated using copper mold casting, determined from DSC measurements.

<table>
<thead>
<tr>
<th>Alloys (at.%)</th>
<th>( T_g ) (K)</th>
<th>( T_{x1} ) (K)</th>
<th>( \Delta T_x ) (K)</th>
<th>( T_{rg} ) (K)</th>
<th>( \Delta H_x ) (kJ/mol)</th>
<th>( D_c ) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}<em>{60}\text{Zr}</em>{37}\text{Ti}_3 )</td>
<td>728</td>
<td>777</td>
<td>49</td>
<td>0.59</td>
<td>5.1</td>
<td>2</td>
</tr>
<tr>
<td>( \text{Cu}<em>{60}\text{Zr}</em>{35}\text{Ti}_5 )</td>
<td>725</td>
<td>773</td>
<td>47</td>
<td>0.60</td>
<td>4.7</td>
<td>2</td>
</tr>
<tr>
<td>( \text{Cu}<em>{60}\text{Zr}</em>{33}\text{Ti}_7 )</td>
<td>722</td>
<td>768</td>
<td>46</td>
<td>0.60</td>
<td>5.0</td>
<td>4</td>
</tr>
<tr>
<td>( \text{Cu}<em>{60}\text{Zr}</em>{32}\text{Ti}_8 )</td>
<td>719</td>
<td>760</td>
<td>41</td>
<td>0.61</td>
<td>4.6</td>
<td>3</td>
</tr>
<tr>
<td>( \text{Cu}<em>{60}\text{Zr}</em>{30}\text{Ti}_{10} )</td>
<td>708</td>
<td>747</td>
<td>39</td>
<td>0.61</td>
<td>4.3</td>
<td>3</td>
</tr>
</tbody>
</table>
to the side with the higher $T_L$ (terminal Cu$_8$Zr$_3$ phase) [see the dashed line in Fig. 5(a)]. In contrast, a pronounced depression of both $T_m$ and $T_L$ occurs as the Ti content is increased, when the Cu content is fixed at 60 at.%, as seen in Fig. 5(b). Exceeding 9 at.% for the Ti content, the $T_m$ no longer changes much, remaining at about 1110 K. This means that the composition probably has reached the boundary of a ternary invariant eutectic ($L \rightarrow Cu_8Zr_3 + Cu_{10}Zr_7 + Cu_2ZrTi$), which will be proven later. Moreover, it was observed that the ternary invariant eutectic temperature (∼1110 K) is about 48 K lower than the binary invariant eutectic temperature for ($L \rightarrow Cu_8Zr_3 + Cu_{10}Zr_7$); see Cu−Zr binary phase diagram. This is an indication that introducing Ti significantly stabilizes the liquid relative to the Ti-free binary Cu−Zr alloys. Additionally, it was noticed that the optimal BMG-forming composition mainly undergoes the univariant eutectic reaction, rather than involving the ternary invariant eutectic; see the dash line in Fig. 5(b).

Additionally, making use of the data of $T_L$, the reduced glass transition temperature $T_g$ ($T_g = T_g/T_L$) of the investigated Cu−Zr−Ti ternary BMGs are calculated and listed in Table I as well. The $T_g$ value of these BMGs is around 0.60. This difference in the $T_g$ value between the BMGs is not significant, even though their GFA is different.

### B. Microstructure of arc-melted BMG-forming alloys

The cooling rate for the arc-melted BMG-forming alloy ingot was estimated to be on the order of 1−10 K s$^{-1}$. Using the Eq. (2) and parameters for the Cu$_{60}$Zr$_{30}$Ti$_{10}$ alloy provided in Ref. 27, the cooling rate of arc-melted Cu$_{60}$Zr$_{30}$Ti$_{10}$ ingot was approximately estimated to be in a range of 2−15 K s$^{-1}$. Upon this cooling rate, the solidification microstructure in the center of the alloy ingot can
be directly correlated with the phase selection when the alloy melt crystallizes before freezing into a glass, i.e., its non-equilibrium solidification pathway prior to glass formation. Therefore, crystalline phases involved in the eutectic reaction that the liquid undergoes during solidification can be revealed.

Figure 6 illustrates the XRD patterns of the arc-melted Cu\(_{60}\)Zr\(_{33}\)Ti\(_7\) and Cu\(_{60}\)Zr\(_{30}\)Ti\(_{10}\) alloys. For the Cu\(_{60}\)Zr\(_{33}\)Ti\(_7\) ternary, crystalline phases Cu\(_{10}\)Zr\(_7\) (orthorhombic) and Cu\(_{10}\)Zr\(_7\) (orthorhombic) can be identified. The Cu\(_{60}\)Zr\(_{30}\)Ti\(_{10}\) alloy exhibits a similar pattern, but a trace amount of ternary compound Cu\(_2\)ZrTi (MgZn\(_2\)-type) is detectable.

Figures 7(a)–7(c) show the backscattered SEM images of the arc-melted ternary Cu\(_{60}\)Zr\(_{33}\)Ti\(_7\) and Cu\(_{60}\)Zr\(_{30}\)Ti\(_{10}\) alloys, together with the binary eutectic Cu\(_{61.8}\)Zr\(_{38.2}\) (e\(_2\)) without Ti for comparison. The lateral surface of the sample was polished for SEM observation, under which it was shown that the microstructure is uniform throughout the sample from the top to the bottom. Two phases with different contrasts can be seen in Fig. 7(a) for the ternary Cu\(_{60}\)Zr\(_{33}\)Ti\(_7\), marked A and B, respectively. The chemical composition for each area, determined with EPMA analysis, was listed in Table II. According to the EPMA analysis, the A and B phases can be verified as the Cu\(_{10}\)Zr\(_7\) and Cu\(_8\)Zr\(_3\) compounds, respectively, each having a supersaturated solubility of Ti. In other words, the Ti dissolved in the Cu\(_{10}\)Zr\(_7\) and Cu\(_8\)Zr\(_3\) is about 6 and 3 at.%, respectively. The volume fraction of Cu\(_{10}\)Zr\(_7\) phase is significantly higher than that of Cu\(_8\)Zr\(_3\) phase. For the binary eutectic Cu\(_{61.8}\)Zr\(_{38.2}\), rod-shaped Cu\(_8\)Zr\(_3\) (darker areas) dispersed in the Cu\(_{10}\)Zr\(_7\) matrix, as shown in Fig. 7(b) (marked as B and A, respectively). These results indicate that the phase selection and morphology of Cu\(_{60}\)Zr\(_{33}\)Ti\(_7\) is quite similar to the binary eutectic alloy Cu\(_{61.8}\)Zr\(_{38.2}\) when the alloys solidified at a cooling rate slightly lower than that of glass formation. The ternary compound Cu\(_2\)ZrTi was not observed in this alloy. In contrast, three phases were observed for the ternary
Cu₆₀Zr₃₀Ti₁₀, as seen in Fig. 7(c). The chemical composition given in Table II allows the A, B, and C phases to be identified as binary Cu₁₀Zr₇ and Cu₈Zr₃, and ternary Cu₂ZrTi, respectively. As a result, it is probable that the ternary invariant eutectic reaction of (L → Cu₈Zr₃ + Cu₁₀Zr₇ + Cu₂ZrTi) was involved during solidification for this alloy. This is evidently different from the case of Cu₆₀Zr₃₃Ti₇.

Furthermore, TEM observation for the arc-melted Cu₆₀Zr₃₃Ti₇ reveals only the coexistence of Cu₈Zr₃ and Cu₁₀Zr₇ compounds in the alloy. No other phases are present. The TEM bright-field image of this alloy in Fig. 8(a) shows the two phases with different contrasts. The selected-area electron diffraction (SAED) pattern taken along the [011] zone axis for the lighter region, as shown in Fig. 8(b), proves that it is the Cu₈Zr₃ phase with an orthorhombic structure, of which the lattice parameters are \(a = 0.787 \text{ nm}, b = 0.815 \text{ nm}, \) and \(c = 0.998 \text{ nm}\). Figure 8(c) shows the SAED pattern for the darker region. The diffraction spots are identified as the [011] diffraction patterns of orthorhombic Cu₁₀Zr₇ with the lattice parameters of \(a = 1.263 \text{ nm}, b = 0.932 \text{ nm}, \) and \(c = 0.933 \text{ nm}\). To determine whether there is any orientation relationship between two crystalline phases, further systematic examination remains necessary.

### C. Compressive properties of CuZrTi BMGs with different Ti content

Figure 9 shows the uniaxial compressive stress–strain curves for three monolithic glasses with different Ti content, Cu₆₀Zr₄₀−₂₇Ti₇ (\(y = 3, 7, 10\)). As seen in Fig. 9, the monolithic glasses mainly exhibit elastic deformation before fracture, without much macroscopic yielding and plastic strain (\(\varepsilon_p\)). The fracture strengths \(\sigma_f\) of the Cu₆₀Zr₃₇Ti₇, Cu₆₀Zr₃₃Ti₇, and Cu₆₀Zr₃₀Ti₁₀ are about 2090, 2160, and 2050 MPa, respectively.

Figure 10(a) shows the appearance of the fractured samples after compression tests for the Cu₆₀Zr₃₃Ti₇ glass under SEM observation. The angle between the fracture surface and compressive loading axis is measured to be 43°, indicating that the deformation and fracture of the glass are controlled by localized shear deformation. Figure 10(b) displays the SEM images of fracture surfaces of Cu₆₀Zr₃₃Ti₇, arc-melted ingot. (b) and (c) correspond to the Cu₈Zr₃ phase (bright region) and Cu₁₀Zr₇ phase (dark region) in (a), respectively.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Area</th>
<th>Cu (at.%)</th>
<th>Zr (at.%)</th>
<th>Ti (at.%)</th>
<th>Normalized phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₆₀Zr₃₃Ti₇</td>
<td>A</td>
<td>57</td>
<td>38</td>
<td>5</td>
<td>Cu₁₀Zr₇</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>72</td>
<td>26</td>
<td>2</td>
<td>Cu₈Zr₃</td>
</tr>
<tr>
<td>Cu₆₀Zr₃₀Ti₁₀</td>
<td>A</td>
<td>58</td>
<td>33</td>
<td>9</td>
<td>Cu₈Zr₃</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>71</td>
<td>26</td>
<td>3</td>
<td>Cu₈Zr₃</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>51</td>
<td>24</td>
<td>25</td>
<td>Cu₂ZrTi</td>
</tr>
</tbody>
</table>

**TABLE II.** Chemical composition determined using EPMA for different phases in the arc-melted Cu₆₀Zr₃₃Ti₇ and Cu₆₀Zr₃₀Ti₁₀ alloys.
IV. DISCUSSION

Our findings indicate that the Cu$_{60}$Zr$_{33}$Ti$_{7}$ alloy is located at the Cu$_{8}$Zr$_{3}$ side of the univariant eutectic groove of (L $\rightarrow$ Cu$_{8}$Zr$_{3}$ + Cu$_{10}$Zr$_{7}$) in the phase diagram. (Ti has solubility in the two terminal phases, Cu$_{8}$Zr$_{3}$ and Cu$_{10}$Zr$_{7}$). The solidification pathway of its melt is expected to undergo the following sequence: primary crystallization to precipitate the Cu$_{8}$Zr$_{3}$ phase, then following the univariant eutectic reaction. In other words, it means that Cu$_{8}$Zr$_{3}$ is the competing crystalline phase with glass formation. Starting from the eutectic point (e$_2$) in Cu–Zr binary subsystem, the univariant reaction temperature was depressed with increasing Ti, along the univariant eutectic groove. This indicates that Ti involvement plays a role in stabilizing the alloy liquid, resulting in a deeper eutectic reaction in contrast to the simple Cu–Zr binary, as seen in Fig. 5(b). This is expected to promote the glass formation. The $D_c$ is increased from 2 mm at Cu$_{64.5}$Zr$_{35.5}$ to 4 mm at Cu$_{60}$Zr$_{33}$Ti$_{7}$. Both compositions are off-eutectic (binary eutectic point or eutectic groove), and skew to the Cu$_{8}$Zr$_{3}$ side with the higher TL, see Fig. 5(b). Such behavior can be understood based on the skewed eutectic coupled zone idea due to the competitive growth of the participating phases. On further increasing the Ti content up to 9 at.%, the ternary invariant eutectic (L $\rightarrow$ Cu$_{6}$Zr$_{3}$ + Cu$_{10}$Zr$_{7}$ + Cu$_{2}$ZrTi) will be involved; see Figs. 5(b) and 7(c). It is plausible that primary crystallization of Cu$_{2}$ZrTi is favored, degrading the GFA. Consequently, the GFA of Cu$_{60}$Zr$_{33}$Ti$_{10}$ (Inoue’s previous alloy; $D_c$ is only 3 mm under our processing condition) is weaker than that of Cu$_{60}$Zr$_{33}$Ti$_{7}$, Figure 11 displays a schematic representation of the BMG formation along, but slightly off, the univariant eutectic groove.

As proposed by Boettinger, microstructures may in many cases be the result of the competition of various forms of crystal growth, and the formation of metallic glass can be promoted due to the limitations on eutectic growth kinetically controlled by diffusion. Such a concept can be used here to understand the glass formation not only for the simple binary deep eutectics, but also for

**FIG. 9.** Compressive engineering stress–strain curves for the as-cast 1-mm-diameter rods of the Cu$_{60}$Zr$_{37}$Ti$_{3}$, Cu$_{60}$Zr$_{33}$Ti$_{7}$, and Cu$_{60}$Zr$_{30}$Ti$_{10}$ bulk glass.

**FIG. 10.** (a) Side views of fractured samples under compression for the Cu$_{60}$Zr$_{33}$Ti$_{7}$ bulk glass and (b) its SEM images of the fractured surface.

This glass, showing vein-like patterns typical of the metallic glasses owing to locally reduced viscosity during shear failure.
The univariant eutectic in ternary systems. In addition, the observation that the ternary alloys correlated with univariant eutectic reaction exhibit a higher GFA may also explain why the GFA of binary alloys such as Cu–Zr can be enhanced by microalloying.

As presented above, significant compositional dependence of compressive plasticity is not observed for the Cu_{60}Zr_{40−y}Ti_{y} (3 ≤ y ≤ 10) series BMGs, even though the T_g decreased with increasing Ti content at a rate of about 2.8 K/at.%. It is different from the case of Cu–Zr–Be BMGs, where the T_g dropped about 3.8 K/at.% with increasing (Zr + Ti) content. The failure behavior of the BMGs with different Ti content is quite similar, all operated and controlled by localized shear bands. The failure strength is comparable to those of other ternary Cu-based BMGs such as Cu–Zr–Al and Cu–Zr–Ag but significantly lower than those of Cu–Hf–Ti and Cu–Hf–Al BMGs.

V. SUMMARY

A round the Cu_{60}Zr_{30}Ti_{10} composition discovered previously by Inoue and collaborators, a search located the best glass-forming composition at Cu_{60}Zr_{43}Ti_{7}, for which a monolithic BMG rod 4 mm in diameter can be fabricated using copper mold casting. This composition is near the univariant eutectic groove of (L → Cu_{60}Zr_{3} + Cu_{10}Zr_{7}) and skews to the side with the higher T_L (Cu_{60}Zr_{3} phase terminal). Compared with the Cu–Zr binary BMG, which is correlated with the eutectic reaction of (L → Cu_{60}Zr_{3} + Cu_{10}Zr_{7}), the improvement of the glass-forming ability is caused by the fact that Ti significantly stabilizes the liquid. Our finding that the glass formation was favored in the vicinity of the univariant eutectic was attributed to the constraints on the coupled growth of two-phases during solidification of the liquid. For the Cu_{60}Zr_{40−y}Ti_{y} (3 ≤ y ≤ 10) series bulk glasses, significant compositional dependence of compressive plasticity is not observed, even though the glass transition temperature T_g decreased much at about 2.8 K/at.% Ti. The compressive fracture strength of Cu_{60}Zr_{37}Ti_{3}, Cu_{60}Zr_{33}Ti_{7}, and Cu_{60}Zr_{3}Ti_{10} bulk metallic glass is around 2090, 2160, and 2050 MPa, respectively.

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