Effects of Niobium Content on Microstructural Development of CuZr BMGC

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Abstract
Stepped-diameter rods of 3- and 4mm diameter were cast to explore the effects of changing the niobium content of a previously studied Bulk Metallic Glass Composite (BMGC) alloy. 4mm specimens were found to be fully crystalline containing a B2 CuZr phase as well as a Cu$_{10}$Zr$_7$ intermetallic phase identified in XRD. 3mm specimens were found to have more varied microstructures, including one composition that produced possible core-shell structured precipitates. No amorphous material was confirmed, however DSC data suggests a phase transformation took place in the 3mm specimens that did not occur in the 4mm specimens.

Introduction
Bulk Metallic Glass Composites (BMGCs) are the subject of great interest in the materials science community. They are derived from Bulk Metallic Glasses (BMGs), which are renowned for their particularly large elastic strain limits, corrosion resistance and strength. These qualities, however, are overshadowed by severe lack of ductility and small plastic strain limits. BMGCs overcome those pitfalls by combining a high-strength glassy matrix with a ductile crystalline secondary phase. These composites have already been shown to exhibit remarkable plasticity when compared to BMGs, as well as extended elastic regimes when compared to crystalline metals. Literature in recent publications has established that the mechanical properties of these BMGCs are dependent on a combination of volume fraction, morphology, and composition of the secondary phase [1], [2], [3]. It follows that the best way to tailor the mechanical behavior of a BMGC would be to control the way the microstructure forms. It has been demonstrated that it is possible to cause changes in microstructure by making small changes in the composition, specifically targeting components with the higher melting temperatures [2], [4]. The alloy Cu$_{47.5}$Zr$_{48}$Al$_4$Nb$_{0.5}$ was selected for this experiment due to previous experience manufacturing and characterizing it [5], and the fact that the Niobium has a significantly higher melting temperature than the other three components. 5 compositions, (Cu$_{48}$Zr$_{48}$Al$_4$)$_{100-x}$Nb$_x$, with X=0, 0.25, 0.5, 0.75, and 1, herein referred to as A-, B-, C-, D-, and E-groups respectively, were manufactured and characterized. It should be noted that the C-group with 0.5 atomic percent niobium has the closest composition to the alloy originally studied by Wu, et al [1]. Here we present the morphological changes that resulted from varying the niobium content of the alloy, and the specific manufacturing processes used.
Experimental Procedure

Specimens were prepared by first arc-melting the elements with purity better than 99.9% in a Ti-gettered argon atmosphere into 30-gram buttons using a water-cooled copper mold. Two buttons were produced for each composition, \((\text{Cu}_{48}\text{Zr}_{48}\text{Al}_{4})_{100-x}\text{Nb}_x\), for \(x = 0, 0.25, 0.5, 0.75, 1.0\). It should be noted that for the B-group \((x=0.25)\) one of the two buttons contained all of the Niobium for the entire casting due to the small amount required. Each button was flipped and remelted three times to ensure homogeneity. Masses of the raw elements and the pre-cast buttons may be found in Table 1.

Table 1: Initial masses of raw materials and final mass of pre-casting buttons. Note that all Niobium for B-group is contains in B1.

<table>
<thead>
<tr>
<th>Component \ Button #</th>
<th>A1/A2</th>
<th>B1</th>
<th>B2</th>
<th>C1/C2</th>
<th>D1/D2</th>
<th>E1/E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (g)</td>
<td>12.141</td>
<td>12.104</td>
<td>12.104</td>
<td>12.066</td>
<td>12.029</td>
<td>11.992</td>
</tr>
<tr>
<td>Zr (g)</td>
<td>17.429</td>
<td>17.376</td>
<td>17.376</td>
<td>17.322</td>
<td>17.268</td>
<td>17.215</td>
</tr>
<tr>
<td>Al (g)</td>
<td>0.430</td>
<td>0.428</td>
<td>0.428</td>
<td>0.427</td>
<td>0.426</td>
<td>0.424</td>
</tr>
<tr>
<td>Nb (g)</td>
<td>0.000</td>
<td>0.184</td>
<td>0.000</td>
<td>0.185</td>
<td>0.277</td>
<td>0.369</td>
</tr>
<tr>
<td>Total (mass of buttons) (g)</td>
<td>30.002/29.997</td>
<td>30.087</td>
<td>29.989</td>
<td>29.992/29.999</td>
<td>29.982/29.980</td>
<td>29.914/29.999</td>
</tr>
</tbody>
</table>

The rod specimens were cast by arc-melting the two buttons of a given composition in a Ti-gettered argon atmosphere and pouring into a stepped-diameter copper mold that can produce both 4mm-diameter and 3mm-diameter rods. To ensure consistent processing conditions between specimens, the casting process was planned out, and the plan was strictly adhered to for all 5 castings. A 700-amp arc was used to melt and mix the two buttons for 34 seconds, followed by a 3-second pour during which the arc was maintained over the liquid minimize its viscosity as it was poured into the mold. Note that the two buttons for the B-group \((x=0.25)\) were premelted for an extra 30 seconds to ensure homogenous composition throughout the liquid before the standard melt and pouring process took place.

Previous experience with this alloy group [5] indicated that the 4mm-diameter specimens would be composites while the 3mm-specimens would be fully glassy, so 3mm-long sections from the top of each 4mm-diameter rod were cut and polished for further characterization. For reference, the sections described above are referred to as “Section 1” for each of their composition groups A-E. All samples were characterized using a Nikon optical microscope, however only the A-group and C-group specimens were analyzed in a JEOL-7001 SEM, a Rigaku X-Ray Diffractometer, and Mettler Toledo Differential Scanning Calorimeter (DSC).

3mm-long sections were also cut from the bottom portion of the 3mm-diameter sections, labeled “Section 2” for each alloy group A-E. These specimens were characterized with the Nikon optical microscope, and Mettler Toledo DSC.

Results & Discussion

Each casting resulted in usable rod sections of both 3mm- and 4mm-diameter. In some cases a gas pocket separated the 3mm-diameter section from the 4mm-diameter section in the
same casting, in others the rod was continuous with a stepped diameter. In previous work [5], it was found that specimens with 4mm-diameter produced the best composite structure, so in the present work the first sections characterized are of 4mm-diameter from the topmost portions of each rod, herein referred to as “section 1” for each composition. Figures 1-5 contain optical micrographs of “Section 1” for each composition, A-E.

Optical microscopy of the 4mm-diameter sections shows what is at least a 2-phase structure, likely crystalline, with the secondary phase being dendritic in nature. Only the C-group alloy exhibited a large, distinct phase separation region towards the edge of the rod (fig. 3).

SEM microscopy of the A-group specimen in Fig. 6 contains a backscattered electron image from the center region of the rod. The A-group composition contains no niobium (Cu$_{48}$Zr$_{48}$Al$_4$), so the heaviest element present is Zirconium. The contrast in image A suggests that the dendritic phase is Al-rich compared to the surrounding material. Figure 7, taken at higher magnification supports the notion that this specimen is crystalline, containing no clearly amorphous structures. SEM examination of the C-group specimen yielded equally interesting results. The center region of the rod appears to contain a 2-phase structure, with the darker phase once again possibly containing a higher proportion of aluminum due to its darker shading in image (A), fig. 8. The micrographs of the edge region of this section were noteworthy as they contain the only large phase separation features yet observed in these specimens (fig. 9). The SEM micrographs reveal that there is a difference in composition between the two phases (image A), and that the composition of the edge phase and the composition of the secondary phase (the darker features on the left side of image A) are at least similar in composition (EDS analysis is necessary to confirm). One feature of note is the large cross-shaped artifact in the upper left, which can be seen in all images (red box). With closer examination at higher magnifications (fig. 10), it is observed in image (A) that there is no significant difference in compositional morphology on either side of the contrast shift seen in image (B).

All observations thus far indicate that the 4mm specimens have a fully crystalline structure. Figure 11 below contains XRD data gathered on Section 1 for A-group and C-group. No broad amorphous peak is present, and there are several crystalline peaks, which confirms that these specimens are fully crystalline in nature. In both A and C groups, several peaks corresponded to the well-known B2 CuZr phase, also found in [1], [3], [5]. Smaller peaks indicate the presence of the cubic Cu$_{10}$Zr$_7$ phase as well.

The 3mm-diameter rods were also sectioned and polished (referred to as “section 2” of their respective compositions). Fig. 12 contains a series of optical micrographs of the 3mm rods. The rods appear to have a 3-phase microstructure, one phase is clearly dendritic, and the darker grey of the other two is likely the B2 CuZr phase, as the circular nature (see images B, D) of the features is very similar to those reported in [1], [5]. It is unclear whether the third phase is crystalline or amorphous in nature from these images. Image (D) is remarkable in that the circular features appear to have a core-shell structure (boxed, with arrows), similar to those reported in [3]. SEM and EDS characterization is necessary to confirm both composition and structure.
The DSC curves for both the 3mm (fig. 13) and 4mm (fig. 14) specimens exhibit some type of phase transformation, but since the transformation peaks in the 3mm specimens are so much thinner and sharper than those of the 4mm specimens, it is reasonable to conclude that the 3mm specimens are actually undergoing some kind of volumetric phase transformation (either amorphous to crystalline, or a transformation between two crystalline phases), whereas the 4mm specimens experienced some sort of grain growth or similar relatively minor structural change.

**Conclusion**

In this work 4mm- and 3mm-diameter rods of the compositions $(\text{Cu}_{48}\text{Zr}_{48}\text{Al}_4)_{100-X}\text{Nb}_X$, $X = 0, 0.25, 0.5, 0.75, \text{and } 1$, were manufactured and characterized with optical and electron microscopy, DSC, and XRD. All specimens, independent of geometry and composition, contained at least two crystalline phases. XRD and DSC data suggest the 4mm specimens are entirely crystalline in nature; no broad peaks observed in XRD nor are any sharp phase transformation events present in the DSC curves. The 3mm specimens are a little more promising; their DSC curves all exhibit a sharp phase transformation peak. Further study is required to determine whether or not the 3mm specimens contain any amorphous material as-cast, or if the phase transformation is merely between different crystalline phases.

Future work will include further characterization of the 3mm specimens in SEM, XRD and EDS to obtain more exact structural and compositional information on the microstructure, particularly on the D-group specimen containing the possible core-shell structured precipitates. The specimen as they are now are too small for mechanical testing, however if further structural characterization continues to be promising, there is enough excess material from the original castings to recast a new set of 3mm-rods for tensile and other mechanical tests.
Appendix A: Figures

Figure 4: A-group (X=0), 100x magnification. Specimen clearly contains at least 2 phases, one clearly dendritic.

Figure 4: B-group (X = 0.25), 100x magnification. Note the large, dendritic structure that dominates the center of the image.

Figure 2: Group C (X = 0.5), 100x magnification, contrast boosted. Area of interest is a distinct phase separation at the edge of the rod. Images recorded using the default settings were unclear, so contrast was boosted in post-processing.

Figure 2: Group D (X = 0.75), 100x magnification. Note smaller average size of secondary phase particles. Image appears out of focus due to tilt of the specimen on the microscope platform.

Figure 5: E-group (X = 1), 100x magnification. Note that the main difference in morphology is the average size of the secondary phase particles.
Figure 7: SEM Micrograph of A-group, section 1, taken of the edge region of the rod.

Figure 7: SEM Micrograph of A-group specimen, center region.

Figure 8: SEM micrograph of C-group, Section 1, center region. Image (A) generated from backscattered electrons, image (B) generated from secondary electrons. Black dots in image (B) are likely some variety of beam contamination, not a part of the specimen.
Figure 10: SEM Micrographs of C-group, Section 1, edge region. Note the left-right phase separation, most evident in SEI (B) and color composite (D).

Figure 10: SEM Micrographs of phase separation region with increased magnification. Note the lack of contrast in image (A) compared to image (B).
Figure 11: XRD data for A and C group 4mm-diameter specimens.
Figure 12: Optical micrographs of the 3mm-diameter specimens. Letter designations correspond to composition. Note the possible core-shell structured features in (D).
Figure 13: DSC Curves generated for 3mm-rod specimens. Note crystallization events are present in each curve.
Figure 12: DSC curves generated from 4mm-diameter specimens. Note how the transformation peaks are significantly broader than those for the 3mm-diameter specimens of the same composition.
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References:


