# Fabrication and mechanical properties of WC particulate reinforced Cu<sub>47</sub>Ti<sub>33</sub>Zr<sub>11</sub>Ni<sub>6</sub>Sn<sub>2</sub>Si<sub>1</sub> bulk metallic glass matrix composites

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The mechanical behavior of the WC particulate (WC<sub>p</sub>) reinforced Cu<sub>47</sub>Ti<sub>33</sub>Zr<sub>11</sub>Ni<sub>6</sub>Sn<sub>2</sub>Si<sub>1</sub> bulk metallic glass (BMG) matrix composites has been examined. The mechanical properties are improved with increasing WC<sub>p</sub> content up to 20 wt%. The ultimate compression strength and plastic strain of the composite containing 20 wt% WC<sub>p</sub> are 2.4 GPa and 2.4%, while those of the monolithic BMG are 1.6 GPa and ~0%, respectively. The multiple shear band formation and crack deflections through WC particles have been identified as the main mechanism for the improved toughness. © 2005 Springer Science + Business Media, Inc.

# 1. Introduction

Bulk Metallic Glasses (BMGs) have attracted a great attention due to their outstanding properties such as high strength and large elastic ranges [1]. The development of several BMG systems has been explored to achieve a large glass forming ability (GFA) [2]. Cu-based BMGs with a large GFA have also been developed, resulting in the extension of BMG materials selection option. It has been reported that Cu-based BMGs show a strength level comparable with other BMG systems, and component additions such as Si and/or Sn in the Cu-Ti-Zr-Ni system lead a significant increase of GFA [3-5]. While the BMGs have shown appealing mechanical properties, a limited ductility of BMGs has often restricted potential structural applications. In order to achieve an extended ductility, a fabrication of BMG composites has been practiced. As a route to produce BMG composites, an in-situ partial crystallization or an addition of secondary phases has been examined, showing that the presence of the secondary phases can improve the ductility [6–8]. One example of the latter option is the WC particulate (WC<sub>p</sub>) reinforced Zr-based BMGs [9]. When WCp is added to the Zr-based BMGs, an enhanced elongation has been achieved during compression tests. The main mechanism for the enlarged ductility has been suggested as a multiple shear band formation through particulates, while monolithic BMGs usually exhibit a catastrophic fracture due to the propagation of highly localized shear bands [9–11]. Further, the examination of the fractured surface after compression tests has shown that a strong interface bonding seems to be a favorable option to increase ductility, when hard second phases are combined into the BMG matrix [9]. While various particulate reinforced BMG matrix composite systems have been examined in order to achieve extended elongation, the particulate reinforced Cu-based BMG matrix composite system has not been examined yet. In this study, the WC particulate and Cu<sub>47</sub>Ti<sub>33</sub>Zr<sub>11</sub>Ni<sub>6</sub>Sn<sub>2</sub>Si<sub>1</sub> (at%) alloy were selected as a reinforcing material and a BMG matrix, respectively, based on the results of the previous reports [9]. In particular, the effect of the amount of WC<sub>p</sub> on mechanical properties has been investigated. Following a fabrication of the Cu-based BMGs with a various amount of WC<sub>p</sub>, the mechanical properties of the composite have been examined through compression tests together with structural and thermal history examinations.

# 2. Experimental

About 20 g alloy buttons with a composition of  $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$  (at%) have been made by arc



Figure 1 DSC traces obtained from the injection-cast  $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$  alloys containing x wt%  $WC_p$  (x = 0, 10, 15, 20).



Figure 2 XRD patterns obtained from the injection-cast  $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$  alloy containing 20 wt% WC<sub>p</sub> (XRD traces obtained from the melt-spun  $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$  alloy and WC particles are also included for comparison).

melting of high purity (>99.9%) elemental components in a Ti gettered Ar atmosphere. In order to fabricate the  $WC_p$  reinforced composite, the alloy button and WC particulates were vacuum-induction melted together in a quartz tube, and injection-cast into a waterchilled Cu mold by a pressurized argon gas. By using this method, 1 mm (in diameter) cylindrical-shaped BMG matrix composites with various weight percents of WC<sub>p</sub> (0, 10, 15 and 20%) have been fabricated. SEM (Secondary Electron Microscope, Hitachi S-2700) and XRD (X-ray Diffraction, Rigaku CN2301) were used for microstructural examination and phase identifications, respectively. The thermal analysis was performed using DSC (Differential Scanning Calorimetry, Perkin Elmer DSC7). Mechanical properties were measured at room temperature under a compressive mode with a strain rate of  $1 \times 10^{-4}$  s<sup>-1</sup>. For the compression tests samples of 1 mm in diameter and 2 mm in height were prepared. The samples were fixed in a jig designed to ensure parallelism of the ends. The surface of the fractured specimen was observed using SEM.

### 3. Results and discussion

Fig. 1 shows the DSC results obtained from the ascast monolithic BMG and BMG matrix composites. The  $T_g$  and  $T_x$  (onset) of the Cu<sub>47</sub>Ti<sub>33</sub>Zr<sub>11</sub>Ni<sub>6</sub>Sn<sub>2</sub>Si<sub>1</sub> BMG were 440°C and 490°C, respectively [5]. When



Figure 3 Compressive stress-strain curves for the Cu<sub>47</sub>Ti<sub>33</sub>Zr<sub>11</sub>Ni<sub>6</sub>Sn<sub>2</sub>Si<sub>1</sub> alloy containing x wt% WC<sub>p</sub> (x = 0, 10, 15, 20) (strain rate:  $10^{-4}$  s<sup>-1</sup>).



*Figure 4* SEM image of the surface appearance of the compressive test specimen after fracture  $(Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$  alloy containing 20 wt% WC<sub>p</sub>).

the weight percent of WC<sub>p</sub> increased from 0 up to 20 wt%, both  $T_g$  and  $T_x$  remained nearly same within the experimental error, indicating that the addition of WC<sub>p</sub> does not affect the crystallization behavior significantly and the value of  $\Delta H$  was lowered in proportional to the increase of WC<sub>p</sub> weight percent. The value of  $\Delta H$  was lowered by about 22%, when the WC<sub>p</sub> amount reached 20 wt%. The estimated exothermic heat of the examined composites is shown in Fig. 1. Further confirmation of the BMG based composites has been made by XRD, as shown in Fig. 2, displaying that the sharp peaks from the WC phase were superimposed on the diffuse halo peak from the amorphous phase.

Fig. 3 shows the results of compression tests of  $WC_p$  reinforced BMG composites together with the monolithic Cu-based BMG. The ultimate compression

strength of the monolithic Cu-based BMG showed about 1.6 GPa without any indications of the plastic deformation. The value was a little lower than those of the other Cu-based BMGs. The Cu<sub>47</sub>Ti<sub>34</sub>Zr<sub>11</sub>Ni<sub>8</sub> BMG showed the ultimate compression strength of about 2.1 GPa with a plastic elongation of about 0.2% [6]. Regarding to the GFA of Cu-based BMGs, it has been reported that the partial replacement of Ni with Sn in Cu<sub>47</sub>Ti<sub>33</sub>Zr<sub>11</sub>Ni<sub>8</sub>Si<sub>1</sub> increased the GFA enabling the fabrication of up to 6 mm diameter rod by injection casting method [5]. Although a limited strength was obtained for the monolithic Cu47Ti34Zr11Ni6Sn2Si1 alloy, the addition of WCp up to 20 wt% increased the strength up to 2.4 GPa, which is a factor of about 1.5 times higher than the monolithic BMG, as shown in Fig. 3. At the same time, the plastic elongation increased up to about 2.4% for the composite. However, the elastic limit decreased from  $\sim 2\%$  for the monolithic BMG to  $\sim 1.4\%$  for the composite BMG containing 20 wt% WC<sub>p</sub>.

The main mechanism for enhancement of the plastic strain is attributed to the multiple shear band formation during compression tests, as shown in the surface of the sample after compression test (Fig. 4). Upon increasing the amount of WC<sub>p</sub>, a larger number of shear steps has been observed at the surface of the compression test sample. In fact, this corresponds to the previous results that multiple shear bands formed during compression test of the BMG matrix composites [9]. Similar results of the strength and elongation increase have been obtained for the ZrC<sub>p</sub> reinforced Zr-based BMG matrix composites [10]. For a clear comparison of the effect of WC<sub>p</sub> amount on mechanical properties, the fractured surfaces of two distinctive composites containing 10



 Amorphous + 10 wt.% WC<sub>p</sub>
 Amorphous + 20 wt.% WC<sub>p</sub>



Figure 6 SEM image of the surface appearance of the fractured specimen after polishing  $(Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$  alloy containing 20 wt% WC<sub>p</sub>).

and 20 wt% WCp are shown in Fig. 5. The vein-like patterns of the fractured surface were clearly observed. The formation of the vein-like pattern is closely related to the localized adiabatic heating during inhomogeneous flow in the metallic glass [12]. When the amount of WC particulates is increased, the evidence of liquid droplets is visible on the fractured surface, reflecting that higher energy during fracture contributed to local melting. The high toughness of the BMG matrix composite containing large amount (20 wt%) of WC particulates supports these observations, as shown in Fig. 3. Also, the crack deflection was observed in the partially polished samples, as marked as arrows in Fig. 6. It clearly shows that the presence of WCp acts as a barrier for the continued crack propagation changing the path into several other directions, which is a favorable option for the enhancement of mechanical properties.

## 4. Summary

The WC<sub>p</sub> reinforced Cu-based BMGs ( $Cu_{47}Ti_{33}Zr_{11}$ Ni<sub>6</sub>Sn<sub>2</sub>Si<sub>1</sub>) have been successfully fabricated and the mechanical properties of the composites have been examined. When the amount of  $WC_p$  increases up to 20 wt%, the ultimate compression strength increases up to 2.4 GPa, a factor of about 1.5 times higher value compared with the monolithic BMG, together with 2.4% plastic elongation. The increase of toughness is attributed to the multiple shear band formation and crack deflections due to the presence of WC particulates.

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