Ceramic Particulate Reinforced Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ Metallic Glassy Matrix Composite Fabricated by Spark Plasma Sintering

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Two-type sintered specimens of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ glassy alloy powder blended with and without 10 vol% ZrO$_2$ ceramic powder, which had the similar relative density, were fabricated by a spark plasma sintering process in order to clarify the reinforced mechanical effect of ZrO$_2$ particulates in the metallic glassy matrix composite. The structure, thermal stability and mechanical properties of the two-type sintered specimens were investigated. Two-type sintered specimens as well as original metallic glassy powder exhibited similar thermal stability. No crystallization of the metallic glassy matrix was demonstrated during the spark plasma sintering process. The plastic ductility of the sintered Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ glassy matrix composite was enhanced by adding the ZrO$_2$ particulates into the metallic glassy alloy. The improvement was originated from the structural inhomogeneity caused by the micro particles inclusion.  

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1. Introduction

The extensive research worldwide on bulk metallic glasses (BMGs) is motivated due to their scientific and engineering significance. A large number of metallic glasses with high glass-forming ability have been found in many alloy systems. However, monolithic metallic glasses face a challenging problem that they fail by the formation of highly localized shear bands under loading at room temperature, which leads to brittle fracture features and catastrophic failure of the materials. Such absence of the plasticity limits the extensive practical applications of BMGs. One way to overcome this problem is to produce the composite materials containing crystalline phase. Attempts have been made to enhance the ductility of BMGs by introducing crystalline phase into the metallic glassy matrix: nanoscale compound particles dispersed in the glassy matrix via thermal treatment, adding particles or fibers during casting or consolidation process, and in situ formed ductile phase precipitates. It was found that the plastic ductility of monolithic BMGs was enhanced by adding some crystalline phase into the metallic glassy matrix composites. This ductility behavior in the metallic glassy matrix composites is achieved by the formation of multiple shear bands initiated at the interface between the reinforcing phase and the metallic glassy matrix, and their confinement in metallic glassy matrix composites. The improved ductility opens up the possibility to overcome the so far limited applications of the monolithic BMGs. However, due to the requirement of high cooling rate for the formation of glassy phase from a liquid state, the metallic glassy matrix composites have been restricted to alloy systems with high glass forming ability. And the dimensions of the metallic glassy matrix composites are limited, and the shape is also rather simple.

Powder metallurgy process should be the best alternative to overcome the problem. Spark plasma sintering (SPS) process, as a novel technique developed for rapid sintering metals, ceramics and composite materials, has a great potential for producing specimens with nearly no crystallization for amorphous materials or minimal grain growth for crystalline materials in a short sintering time. The SPS process is a type of solid compression sintering technique which is similar to hot-pressing (HP) sintering process, so that the sintered specimens with the large-size and complicated shape can be easily achieved. In the SPS process, a pulse electrical current flows directly in the sintered materials. A very high heating efficiency is achieved. Furthermore, it is also postulated that the high electric-pulse power might generate plasma in the gaps between powder particles, although the plasma generation during the SPS process has still not been experimentally verified. The plasma can partially eliminate adsorbed gases and oxide films on nonoxide particles, and activate the surface of the powders. The sintering can be carried out at a lower temperature with a shorter time than that of conventional sintering processes. Therefore, crystallization of the metallic glassy alloy and coarsening of the dispersed particles can be avoided. However, up to now, little report has been presented about the SPS consolidation of metallic glassy matrix composite.

It is well known that Zr-Cu-Al-Ni alloy is one of the best glass formers. The alloy is very robust against heterogeneous nucleation at surfaces or interfaces, making it desirable for use as the matrix in the development of novel bulk metallic glassy matrix composites. For the reinforcements, in traditional metal matrix composites, the most widely used reinforcements are ceramics, such as ZrO$_2$, SiC, Al$_2$O$_3$. Therefore, the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ glassy alloy powder and the ZrO$_2$ ceramic powder were chosen to use in this study.

In the present study, we will address to clarify the reinforced mechanical effect of ZrO$_2$ particulates in the metallic glassy matrix composite. Two-type sintered specimens of the Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_{5}$ glassy alloy powder blended with and without 10 vol% ZrO$_2$ ceramic powder, which had the similar relative density, were prepared by the SPS process. The structure, thermal stability and mechanical properties of the two-type sintered specimens were investigated. The reinforced effect of ZrO$_2$ particulates is discussed.
metallic glassy powder, and 600 MPa for the mixed powder. The details of heating, temperature measurement and control, and loading pressure control in the SPS process have been described in a previous paper. The sintered specimens obtained were a cylindrical shape with a diameter of 10 mm and a height of about 5 mm.

The structures of the powders and sintered specimens were examined by X-ray diffractometry (XRD) in reflection with a monochromatic Cu Kα radiation. Thermal stability associated with the glass transition temperature (Tg), supercooled liquid region (ΔT), and crystallization temperature (Tc) was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K s⁻¹. The density of the sintered specimens was determined by measuring their mass and dimension of the samples (mass per volume). Mechanical properties under a compressive load were measured at room temperature using a conventional mechanical testing system (Instron 4201). The test specimens with a rectangular shape of 2.5 mm in width, 2.5 mm in thickness and 5.0 mm in height were used in the present study. The initial strain rate used was 5 × 10⁻⁴ s⁻¹.

3. Results

Using the gas-atomized Zr₅₅Cu₃₀Al₁₀Ni₁₅ glassy powder or a mixed powder of Zr₅₅Cu₃₀Al₁₀Ni₁₅ glassy powder blended with 10 vol% ZrO₂ powder, the sintering was performed by the SPS process. The density of the obtained specimens was measured. The results are given in Table 1. The similar relative density is seen for two-type sintered specimens. This indicates that there is similar porosity, or same free volume in the two sintered specimens.

The structures of the sintered specimens and the original powders were analyzed by XRD. Figure 2 shows the XRD patterns obtained from the sintered specimens and the original glassy alloy powder. Figures 2(a), 2(b) and 2(c) show the XRD patterns of the sintered Zr₅₅Cu₃₀Al₁₀Ni₁₅ glassy matrix composite with 10 vol% ZrO₂ powder, the sintered monolithic Zr₅₅Cu₃₀Al₁₀Ni₁₅ BMG specimen, and the original Zr₅₅Cu₃₀Al₁₀Ni₁₅ glassy alloy powder, respectively. The XRD pattern of the sintered monolithic Zr₅₅Cu₃₀Al₁₀Ni₁₅ BMG specimen consists only of a broad diffraction peak and no sharp peak corresponding to crystalline phase is observed, in agreement with that of the original Zr₅₅Cu₃₀Al₁₀Ni₁₅ glassy alloy powder. The XRDPattern of the sintered glassy matrix composite specimen shows sharp peaks diffracted from the ZrO₂ (as indicated in Fig. 2(a)) superimposed on a broad halo peak, indicating that the matrix of the sintered composite consists of a fully glassy phase.

Figure 3 shows the DSC curves measured from the sintered specimens and the original glassy alloy powder

Table 1 Density and thermal properties of the Zr₅₅Cu₃₀Al₁₀Ni₁₅ BMG and the ZrO₂ particulate reinforced composite as well as original metallic glassy powder.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>SPS conditions</th>
<th>ρ (g/cm³)</th>
<th>ρ/ρ₀ (%)</th>
<th>Tₛ (K)</th>
<th>Tₓ (K)</th>
<th>ΔT (K)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolithic glass</td>
<td>623 K under 30 MPa, 10 min</td>
<td>6.51</td>
<td>95.3</td>
<td>683</td>
<td>771</td>
<td>88</td>
<td>50.0</td>
</tr>
<tr>
<td>+10%ZrO₂</td>
<td>623 K under 600 MPa, 10 min</td>
<td>6.39</td>
<td>95.2</td>
<td>683</td>
<td>773</td>
<td>90</td>
<td>45.6</td>
</tr>
<tr>
<td>Original powder</td>
<td></td>
<td>684</td>
<td>774</td>
<td>90</td>
<td>50.6</td>
<td></td>
<td></td>
</tr>
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</table>
with a continuous heating rate of 0.67 K s\(^{-1}\). The features of the DSC curves of the sintered metallic glassy matrix composite specimen (Fig. 3(a)) and the sintered monolithic Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) BMG specimen (Fig. 3(b)) are similar to that of the original glassy alloy powder (Fig. 3(c)), namely, an endothermic reaction due to the glass transition, followed by a large supercooled liquid region and two exothermic reactions due to crystallization events. The sintered metallic glassy matrix composite specimen as well as the sintered monolithic Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) BMG specimen shows that the glass transition temperature (\(T_g\)), the onset temperature of the first-stage crystallization (\(T_X\)), and the extent of the supercooled liquid region (\(\Delta T = T_X - T_g\)) are similar to those from the original metallic glassy powder. These thermal stability data are summarized in Table 1. It indicates that no crystallization of the metallic glassy matrix occurred during the SPS process. Furthermore, the crystallization enthalpy (\(\Delta H\)) of 50.1 J/g for the sintered monolithic Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) BMG specimen is similar to that for the original glassy alloy powder, while the crystallization enthalpy (\(\Delta H\)) of the sintered metallic glassy matrix composite specimen is 45.6 J/g. It is about 90% of that of the original Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy matrix, which is 50.6 J/g, as given in Table 1 and Fig. 3. This further demonstrated that the crystallization of the Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy matrix did not take place during the SPS process.

Figure 4 shows nominal compressive stress–strain curves of the sintered Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy matrix composite with 10 vol% ZrO\(_2\) powder (a) and the sintered monolithic Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) BMG specimen (b).

Fig. 2 XRD patterns of the sintered Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy matrix composite with 10 vol% ZrO\(_2\) powder (a), the sintered monolithic Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) BMG (b), and original Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy powder (c).

Fig. 3 DSC curves of the sintered Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy matrix composite with 10 vol% ZrO\(_2\) powder (a), the sintered monolithic Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) BMG (b), and original Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy powder (c).

Fig. 4 Compressive stress–strain curves of the sintered Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) glassy matrix composite with 10 vol% ZrO\(_2\) powder (a) and the sintered monolithic Zr\(_{55}\)Cu\(_{30}\)Al\(_{10}\)Ni\(_{5}\) BMG specimen (b).
4. Discussion

The present experimental results show that no crystallization of the metallic glassy matrix occurred during the SPS process. This may originate from the low sintering temperature of 623 K, which was much lower than the crystallization temperature \( T_x \) as well as the glass transition temperature \( T_g \) of the \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy alloy powder. They were measured to be 774 K and 684 K, respectively, at a heating rate of 0.67 K\ s\^{-1}, as given in Table 1. It is known that the SPS process is an electrical sintering technique which applies an ON-OFF DC pulse voltage. The pulse electric current directly flows through the sintered powder materials in the SPS process. Thus the temperature at the contact interfaces between powder particles should be higher than the average temperature for the sintered specimens due to the focused current and Joule heat at the bonded interface between powder particles, which has been demonstrated in our previous investigations of Al-Mg alloy powders sintered by the SPS process.\(^{14-16}\) This local high temperature can enhance the formation and growth of the neck between powder particles, and improve the properties of the sintered BMG specimens. On the other hand, Tokita\(^{12}\) indicated that the application of the pulse voltage in the SPS process enhanced thermal diffusion. The heat is transferred immediately and diffused to whole powder particle so that intergranular bonding portion is quickly cooled. This is in favor of the sintering of glassy materials or metastable phase materials. Kawamura et al.\(^{17}\) demonstrated that the crystallization was avoided because the cooling rate was higher than the critical cooling rate of the \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy alloy prepared by spark welding.

Therefore, it is reasonable that the crystallization of the metallic glass can be prevented during the SPS process. Furthermore, redistribution of the glassy matrix and the dispersed particles does not exist during solid state sintering, which results in more homogeneous products than those prepared by the casting method. Hence, this is a promising technique for the fabrication of metallic glassy matrix composite without size and shape limitations.

Next, we should discuss the effect of the \( \text{ZrO}_2 \) particulates on the mechanical properties of the sintered \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy matrix composites. As shown in Fig. 4 and Table 2, comparing with the sintered monolithic \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) BMG specimen, both of the compressive strength and plastic ductility in the sintered \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy matrix composite were enhanced by adding the \( \text{ZrO}_2 \) particulates into the metallic glassy alloy. The compressive strength increased from 1420 MPa for the sintered monolithic \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) BMG specimen to 1500 MPa for the sintered \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy matrix composite specimen. Meanwhile the compressive plastic ductility after the elastic strain increased from 0.74% for the sintered monolithic \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) BMG specimen to 1.55% for the sintered metallic glassy matrix composite specimen. It is a very large improvement in comparison with that of the as-cast \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) metallic glassy rod specimen, which is almost zero.\(^{18}\) Due to the similarity of free-volume in the sintered \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy matrix composite and in the sintered monolithic \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) BMG specimen, the effect of free-volume on the plastic ductility in the sintered composite specimen can be determined. Therefore, except for the effect of the free-volume, the improvement of the compressive strength and plastic ductility in the sintered \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy matrix composite should mainly originate from the reinforcement \( \text{ZrO}_2 \) particulates. Conner et al.\(^{19}\) have reported that particulates of W, WC, Ta or SiC can restrict the propagation of shear bands and promote the generation of multiple shear bands. In the present study, the existence of the \( \text{ZrO}_2 \) particulates, on the one hand, makes shear band propagation more difficult, which leads to an increase of compressive strength. On the other hand, the \( \text{ZrO}_2 \) particulates also lead to the generation of multiple shear bands.\(^{10,20}\) Choi-Yim et al.\(^{20}\) have demonstrated that the formation of multiple shear bands is initiated by particles, which are blocking the propagation of the single shear band.

Based on the aforementioned analysis and discussion, it is clear that the improvement of the compressive strength and the plastic ductility originates from the structural inhomogeneity caused by the micro particles inclusion. The \( \text{ZrO}_2 \) ceramic particulates act as a resisting media causing deviation, branching and multiplication of shear bands.

5. Conclusions

Two-type sintered specimens of the \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy alloy powder blended with and without 10 vol% \( \text{ZrO}_2 \) ceramic powder, which had the similar relative density, were prepared by the SPS process. The structure, thermal stability and mechanical properties of the two-type sintered specimens were investigated. Two-type sintered specimens as well as original metallic glassy powder exhibit similar thermal stability. No crystallization of the metallic glassy matrix is demonstrated during the SPS process. The plastic ductility of the sintered \( \text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5 \) glassy matrix composite is enhanced by adding the \( \text{ZrO}_2 \) particulates into the metallic glassy alloy. The improvement originates from the structural inhomogeneity caused by the micro particles inclusion.

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