Microwave Processing of Metallic Glass/polymer Composite Material in A Separated H-Field

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1. Introduction

As a rapid developing technique, microwave heating has shown its potential in the field of material processing. Compared with conventional heating, it can offer some interesting advantages including significant processing time and energy savings, high heating rate, lower environmental hazards and provision of high product quality and reliability since it is a volumetric heating in that thermal energy is internally and instantaneously generated within the material by the interaction between the material and electromagnetic field, instead of originating from external radiant or resistance heating [Clark & Sutton, 1996; Katz, 1992; Roy et al., 1999, 2002; Clark et al., 2000]. Furthermore, some excess effects, which are referred as nonthermal, or athermal effects, may also occur during microwave heating by the interaction of the material with the electromagnetic field [Bergese, 2006; Saitou, 2006; Roy et al., 2002]. It is generally known that the way microwaves interact with matter depends mainly on the electrical conductivity, complex permittivity, and complex permeability of the materials. Currently, microwave heating is applied widely to food, rubber, semiconductors, polymers, ceramics and metallic materials. For dielectric materials, the heating mechanisms in microwave field are mainly the polarization dissipation of electric dipoles under the alternating electric (E-) field and direct conduction effects. However, microwave heating of metals is different from that observed in dielectric materials. As good electrical conductors, bulk metals can not be well heated up because microwaves interaction with metals is restricted to its surface, but fine metal powders may be couple with microwaves at room temperature by Joule heating and magnetic-induced effects. Now a variety of metallic materials have been successfully sintered and processed in a pure microwave system or a hybrid heating system in which an external microwave susceptor is used [Anklekar, et al., 2005; Gedevanishvili, et al., 1999]. Although the mechanisms of microwave heating have not been fully understood until now, there is still an increasing interest in microwave processing of various materials, especially new materials with potential applications.
Metallic glasses are MGs known as a new class of metallic materials with the unique combination of physical, chemical and mechanical properties due to their disordered atomic arrangement different from that in crystalline metallic materials [Inoue, 2000; Johnson, 1999; Wang et al., 2004]. Compared with its crystalline counterparts, MGs exhibit significant viscous flow if they are heated to supercooled liquid region (temperature range between glass transition ($T_g$) and crystallization onset temperature ($T_x$)), which can be utilized for heating and sintering process. This makes it a possibly good candidate for microwave heating. In fact, microwave heating and sintering of metallic glassy powders and their composites has been performed in a single-mode cavity [Yoshikawa, et al., 2007; Louzguine-luzgin, et al., 2009], and nanocrystallization of some metallic glassy powders and ribbons has been induced in the E-field [Nicula, et al., 2009]. Otherwise, microwave processing of metallic glass matrix composites has also been reported because the composite materials may exhibit the desired properties that can not be produced by conventional monolithic materials [Li, et al., 2008; Xie, et al., 2009].

Based on the above consideration, we tried to heat of the powdered mixture MG of and polymer in microwave field and intended to develop a composite material based on MG and polymer using microwave heating technique because MGs and typically polymers show complementary properties, such as electrical, optical and mechanical characteristics and the liquidus or glass transition temperature of the commonly-used thermoplastics are relatively low (not more than 450°C) and very close to the $T_g$ of some MGs. If two components can be combined in a single material, some interesting properties may be expected in the proposed composites.

The present paper describes microwave processing of the powdered mixtures of metallic glasses and polymers using a single-mode 915 MHz applicator in a separated magnetic (H-) field. A single-mode applicator is chosen because it has high field strength, the most efficient by far, can be operated continuously and used to focus the microwave field at a given location. We investigated the heat response of the powdered mixtures of the Cu$_{50}$Zr$_{45}$Al$_5$ metallic glass and polyphenylene sulfide (PPS) [$C_6H_4S_n$] in a separated microwave H-field. PPS was chosen because of its good thermal stability, excellent chemical resistance, and inherent flame resistance. The effect of the PPS content in the mixtures on the heating behaviors of the composites was also investigated.

2. Experimental procedure

The Cu$_{50}$Zr$_{45}$Al$_5$ metallic glassy powders were fabricated by a high-pressure gas-atomized method. The preparation procedure has been presented elsewhere [Xie, et al., 2007]. Size distribution of the gas-atomized alloy powders was measured by a conventional sieving method. PPS used in this work was in the form of off-white neat powder and its average molecular weight was about 10,000. The blended powders were obtained by mixing Cu$_{50}$Zr$_{45}$Al$_5$ metallic glassy alloy powders with the size under 90 μm and PPS powders according to various volumetric ratios in a mixer. To obtain larger-size samples and improve sintering, we have designed and built a single-mode microwave applicator (915MHZ, 5kW) with the pressure loading system. The illustration schematic of a single-mode 915 MHz microwave system is shown in Fig. 1. It consists of a single-mode 915 MHz generator with a power output adjustable from 1 to 5 kW in steps of 40 W, a waveguide, three-stub tuner, separator, a single-mode tunable applicator, a pressure loading system, an infrared pyrometer and a computer control system. Microwave-induced heating was
performed in a separated H-field maximum. The samples were placed in an alumina (Al₂O₃) mould because Al₂O₃ has not obvious heat response in the H-field. The applied pressure was kept at about 5 MPa for avoiding the fracture of the alumina mould during heating process. To order to initiate microwave absorption, the resonating cavity was tuned by a remotely controlled three-stub tuner and the slide plunger at the end of the waveguide. The temperature was controlled by adjusting the input power (P). The temperature measurement was performed in situ using an infrared pyrometer through a quartz window on the side of the press. The pyrometer was calibrated by comparison of the reading with thermocouple in a resistance furnace. It is not possible to measure the sample temperature under about 450 K. All experiments were carried out under a flowing nitrogen gas or low vacuum.

Fig. 1. Illustration schematic of a single-mode 915 MHz microwave system

The structures of the initial powders and the sintered composites were determined by X-ray diffractometry (XRD) in reflection with a monochromatic Cu-Kα radiation. The thermal stability of metallic glassy powder was examined using differential scanning calorimetry (DSC) at a heating rate of 40 K/min. The density of the bulk sintered specimen was calculated by measuring the mass and dimension of the sample (mass per volume). The microstructures of the sintered specimens and initial metallic glassy alloy powders were characterized by scanning electron microscopy (SEM).

3. Results and discussion
3.1 Characterization of Cu₅₀Zr₄₅Al₅ gas-atomized powders
Here the characteristics of the gas-atomized Cu₅₀Zr₄₅Al₅ are determined. Figure 2 shows the XRD pattern and DSC curve of Cu₅₀Zr₄₅Al₅ alloy powders with particle size under 125 µm. It can be seen in Fig. 2(a) that only typical broad diffraction maxima without any observable sharp diffraction peaks corresponding to crystalline phases occur, indicating that a fully amorphous phase is formed in the particle size range below 125 µm. As shown in Fig. 2(b), a distinct glass transition characteristic followed by two crystallization events occurs, and the values of Tᵥ, Tₓ, and supercooled liquid region width (ΔT) were determined to be 708 K, 776 K and 68 K, respectively, which are similar to the ones reported for the as-cast Cu₅₀Zr₄₅Al₅ rod and ribbon[Inoue & Zhang, 2002]. Figure 3 shows a typical SEM micrograph of the gas-atomized Cu₅₀Zr₄₅Al₅ alloy powders with particle sizes under 125 µm. Most of the gas-
atomized powders have a spherical morphology with clean surface. On the outer surface of the particles no observable contrast revealing the formation of crystalline phase is seen. These results show that the gas-atomized method is flexible for fabricating metallic glassy powders.

![XRD pattern and DSC curve of Cu<sub>50</sub>Zr<sub>45</sub>Al<sub>5</sub> alloy powders with particle size below 125 µm.](image)

![SEM micrograph of the gas-atomized Cu<sub>50</sub>Zr<sub>45</sub>Al<sub>5</sub> alloy powders with particles sizes under 125 µm](image)

**3.2 Microwave processing of the mixtures of Cu<sub>50</sub>Zr<sub>45</sub>Al<sub>5</sub> metallic glassy powder and PPS powder**

We firstly simulated the electromagnetic field distribution in the waveguide based on the finite element method and by using a JAMG-Studio program. The results have indicated that the separated E- and H-field maxima can be obtained by adjusting the position of the alumina loading pressure system in the waveguide [Xie, et al., 2009]. Using this applicator, a two-phase Cu<sub>50</sub>Zr<sub>45</sub>Al<sub>5</sub>/Fe sintered sample was successfully heating up in H-field...
maximum [Louzguine-luzgin, et al., 2009]. The combination of two materials better offers temperature control on heating compared to heating of metallic glass separately. We also processed the Cu$_{50}$Zr$_{45}$Al$_5$ metallic glass matrix composites containing Sn powders in H-field maximum with an applied pressure of about 5 MPa[Li, et al., 2010]. Now we tried to heat a two-phase material which consists of Cu$_{50}$Zr$_{45}$Al$_5$ and PPS in H-field maximum. We investigated the heat response of the powdered mixture of the Cu$_{50}$Zr$_{45}$Al$_5$ metallic glass and PPS in H-field maximum. Figure 4 shows the temperature profiles and energy consumption of the PPS powder and blended powders heated by microwaves in a separated H-field. It can be seen that all curves of the temperature and energy consumption are not smooth because microwave absorption capacity of the material is very sensitive to the tuner adjustment. It has been reported that fine metallic glassy powders can be heated up like most of pure metals in H-field likely by the eddy current loss effect[Buchelnikov, et al., 2008]. Compared with metallic glassy powders, PPS did not show obvious heat response under a flowing nitrogen gas with the increase of $P$, because most of polymers are loss dielectric constant materials at room temperature. In H-field magnetic effect did not contribute to microwave absorption of PPS powders. Only under low vacuum the obvious increase of the temperature was detected by microwave-induced plasma at the surface of the sample which is not a normal heating process. The addition of Cu$_{50}$Zr$_{45}$Al$_5$ metallic glassy powders strongly affected the heating behaviors of the composites in the H-field. In the case of 75 vol.% PPS, although the temperature was not detected like pure PPS because its surface temperature was too low, its inner temperature was far higher than its surface temperature due to the reverse thermal gradient inside the composite, temperature decreasing rapidly from inside to outside. This is attributed to conductive and radiant heat loss from the surface and selecting heating achieved by the differential coupling of metallic glassy powder and PPS with microwaves. With the further increase of the content of Cu$_{50}$Zr$_{45}$Al$_5$ metallic glassy powders, the relatively uniform temperature distribution could be realized in the cases of 25 and 50 vol.% PPS. This also means that the increase of the temperature in the blended powders at room temperature depends mainly on Cu$_{50}$Zr$_{45}$Al$_5$ metallic glass and obvious heat response only occurred at a sufficient content of Cu$_{50}$Zr$_{45}$Al$_5$ metallic glass.

Fig. 4. Temperature profiles and energy consumption of the PPS powder and blended powders heated by microwaves in a separated H-field
Figure 5 shows the XRD patterns of the initial blended powders and composites with 25, 50 and 75 vol.% PPS powder heated by microwaves under a flowing nitrogen gas. As shown in Fig. 5(a), in the case of 50 vol.% PPS, except for the phase corresponding to PPS, only typical broad diffraction maxima was seen without any detectable sharp diffraction peak corresponding to a crystallization peak, indicating that an amorphous phase was retained. Partial crystallization was induced in the case of 25 vol.% PPS because of its relatively high sintering temperature. Different from the composites with 25 and 75 vol.% PPS, a gradient structure in the composite with 75 vol.% PPS was induced by microwave heating in a separated H-field. To confirm its thermal gradient, the structural changes from the center to surface were investigated. The composite have had three different zones. It is shown that in Fig. 5(b) that zone A, close to the surface of the sample, did not show obvious heat response and had a similar structure as the initial blended powders. Zone C was located in the central region of the sample and exhibited a porous structure. Due to the decomposition of PPS, the formation of cubic $\text{ZrO}_2$, $\text{ZrS}_{0.67}$ and $\text{ZrH}_{0.25}$ phase was detected except for $\text{Cu}_{10}\text{Zr}_7$ and $\text{AlZr}_2$ phase during microwave processing. In the zone B, PPS powders were cured by microwaves and a high fraction of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ metallic glassy phase was also retained. Such a gradient structure formed by microwave heating is closely linked with different dielectric properties of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ metallic glass and PPS and their contents in the composite. Due to the low content of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ metallic glass, the composite has a poorer heat conductivity compared to those with a higher fraction of $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ metallic glass, so the reverse thermal gradient was more easily induced in a short time.

![Fig. 5. XRD patterns of the initial blended powders and composites with 25, 50 and 75 vol.% PPS powder heated by microwaves under a flowing nitrogen gas.](image)

Table 1 lists the common features and relative densities of Pure PPS powder and the composites with 25, 50, 75 and 90 vol.% PPS powder heated by microwaves in a separated H-field. Pure PPS sample obtained under low vacuum shows very low relative density (57%) because the plasma induced by the interaction between microwaves and atmosphere interrupted the normal heating process and the actual sintering temperature is lower than the reading temperature by pyrometer. Under a flowing nitrogen gas, the introduction of 10 vol.% $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$ metallic glassy powders only makes the mixture be weakly sintered. In the case of 75 vol.% PPS, the powdered mixture was heterogeneous heated and sintered to lead to the formation of a gradient structure. The composite with 50 vol.% PPS obtained
Table 1. Common features and relative densities of pure PPS powders and the composites with 25, 50, 75 and 90 vol.% PPS powder heated by microwaves.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Atmosphere</th>
<th>Relative Density</th>
<th>Common Feature</th>
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<tbody>
<tr>
<td>Cu₅₀Zr₄₅Al₅+25 vol.% PPS</td>
<td>N₂</td>
<td>84%</td>
<td>Sintered and partial crystallization</td>
</tr>
<tr>
<td>Cu₅₀Zr₄₅Al₅+50 vol.% PPS</td>
<td>N₂</td>
<td>72%</td>
<td>Sintered and amorphous</td>
</tr>
<tr>
<td>Cu₅₀Zr₄₅Al₅+50 vol.% PPS</td>
<td>Vacuum</td>
<td>59%</td>
<td>Weakly sintered and amorphous</td>
</tr>
<tr>
<td>Cu₅₀Zr₄₅Al₅+75 vol.% PPS</td>
<td>N₂</td>
<td>Sintered and gradient structure</td>
<td></td>
</tr>
<tr>
<td>Cu₅₀Zr₄₅Al₅+90 vol.% PPS</td>
<td>N₂</td>
<td>Weakly sintered</td>
<td></td>
</tr>
<tr>
<td>PPS</td>
<td>N₂</td>
<td>Not sintered</td>
<td></td>
</tr>
<tr>
<td>PPS</td>
<td>Vacuum</td>
<td>58%</td>
<td>Weakly sintered</td>
</tr>
</tbody>
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under a flowing nitrogen gas also has a higher relative density than that under low vacuum. Bulk Cu₅₀Zr₄₅Al₅ metallic glass/PPS composite with a high relative density (84%) was obtained by microwave heating of the blended powders containing 25 vol.% PPS. This shows that the higher sintering temperature leads to the melting of PPS particles and then the resulted composites are much denser with the significantly reduced number of voids. The compressive strength of these composites was also measured and no more than 100 MPa, similar to that of common polymers. These results further manifested that a better sintering quality could be obtained in the composite with a high fraction of Cu₅₀Zr₄₅Al₅ metallic glassy phase.

Figure 6 shows the appearance and microstructure of the composite with 25 vol.% PPS powder heated by microwaves in H-field under a flowing nitrogen gas. As shown in Fig. 6(a), a bulk sintered composite with a relative density of about 84% was obtained under an applied pressure of about 5 MPa. It can be seen in Fig. 6 (b) that PPS powders were melted by microwave heating and permeated into the voids and interstices between the Cu₅₀Zr₄₅Al₅ particles. Figure 7 presents the SEM micrograph of the polished cross section of the zone B of the composite with 75 vol.% PPS powder heated by microwaves under a flowing nitrogen gas. In the zone B, PPS powders were rapidly and well consolidated by microwaves heating and the wetting seemed good with no obvious cracking observed on the interface between metallic glassy particle and PPS particle. A good bonding state between Cu₅₀Zr₄₅Al₅ metallic glassy particles and PPS was seen. Recently it has been reported that some MGs with low glass transition temperature have similar viscosities at the same temperature as some polymers [Kündig, et al., 2007]. In addition, Zr₅₅Cu₃₀Al₁₀Ni₅ metallic glass was also successfully deposited on various engineering polymer substrates by magnetron sputtering as thin homogeneous layers of about 400 nm and a good adhesion was achieved[Sojnila, et al., 2009]. The above results show that microwave-induced heating process can offer a possibility to fabricate a single composite material that consists of metallic glass and polymer.
4. Conclusion

In the present work, using a single-mode 915 MHz microwave applicator, we investigated the heating behaviors of the mixtures of Cu$_{50}$Zr$_{45}$Al$_5$ metallic glassy powder and PPS powder in a separated H-field. The Cu$_{50}$Zr$_{45}$Al$_5$ metallic glass/PPS composites were fabricated with an applied pressure of about 5 MPa under a flowing nitrogen gas. The mixtures with a high fraction of Cu$_{50}$Zr$_{45}$Al$_5$ metallic glassy phase could be heated well and exhibited a relatively uniform structure. With the increase in PPS content above 90 vol.%, the mixture was hardly heated up under a nitrogen-flow atmosphere, but was heated well in low vacuum by microwave-induced plasma heating. A bulk sintered composite with retention of an amorphous structure were obtained. The bonding state between metallic glassy and PPS particles was found. The gradient structure could be formed by microwave processing of the composites with a high fraction of PPS phase. It is evident that microwave induced heating process in the mixture of Cu$_{50}$Zr$_{45}$Al$_5$ metallic glassy powder and PPS powder in a separated H-field offers a possibility to fabricate metallic glass/polymer composites with large dimensions.
5. References


Roy, R.; Agrawal, D.K.; Cheng, J.P. &


The book offers comprehensive coverage of the broad range of scientific knowledge in the fields of advances in induction and microwave heating of mineral and organic materials. Beginning with industry application in many areas of practical application to mineral materials and ending with raw materials of agriculture origin the authors, specialists in different scientific area, present their results in the two sections: Section 1-Induction and Microwave Heating of Mineral Materials, and Section 2-Microwave Heating of Organic Materials.

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