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Porous bulk metallic glass fabricated by powder hot pressing

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Abstract: A synthesis method for the production of porous bulk metallic glass (BMG) was introduced. This method utilizes the superplastic forming ability of amorphous powder in the supercooled liquid (SCL) state and intenerating salt mixture as a placeholder to produce BMG foam by using a hot die pressing method. Scanning electron microscope (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were employed to characterize the morphologies of foaming structure, the crystallization and the percentage of crystallization of the as-produced porous BMG. The results suggested that the formation of porous structure by superplastic forming process is feasible. Good bonding effect was observed between amorphous powder particles. Less than 6.5% of crystalline phases were formed during hot pressing, and less than 5.5% of residual salt was enclosed in the foam. To remove any residual salt particles, salt preforms with three-dimensional network and good connectivity is necessary.

Key words: porous bulk metallic glass; hot pressing; placeholders; superplastic forming

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1. Introduction

Since porous BMGs (Bulk metallic glass) exhibited ductility and biologic compatibility [1], many researchers were focused on the fabrication of such excellent materials. Schroers *et al.* [2] demonstrated the first porous BMG by entrapping gas in a liquid Pd₄₃Ni₁₀Cu₂₇P₂₀ alloy. Wada and Inoue [3] reported foaming of the same alloy by casting around soluble NaCl placeholders. Shortly afterwards, Brothers and Dunand [4] developed an alternative method based on liquid filtration of beds of hollow carbon microspheres, appropriate for use with reactive commercial BMG alloys, *e.g.* Zr-based alloys. In his another report, a method based on a salt replication process for the processing of open celled foams from the commercial BMG alloy Vit106 (Zr₅₇Nb₅Cu_{15.4}Ni_{12.6}Al₁₀) was also described [5]. Recently, Ren *et al* [6] fabricated a porous BMG of 8 mm in diameter, which is the largest porous BMG reported up to now.

Until now, Bulk amorphous foam generally fabricated by liquid route, which produce many problems. Two important problems of these are the reduction of glass forming ability (GFA) of based alloy and the contamination of liquid alloy during processing. In

this paper, a SCL (Supercooled liquid)-state foaming route by blending placeholders, which usually salts with controllable intenerating temperature, with amorphous metal powder to produce a porous BMG, was introduced. Reports offer evidence that amorphous metal powders can be consolidated in the SCL region with little or no loss of strength by using hot pressing [7], warm rolling [8], and conventional area reduction [9-10] or equalchannel angular [11] warm extrusion techniques. It is easy to envision an incorporation of placeholders into these consolidated compacts, providing a natural method for making low-density porous materials with low processing temperatures.

2. Experimental

A pre-alloying ingot with a nominal composition of Zr₅₅Cu₃₀Al₁₀Ni₅ was prepared by induction melting the mixture of Zr, Cu, Al and Ni with a purity of 99.5wt% or better in a BN (boron nitride) crucible under high vacuum. The Zr₅₅Cu₃₀Al₁₀Ni₅ powders were produced from the pre-alloying ingots by high pressure Ar gas atomization at a dynamic pressure of 3.5 MPa after heating to 1623 K using an annular nozzle having a melt delivery inner diameter of 2.7 mm. Following atomization, powders were screened to size ranges of

powder particles having diameters not larger than 25 μm . The particle size of the metal powder is not critical but the metal particles must be considerably smaller than salt particles that are chosen as the placeholder [12].

During SCL region processing, heating into the SCL region would enhance the kinetics of crystallization. Consequently the time allowed for processing would be limited. Therefore, the processing temperature for the hot pressing has to be carefully determined by considering the simultaneous plastic forming and crystallization. An ideal processing window can be obtained when the time scale characterizing plastic forming is shorter than that characterizing crystallization. To determine the appropriate hot press time available before crystallization at a certain temperature, a time-temperature transformation (TTT) plot was constructed for the amorphous powder, as shown in Fig. 1, by performing isothermal DSC scans. This was accomplished by first heating the powder to selected annealing temperatures above T_g and then measuring the time until the sample starts to crystallize, which is indicated by the onset of an exothermic reaction.

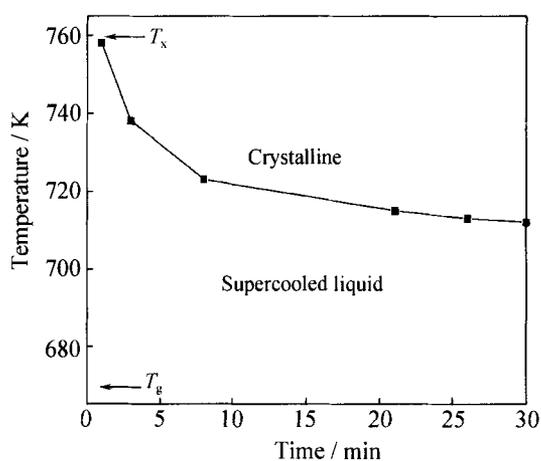


Fig. 1. TTT diagram for the onset of crystallization of gas atomized powder isothermal heated to selected temperature.

A mixture of NaCl and CoCl_2 (NaCl:CoCl₂=7:10 in mass ratio) was first melted at 873 K for 1 h in low vacuum and then cracked and screened to an average size of 300 μm . The placeholder was prepared from such a mixture with a relatively low melting temperature. The measuring intergenerating temperature of the mixing salt is 643 K. The particle size of the salt powder selected will be according to the intended cell size of the final foam.

The amorphous powder and salt powders were mixed with a volume fraction of amorphous powder of 0.3 of all solid materials excluding pores in the mix-

ture. Ethanol was used as the binder and a small amount, roughly 1 vol% of the amorphous powder/salt mixture, was added during mixing. The amorphous powder/salt powder mixture was poured into a copper can and both ends of the can were vacuum sealed after outgassed. The dimension of the copper can is 30 mm deep by 20 mm inner diameter cavity and 23 mm outer diameter.

The experiment was performed using hot die pressing for consolidation. The can was placed into a hot die which was isothermal heated at 713 K. Once the copper can was placed into the hot die, the hot pressing under a constant ram pressure of 800 MPa through a die was applied. The hot pressing time was set as 15 and 18 min respectively. After pressing, the copper can was first quenched into water at ambient temperature, and then removed the copper coat. The salt was removed by flowing water, leaving the resultant foam. To determine the crystallization degree of the as-produced foams, a rod of 3 mm in diameter with the same composition was made by copper mold casting for comparison.

The structure of the as-produced foam samples was examined by an S-3400 scanning electron microscope (SEM). X-ray diffraction (XRD) analyses and mass measurements were also carried out to determine the extent of amorphous structure and salt removal.

3. Results and discussions

The typical cellular structure of the as-produced foams is shown in Fig. 2. Fig. 2(a) shows a SEM macrograph of the foam. The foam exhibits uniformly distributed open cells and a network of well-bonded metal particles. It has a porosity of 70% and cell size in the range from 250 to 450 μm . Fig. 2(b) shows the cellular structure of the as-produced foam. The powder particles are well connected and some tiny holes among the connected particles are observed. Fig. 2(c) shows the wall structure in a typical cell. The bonding region between particles as indicated by arrows indicates that strong bonding has formed between the particles. Many tiny cross lines were observed on the surface of the particles, showing that the particles have suffered severe deformation during hot pressing.

XRD was adopted to analyze the amorphous structure of the as-produced foam, as shown in Fig. 3. It is obvious that the two as-produced foams are almost in amorphous state with a broad diffraction. While some tiny crystalline diffraction peaks superimposed on the amorphous halo are also observed. To determine the volume fraction of crystalline phases, DSC scans were performed on a condensed BMG (with a diameter of 3

mm produced by copper mold casting) and BMG foam (produced by hot pressing for about 18 min) as shown in Fig. 4. Both of the condensed BMG and BMG foam show distinct glass transition temperature and SCL region, followed by crystallization of the amorphous phase. There is no obvious difference between those characteristic temperatures. The glass transition temperature, T_g , crystallization temperature, T_x , the temperature interval between T_g and T_x , *i.e.* SCL region ΔT_x , and crystallization enthalpy ΔH are summary in Table 1. It is clearly seen that crystallization enthalpies between the two materials are different. So the percentage of crystalline phases can be estimated from the relatively different enthalpies, about 6.5% crystalline phases existing in the BMG foam. Such estimation is coincident with the XRD results.

In most cases, the salt particles in the hot pressing preforms could not be dissolved completely. Some salt particles remained in the resultant foam. The residual salt can be estimated according to the expression suggested by Zhao *et al* [12]. For each specimen, the mass of the initial amorphous powder, the salt powder, a sample cut from the hot pressing preform, and the resultant amorphous foam were measured using a balance with an accuracy of 0.001 g. The fraction of the residual salt in the amorphous foam with respect to the total salt in the initial hot pressing preform, ϕ , was determined by [12]

$$\phi = \frac{W_f - W_p f_{\text{amor}}}{W_p (1 - f_{\text{amor}})},$$

where W_f and W_p are the masses of the amorphous foam and the corresponding pre-dissolution hot pressing preform respectively, and f_{amor} is the mass fraction of amorphous powder in the initial mixture. The calculation result shows that the fraction of the residual salt powder in the foam with respect to the total salt in the preform is less than 5.5%. The relative density of the foam is therefore expected to be a little higher than the value estimated from the initial amorphous powder fraction. With a high volume fraction of salt in the preform, most salt particles are in contact with each other and form a continuous three-dimensional network. Because all the salt particles in the network can be dissolved away by water, there is only small amount of residual salt particles in the resultant foam. In contrast, with a low volume fraction of salt in the preform some salt particles are enclosed completely by the amorphous matrix. Those isolated salt particles can not be dissolved away and remained in the foam. Therefore hot pressing the mixture of salt and amorphous powder is only suitable to those of foams with high porosity and open celled foam re-

quirement. To fabricate adjustable porosity of foam material, a salt perform with three-dimensional network and a required porosity is necessary. This will be reported elsewhere.

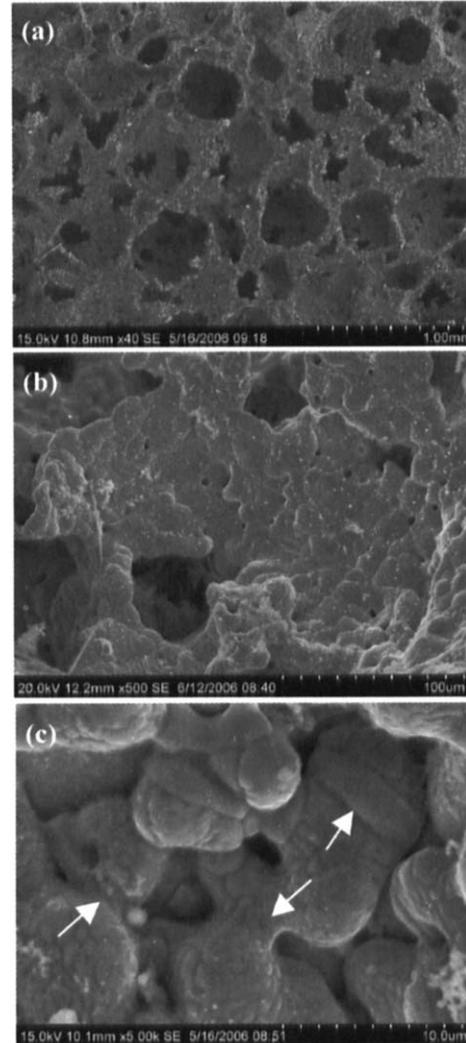


Fig. 2. SEM morphology: (a) the as-produced foam synthesized by hot pressing; (b) the cellular structure of the as-produced foam; (c) magnified view of the inner wall of the foam.

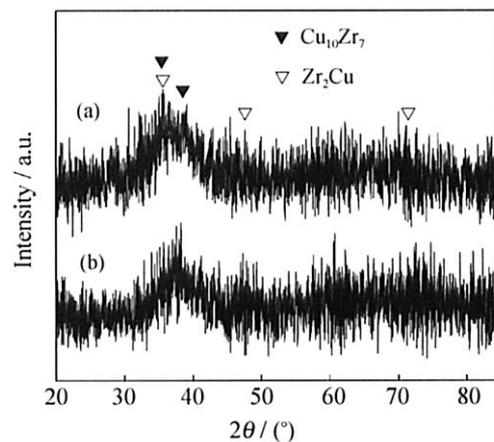


Fig. 3. XRD patterns from as-produced foams synthesized by hot pressing for (a) 15 min and (b) 18 min, respectively.

The amount of tiny holes in the cell wall or struts is determined by the particle morphology and size of the amorphous and salt powder as well as the compacting pressure. It is truth from Figs. 2(b) and 2(c) that there exist some tiny holes, less than 3 μm in diameter. Under the current compacting conditions, the tiny holes might reduce the strength and increase the porosity of BMG foam. Considering the enclosed residual salt existed in the foam that has reduced the porosity of the foam, the porosity of the foam is somewhat unaffected.

The large resistance of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ BMG to crystallization results in an SCL region that is accessible on a convenient time scale for processing, as shown in Fig. 1. This allows for a superplastic foaming (SPF) process, where the amorphous powder behaves like a plastic. An ideal amorphous powder for SPF would be identified by a large supercooled liquid region, no embrittlement during heating treatment. An amorphous powder with a low T_g is desirable due to it reduces heating temperature and contamination comes from oxidation.

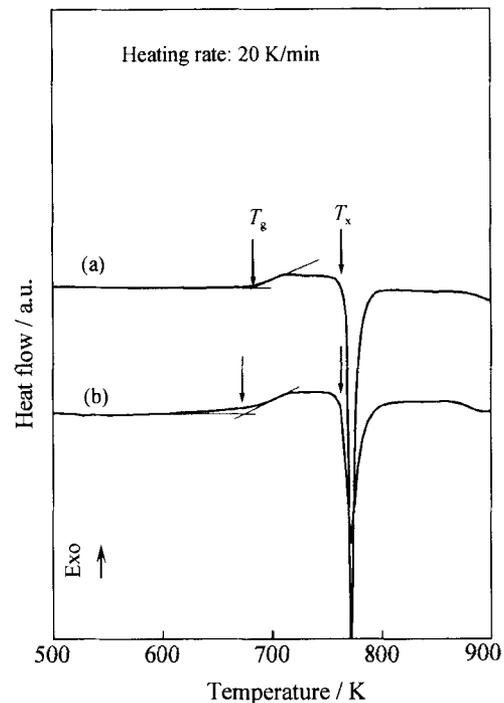


Fig. 4. DSC curves of as-cast BMG with a diameter of 3 mm (a) and as-produced foam (b).

Table 1. Characteristic temperatures and crystallization enthalpies of condensed $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ BMG and MBG foam at heating rate of 20 K/min

Sample	T_g / K	T_x / K	ΔT_x / K	ΔH / ($\text{J}\cdot\text{g}^{-1}$)
BMG (3 mm in diameter)	672	762	90	52.06
Foam	682	764	82	48.70

It should be noticed that when the designed mixture of salt powder is heated in the SCL-state of amorphous powder, the mixing salt interpenetrates and will not be as obstacles but as transfers of pressure during pressing, because the salt liquid is incompressible.

4. Conclusions

A new process, SPF, has been developed for manufacturing BMG foam. In SPF, amorphous powder and salt powder were first mixed at specified ratio, outgassed and sealed in a copper can. The copper can was then isothermal heated and compacted into a preform. During hot pressing, the amorphous powder was deformed plastically in the SCL region. A BMG foam can be successfully synthesized by this method. The particles among amorphous powder were well bonded. XRD and DSC results show that less than 6.5% of crystalline phases were formed during hot pressing, and less than 5.5% of residual salt was enclosed in the foam. To remove any residual salt particles, salt preform with three-dimensional network and good connectivity is necessary.

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