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Influence of viscous flow on the deformation behavior of bulk metallic glassy alloys in supercooled liquid region

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ABSTRACT

We present the investigation of the effect of viscosity on the deformation behavior of metallic glasses at supercooled liquid region during hot extrusion. Also the change of the specific surface area in porous Hf-based metallic glass and Ni-based metallic glass were compared. The homogeneously distributed ruggedness-shape surface of ligament was observed in the Hf-based metallic glass which has lower viscosity comparing to that of Ni-based metallic glass. For lower viscosity, it is very desirable to fabricate large surface area porous metallic glass due to a change of the surface morphology of the ligaments from smooth-like to rugged-like appearance, thus suggesting an optimum regime for increasing the specific surface area by controlling viscosity of metallic glass at a given processing condition.

1. Introduction

Bulk metallic glasses (BMGs) are known to have unique properties, such as high strength, high corrosion resistance and high electrochemical potential, etc. [1]. Porous metallic materials are widely used in many fields including aerospace, atomic energy, electrochemistry, petrochemistry, medicine and environmental protection applications [2,3]. Also, the high surface area of foams produced from superplastic characteristic of metallic glasses (MGs) make them viable candidates as functional materials such as high-sensitivity sensors, catalysts or hydrogen storage media. Therefore, synthesis of porous structures using metallic glasses due mainly to their electrochemical properties combined with desirable strengths at relatively low densities is preferred to both structural and functional applications [4–8].

Fabrication of amorphous metal foams has been reported by several methods using specific metallic glass alloys that have high glass forming ability [4–8]. However, there is critical restriction; the BMG alloy system must have a high glass forming ability to allow generation of the foam without crystallization during cooling. Recent attention has been directed toward synthesizing porous structures with MGs due to their favorable properties such as high strength, large elastic stains and, in the case or particular compositions, strong corrosion resistance [5,9,10]. The fabrication of a MG foam was introduced powder metallurgy route to having uniformly dispersed pores by a sequential process involving warm extrusion of metallic glass powders blended with a second, fugitive powder, followed by dissolution of the latter [5,9,10]. Deformability of metallic glass powders can only be achieved in the supercooled liquid regions by their superplasticity at elevated temperature. Therefore viscous flow of metallic glass is important parameter for shaping operation at supercooled liquid region.

In the current study, we describe the effect of viscosity at supercooled liquid region of metallic glass on the formability of metallic glass powders related and investigated the characterization of porous structures obtained from different metallic glass alloys.

2. Experimental details

Initially both $Hf_{44.5}Cu_{27}Ni_{13.5}Nb_5Al_{10}$ (at%) metallic glass alloy powder and $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ (at%) metallic glass powder were prepared by high pressure inert gas atomization under Ar atmosphere at Korea Institute of Industrial Technology (KITECH) (>99.9% purity). The sizes of Hf-based metallic glass powders used as starting materials have from 45 to 106 μm and the sizes of Ni-based metallic glass powders have from 63 to 75 μm, respectively.

The Hf-based and Ni-based metallic glass matrix precursors containing 40 vol.% fugitive brass phase were produced by warm extrusion of blended, gas-atomized powders, respectively. Details

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Table 1
Summary of physical properties of porous metallic glass foams.

Samples	Processing temperature (K)	Density of bulk MG (g/cm^3)	Density of foam (g/cm^3)	Porosity (Vol.%)	Viscosity at processing Temp. (Poise)	Surface area (m^2/g)
$Hf_{44.5}Cu_{27}Ni_{13.5}Nb_5Al_{10}$ MG foam	836	10.54	6.63	37	6×10^4	0.23
$Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ MG foam	845	7.52	4.62	41	2×10^5	0.44

of the composite precursor synthesis and warm extrusion processes are described elsewhere [9–11]. The density of the machined precursor specimen was determined by pycnometry. After machining, the extruded precursor sample which has cylindrical-shaped rods 8.5 mm in diameter and 26.4–51.2 mm lengths by immersion into a 50:50 concentrated-HNO_3:H_2O solution for 48 h at room temperature. Structural characterization was performed using a Philips APD 3520 X-ray diffractometer with monochromatic Cu-K$_\alpha$ radiation and a JEOL 5910LV scanning electron microscope (SEM). The thermal properties of the samples were measured with a Perkin–Elmer Pyris-1 differential scanning calorimeter (DSC) at a heating rate of 40 K/min. A thermo-mechanical analyzer (TMA)-7 was used at a heating rate of 10 K/min under flowing of Ar for viscosity measurement. The specific surface area of the porous MG was determined using the Brunauer–Emmett–Teller (BET) equation from data obtained with a Quantachrome Autosorb-6 Physisorption multiple-point Analyzer. Pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method.

3. Results and discussions

As summarized in Table 1, the nominal volume fraction of brass in the as-extruded precursors was 40% and the measured density of Hf-based MG was 10.54 g/cm^3 and the density of Ni-based MG was 7.52 g/cm^3, respectively. The density of Hf-based MG foam, which was measured from the foam's mass following dissolution of the brass, was 6.63 g/cm^3 and the density of Ni-based MG foam was 4.62 g/cm^3 which corresponds to 62.9% and 58.3% of the density of Hf-based MG and Ni-based MG, respectively, indicating that almost of the fugitive brass phase was removed by dissolution process.

SEM images obtained from the porous MG foams after dissolution processing are shown in Fig. 1. The microstructure of MG foams is composed of homogeneously dispersed porous cells and continuously connected metallic glass struts, which together correspond, respectively, to the elongated brass particles and metallic glass powders. The macrostructure of the Hf-based MG foam, the inset image of Fig. 1a, is shown as the cylindrical-shaped rods of about 8.5 mm in diameter and 51.2 mm length. The macrostructure of the Ni-based MG foam, the inset image of Fig. 1b, is shown as the cylindrical-shaped rods of about 8.5 mm in diameter and 26.4 mm length, respectively.

Detailed microstructural views of $Hf_{44.5}Cu_{27}Ni_{13.5}Nb_5Al_{10}$ MG foam and $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ MG foam are shown in Fig. 1a and b, respectively; both MG foams show the longitudinal structure along the extrusion direction consists of ellipsoidal pores size up to 50 μm in diameter and about 150 μm in length located between continuously connected metallic glasses obtained through dissolution of the fugitive phase (brass) in aqueous solution. As a result of the homogeneous deformation of the spherical gas-atomized metallic glass powders, the struts have a high aspect ratio, which has been suggested to be preferred for enhancing plasticity compared to pores with an equiaxed nodal shape [9].

The homogeneously distributed ruggedness-shape surface of ligament was observed in the Hf-based MG foam, shown in Fig. 1a, comparing to the smooth surface of ligament in Ni-based MG foam, shown in Fig. 1b. The rugged surface of ligament in Hf-based MG foam is supposed to introduce from mark of surface morphology of deformed brass fugitive phase which has higher flow stress compare to the flow stress of Hf-based MG at interface between Hf-based MG and brass during extrusion. The smooth surface of ligament in Ni-based MG is considering that the flow stress of Ni-based MG is higher than the flow stress of fugitive phase at extrusion temperature.

Fig. 2a shows the constant-rate heating DSC (40 K/min) scans of the $Hf_{44.5}Cu_{27}Ni_{13.5}Nb_5Al_{10}$ gas-atomized powder and foam, respectively. The DSC curve of Hf-based MG foam exhibits a distinct glass transition, followed by the supercooled liquid (SCL) region before a primary crystallization event occurs at higher temperature. The onset temperature of the glass transition, T_g, estimated as the point of intersection between the linearly extrapolated curve below the transition with the steepest tangent of the rise in the heat flow

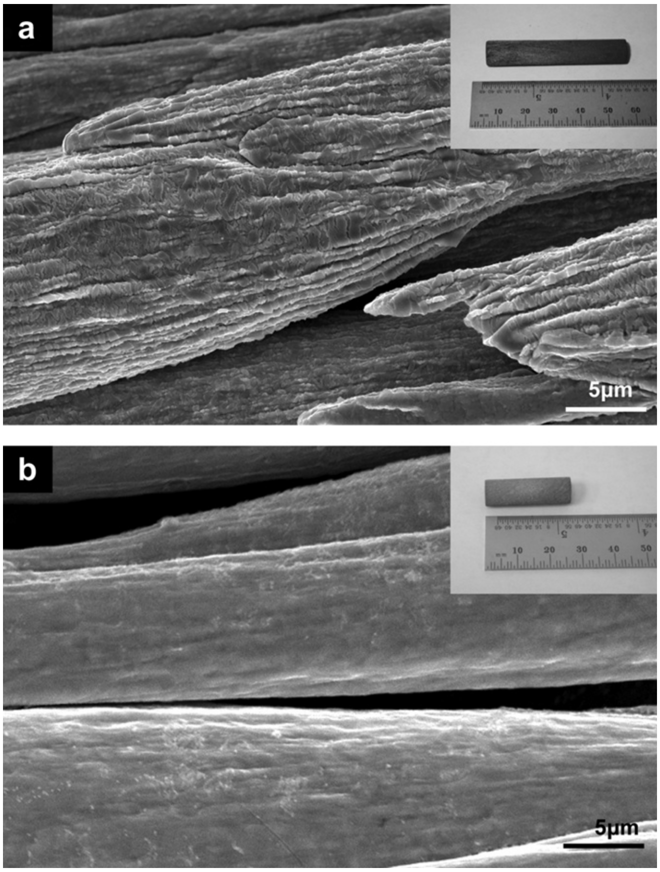

Fig. 1. (a) SEM image of a $Hf_{44.5}Cu_{27}Ni_{13.5}Nb_5Al_{10}$ MG foam. Pores are uniformly distributed throughout the sample with rugged surface morphology of ligament. Inset optical image shows macrostructure of Hf-based MG foam after dissolution. (b) SEM images of a $Ni_{59}Zr_{20}Ti_{16}Si_2Sn_3$ MG foam. Pores are uniformly distributed throughout the sample with smooth surface morphology. Inset optical image shows macrostructure of Ni-based MG foam after dissolution. The volume fraction of porosity is around 40% with an average size of up to 50 μm.