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Thermo-plastic expansion of amorphous metallic foam

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Abstract

Amorphous $Pd_{43}Ni_{10}Cu_{27}P_{20}$ foam is produced at 38%, 49%, and 70% porosity by isothermally expanding a 25%-porosity amorphous precursor in the supercooled liquid state for varying durations. The foam morphologies exhibit good spatial homogeneity as well as good size uniformity of bubbles, which is a consequence of the high viscosity of the supercooled liquid state which inhibits floatation and dampens the growth kinetics. The expansion capability of amorphous metals into high-porosity foam demonstrated in this study is attributed to the plastic deformability of the supercooled liquid state, which enables large plastic membrane elongations during foaming.

Keywords: Amorphous material; Metals; Liquid quenching; X-ray diffraction; Strain

1. Introduction

Families of metallic glass-forming systems exhibiting a remarkable kinetic stability against crystallization have been developed over the last decade [1,2]. Such systems are characterized by supercooled liquid states (metastable states to which glass relaxes before undergoing crystalline transition) that maintain stability for periods of up to 10^3 s at temperatures extending more than 100° above the glass transition [3]. The viscosity characterizing these states varies smoothly and predictably from viscous fluid to solid, taking values that typically range between 10^5 and 10^{12} Pa s [4]. The kinetic stability characterizing these systems combined with their excellent rheological properties opens the possibility for isothermal forming processes similar to those employed in the processing of plastics or conventional glasses [5].

This "thermo-plastic" forming capability of amorphous metals constitutes a key quality that can be exploited to considerably advance their plastic processing [6]. Thermoplastic forming performed on vitrified feedstock effectively decouples the forming stage from the vitrification stage, which requires rapid quenching of the product. Such decoupling renders the requirement for product rapid quenching redundant, and hence the limitations on size imposed by the rate of heat removal (referred to as critical casting thickness) are relaxed.

Expansion of closed-cell amorphous metal foam appears to be an attractive application of thermo-plastic forming [7]. The challenge in producing high quality metal foam is accomplishing a uniform and homogeneous foam morphology that would give rise to enhanced structural and functional characteristics [8]. Since crystalline metals cannot undercool substantially, foaming can be performed in either the equilibrium liquid or the crystalline solid state. Foam processing in the equilibrium liquid state can result in highly porous foams [9], whose morphologies however would evolve essentially "uncontrolled", owing to very low viscosities promoting under-damped growth and bubble sedimentation. By foaming in the crystalline solid state, substantial control over the evolution of morphology is introduced, however, the limited superplastic deformability of crystalline metals imposes constraints on the attainable porosity [10].

Conversely, the highly viscous supercooled liquid states render glass-forming metallic systems much more attractive for metallic foam processing [11]. The high viscosity characterizing supercooled liquids can inhibit sedimentation and dampen growth giving rise to "controlled" expansion. Moreover, the outstanding "plastic" deformability of the supercooled liquid

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state [12] can result in high-porosity foam expansion. Additionally, since amorphous metals exhibit significantly higher strength and elastic strain limit as compared to crystalline metals [5], they can potentially produce structurally more advanced foams.

Recently, high-porosity closed-cell amorphous metallic foams have been successfully processed in the equilibrium liquid [13,14]. The foam morphologies however exhibit size distributions that are effectively bi-modal, which is a consequence of a rather uncontrolled foaming process in the liquid state. As demonstrated in another study [15], thermo-plastic expansion of amorphous metallic foam can be accomplished by expanding an amorphous precursor in the supercooled liquid state. As in these previous studies the $Pd_{43}Ni_{10}Cu_{27}P_{20}$ glass-forming alloy was considered here for thermo-plastic foam processing due to its robust glass-forming characteristics. The glass transition, crystalline transition, and melting temperatures of this alloy are 300, 395, and 530 °C, respectively [2]. Hydrated B_2O_3 was considered as gas-releasing agent due to its chemical inertness and fluxing ability with the glass-forming alloy.

2. Experimental

The alloy ingot was prepared by first pre-alloying Pd (99.9 mass%), Ni (99.9 mass%), and Cu (99.99 mass%) by induction heating, and then alloying P (98 mass%) by slow furnace heating in a sealed tube.

The foam precursor ingot was prepared by enclosing hydrated B_2O_3 powder with the alloy ingot at a mass ratio of 1:10 in a quartz tube sealed in argon at 0.65 bar. The tube was placed in a furnace at 900 °C for 10 min. The decomposing agent released water vapor, most of which was entrained in the molten alloy in the form of microscopic gas bubbles. The ingot was subsequently quenched to produce an amorphous foam precursor.

Foam expansion was performed in three isothermal stages of varying duration. In each stage, a precursor specimen mounted on a thermocouple was heated to 360 °C in a helium atmosphere under 1 bar pressure. After thermal equilibration had been recorded, pressure was reduced to 10^{-3} mbar to activate expansion. Foaming was allowed to proceed for a given duration followed by water quenching.

3. Results

Optical micrographs of the sectioned foam precursor and the three foam articles expanded for 60, 120, and 180 s, are shown in Fig. 1. Their porosities measured by the Archimedes method

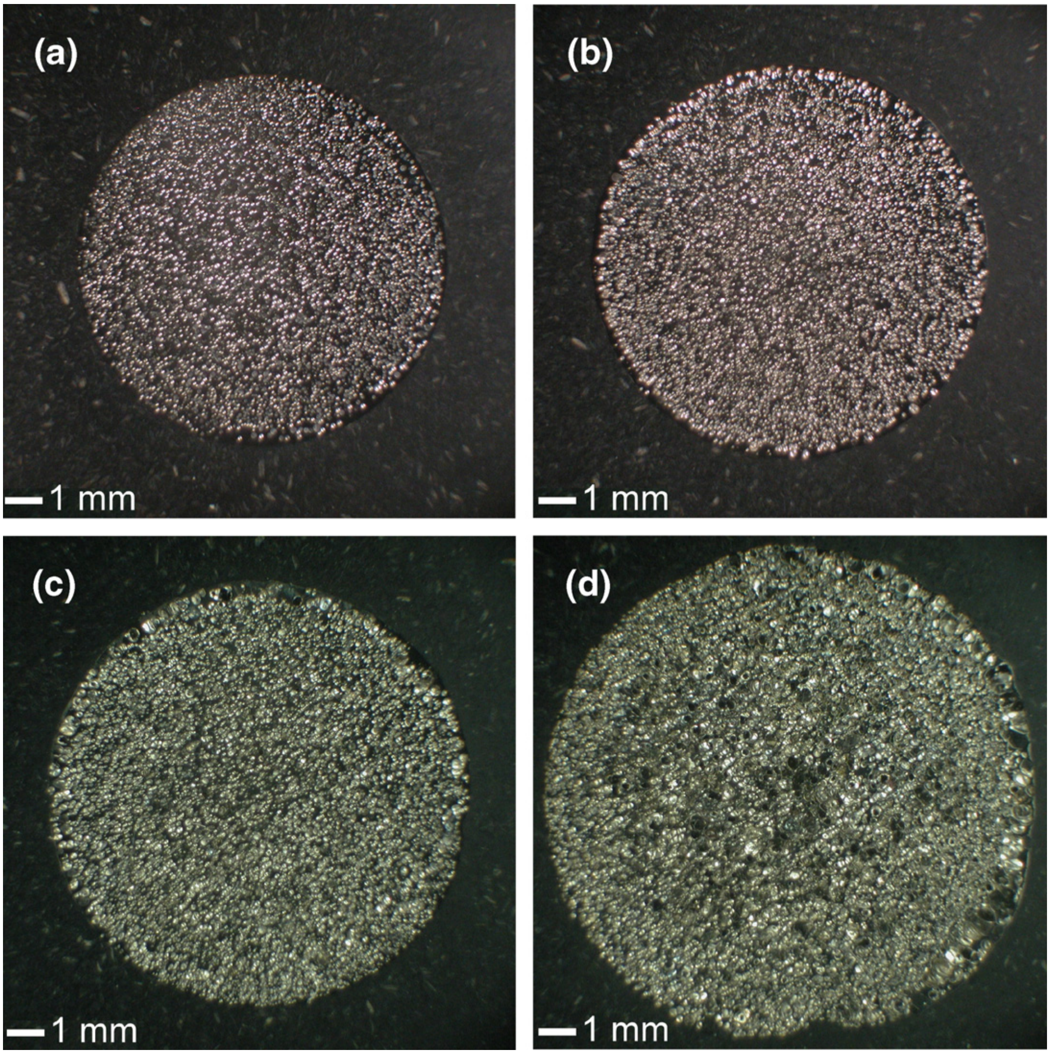

Fig. 1. Optical micrographs of the sectioned precursor and foam products: (a) 25% porosity (foam precursor); (b) 38% porosity (foam expansion for 60 s); (c) 49% porosity (foam expansion for 120 s); (d) 70% porosity (foam expansion for 180 s).

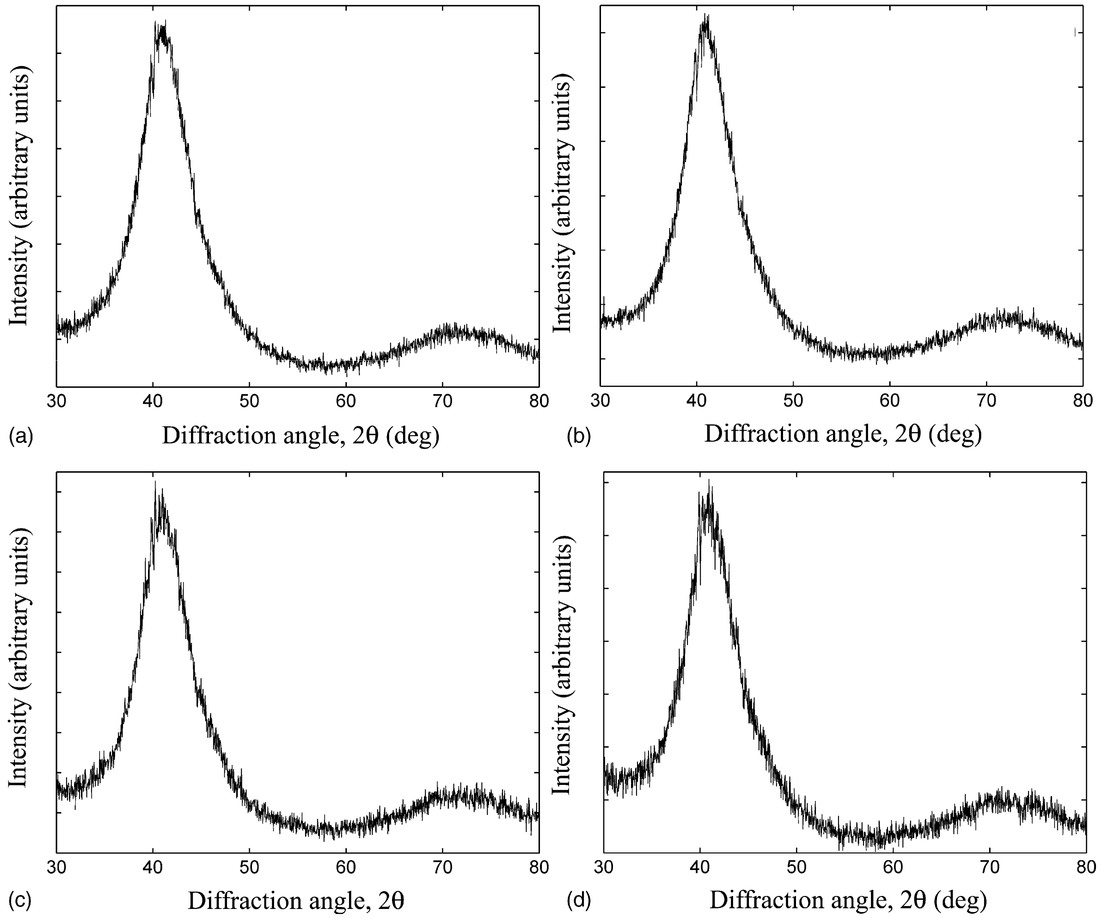

Fig. 2. X-ray diffractograms of the precursor and foam products: (a) 25% porosity; (b) 38% porosity; (c) 49% porosity; (d) 70% porosity.

were found to be 25%, 38%, 49%, and 70%, respectively. The amorphous nature of the products was verified by X-ray diffraction. The diffractograms are shown in Fig. 2. Micrographs of the sectioned foam precursor and the three foam articles on a 2:1 and 20:1 magnification scale are presented in Figs. 3 and 4.

4. Discussion

The images in Fig. 3 illustrate that foam morphologies exhibit good spatial homogeneity as well as good uniformity in bubble sizes. The development of good morphological characteristics is a consequence of the high viscosity of the supercooled liquid state which inhibits floatation and dampens the growth kinetics. The images in Fig. 4 suggest that expansion during thermoplastic foaming evolves by a departure from the spherical symmetry of bubbles towards the development of a cellular structure comprising a network of intracellular membranes. Further expansion progresses by growth of the cellular structure contributed by mechanisms involving plastic membrane stretching.

It is therefore evident that that up to some critical porosity, over-damped growth of bubbles constitutes the principal mechanism of expansion. This critical porosity is associated with the density of random close packing of spheres, which for a monosized system is reported to be 63.7% [16]. This fraction can be taken to approximately represent the "threshold" porosity, beyond which bubbles become supercritically packed and expansion advances by mechanisms involving plastic stretching of membranes. Ultimate necking and rupture of the membranes would give rise to gas percolation and eventual cessation of the expansion process. It is therefore conceivable that the maximum attainable porosity during thermo-plastic foaming is essentially limited by the ductility of the supercooled liquid state.

In solid-state foaming of crystalline metals, attainable porosities are reported to be limited to less than 50% [10]. This is a consequence of the limited superplastic deformability exhibited by crystalline materials. Owing to enormously high viscosities, superplastic deformation in crystalline materials is contributed by creep mechanisms rather than by flow, and consequently the attainable plasticity is limited. In contrast, visco-plastic deformation in supercooled liquids is associated with flow mechanisms which give rise to "near-ideal" plastic behavior. In principle, an ideal plastic behavior would be characterized by a strain-rate sensitivity exponent of 1.0 and would be associated with Newtonian flow and essentially infinite ductility. Indeed, fiber drawing experiments performed in the supercooled liquid state at substantially low strain rates were found to produce plastic elongations on the order of 100,000% [12]. This excellent plastic deformability exhibited by the supercooled liquid state renders amorphous metals suitable for high porosity thermo-

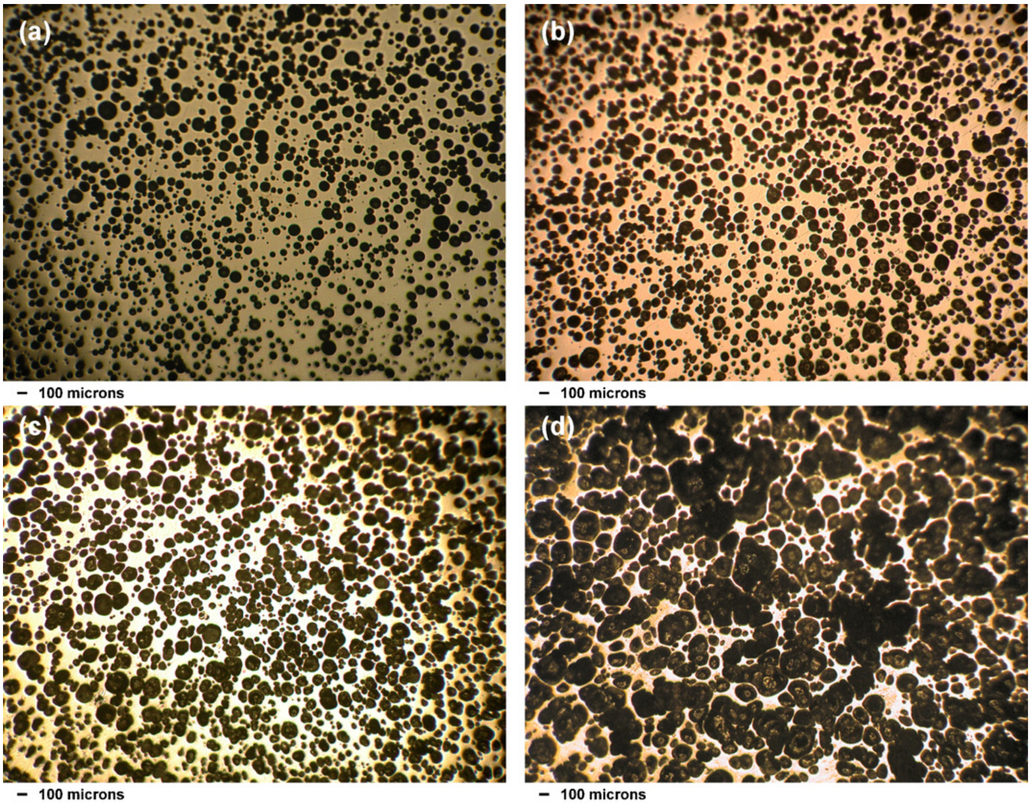

Fig. 3. Optical micrographs of the sectioned precursor and foam products on a 2:1 magnification: (a) 25% porosity; (b) 38% porosity; (c) 49% porosity; (d) 70% porosity.

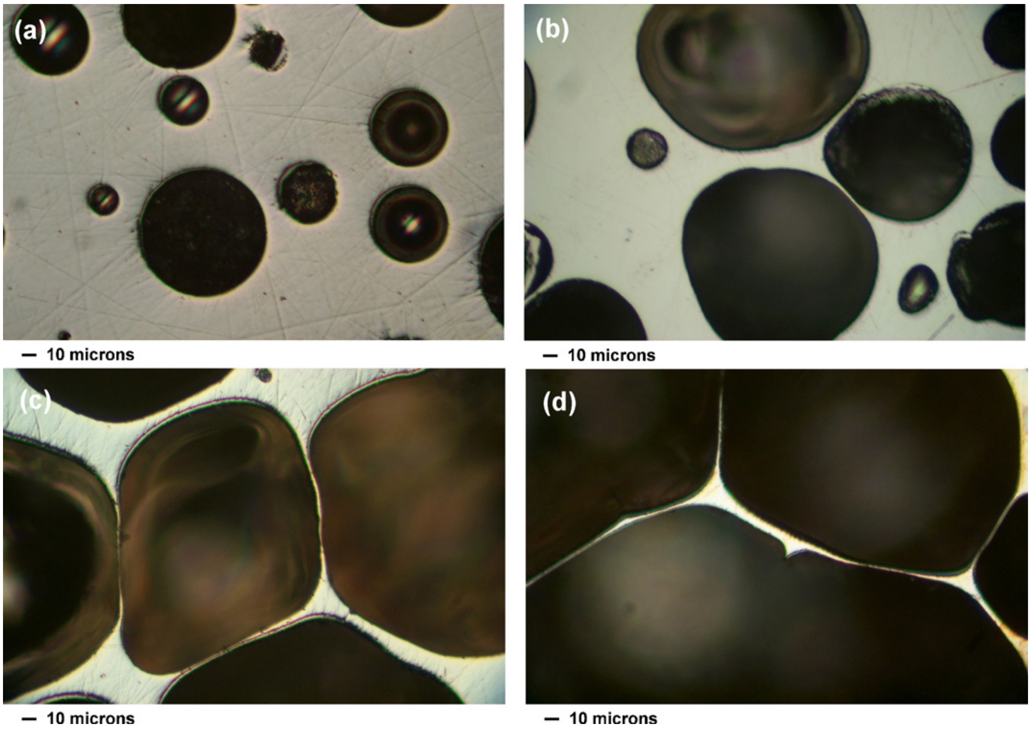

Fig. 4. Optical micrographs of the sectioned precursor and foam products on a 20:1 magnification: (a) 25% porosity; (b) 38% porosity; (c) 49% porosity; (d) 70% porosity.

plastic foaming. Specifically, the strain-rate sensitivity exponent of $Pd_{43}Ni_{10}Cu_{27}P_{20}$ liquid at 360 °C is reported to be near unity for strain rates less than $10^{-2}\,s^{-1}$ [17]. Since the rate of global volumetric strain during foaming in the present experiments was on the order of $10^{-2}\,s^{-1}$, it can be argued that near-ideal plastic conditions prevailed in the course of these foaming experiments.

5. Conclusions

This study exemplifies the potential of bulk-glass forming metallic alloys to form closed-cell amorphous foam. It is demonstrated that by means of a thermo-plastic foam expansion process, metallic foam exhibiting good morphological characteristics can be produced at substantially high porosity. The foam expansion capability of amorphous metals is attributed to the plastic deformability of supercooled liquids, which contributes to overcome the constraints in attainable porosity encountered in the technology of metal foam processing.

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