Scripta Materialia xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

Micropatterning kinetics of different glass-forming systems investigated by thermoplastic net-shaping

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ARTICLE INFO

Article history:
Received 19 January 2017
Received in revised form 19 February 2017
Accepted 22 February 2017
Available online xxxx

Keywords:
Thermoplastic net-shaping
Glass-forming ability
Formability kinetics
Thermophysical properties
Supercooled liquid fragility

ABSTRACT

The formability difference between good and marginal glass-forming systems is investigated by micro-surface patterning of hierarchical features using thermoplastic net-shaping (TPN). For each alloy, a remarkable change in the flow behaviour is observed as the applied force along with the pressing time and temperature are optimized. The flow kinetics of glassy alloys with different glass-forming abilities is best described by the formability parameter *S*, which is defined by the ratio of the width of the supercooled to undercooled liquid region $(T_l - T_g)/(T_x - T_g)$. Reproducible micro-engineered surfaces with high uniformity can be established by controlled TPN processing.

1. Introduction

Unlike the majority of other metallic materials with crystalline atomic structure, bulk metallic glasses (BMGs) do not have any grains or grain boundaries and have an amorphous structure [1,2]. These new-generation alloys with high glass-forming ability and slow crystallization kinetics possess a large number of ideal attributes for commercial applicability [3–7]. For example, the key features relevant for structural applications are: i) very high strength and hardness along with good load bearing capability and high wear resistance; ii) low Young's modulus and high elasticity of about 2%; iii) excellent corrosion resistance even under extreme environments, and iv) excellent (micro)formability that allows producing precise and versatile geometries on length scales ranging from tens of nanometers to several centimeters, which is of great interest for various fields such as MEMS/NEMS, biomimetics, functional surface coatings, friction stir welding, etc.

Ti-based BMGs have a higher corrosion potential and lower corrosion current density compared to conventionally used Ti–6Al–4V alloys, indicating a better corrosion resistance [8]. Moreover, it has been found that Zr- and Ti-based BMGs have excellent endurance against phosphate buffer saline solution as well as higher fatigue strength under high cycle fatigue testing [9,10]. In terms of wear resistance, it has been very recently found that Ti-BMGs and composites [11] as well as Zr-based BMG types [12] have 1.5 to 2 times better wear resistance than Ti-based crystalline alloys, as measured by Vickers microhardness testing. The grain-free microstructure also yields twice to three times higher fracture strength and hardness as-compared to other conventionally used crystalline Zr- and Ti-based alloys [9,13]. Observations of the microstructure and mechanical properties of welded joints obtained by friction stir welding revealed the original and fully amorphous nature of the BMG, and the adopted method enables significant improvements in safety and durability of commercial products and vehicles [14].

In this contribution, two specific BMGs ($Zr_{48}Cu_{36}Al_8Ag_8$ and $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Ga_2$) with different formability were investigated. The first part of this contribution describes the transfer of micropatterns onto BMG surfaces via thermoplastic net-shaping (TPN) and post-

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http://dx.doi.org/10.1016/j.scriptamat.2017.02.038

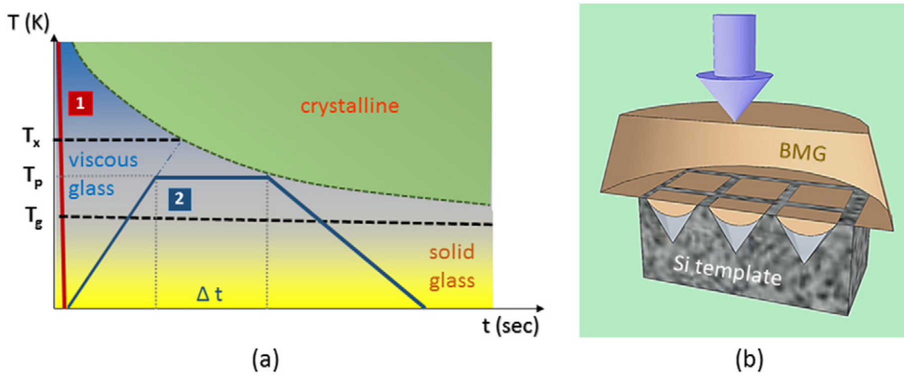

Fig. 1. (a) Schematic Time-Temperature-Transformation (TTT) diagram of the two step-production process; (1) Direct casting into plate geometry followed by (2) reheating into the SCLR and thermoplastic net-shaping for a given time Δt. (b) Filling of the BMG into micro-sized hierarchical inverted pyramid patterns etched into the Si template using the concept of thermoplastic net-shaping. The sketch displays the cross-section of the molded BMG (transparency applied for visualizing the inner section during molding into etched cavities of the Si template).

morphological characterization of the hierarchically generated features. The second part focusses on thermophysical properties, and comparison of the formability kinetics of the considered alloy types.

2. Thermoplastic net-shaping of BMGs

To evaluate the thermoplastic formability of different BMG alloys for meso-scale surface patterning, high temperature compression molding was adopted as net-shaping method. Since the desired BMG properties are otherwise lost (i.e. crystallized BMGs can no longer be deformed), any fabrication process must bypass crystallization during solidification and post-processing [15–18]. The overlap between the time interval of processing and the onset of crystallization was circumvented by directly quenching the glass into plates through centrifugal casting, and reheating to their processing temperatures, as shown in Fig. 1a ($T_g<T_p<T_x$, where T_g is the glass-transition, T_x the crystallization and T_p the processing temperature of the considered BMG). The main benefit of TPN is to decouple the casting and forming processes so that the material can be deformed within a much longer time window [19, 20]. Hence, complex shapes with high dimensional accuracy are feasible by this two-step production method. The sluggish kinetics in the supercooled liquid regime (SCLR) enables controlled Newtonian flow of the viscous glass into the desired cavities (Fig. 1b). Another important advantage of TPN is that due to sluggish relaxation kinetics in the SCLR, no fast cooling is required, which extends the use of this method in high vacuum chambers with slow cooling to minimize the surface oxidation during and after pressing.

To evaluate the filling depth of the BMGs, maximum pressing loads of 10, 25, 40, and 55 kN were selected. The data in Fig. 2 shows that the formability kinetics in the SCLR determine the filling depth of the patterns, which were observed by scanning electron microscopy (SEM) imaging. When the applied load is only 10 kN, the flow kinetics of both alloys are similar. The square base with a thickness of ~1 μm is formed within 2 min pressing time. As the applied load increases to 25 kN, the filling depth for the Zr-BMG becomes ~5 μm, whereas the Ti-BMG fills the cavity only by 1.5 μm. A transition in terms of the flow kinetics is obtained when the applied load reaches to 40 kN. An array of fully formed pyramids with a total height of 23.3 μm measured by using high-resolution SEM can be obtained. Irregularities and excess material are observed at the summit of the pyramids as the load is raised above 40 kN, which is due to the local fracture of the Si template with negative features. For this reason, optimized patterning for the Zr-BMG should be conducted at or

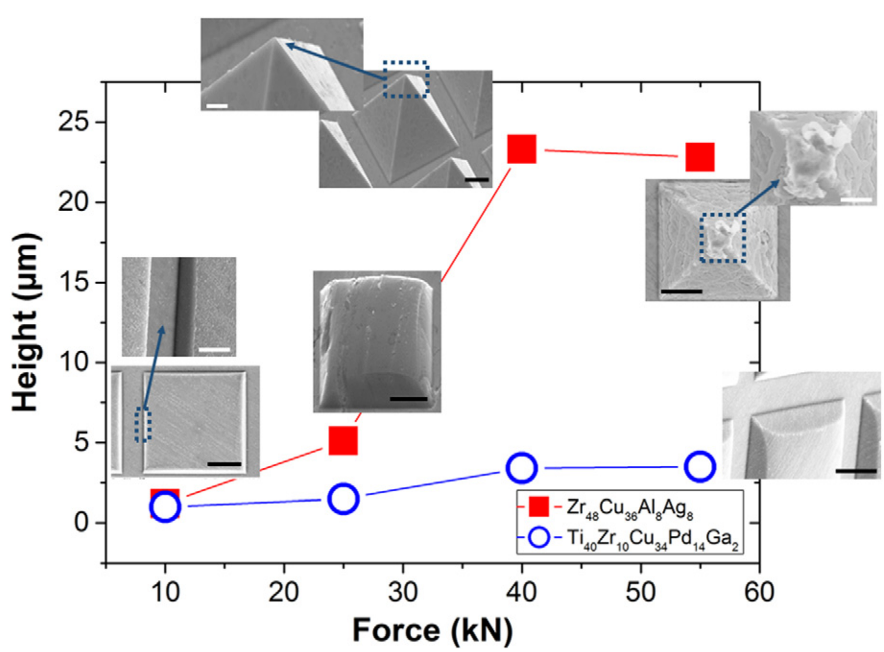

Fig. 2. Comparison of the filling height of the cavities vs applied load for two different BMG types. The SEM images illustrate the evolvement of the pyramidal shapes (Zr-BMG – filled red square symbols) or bumps (Ti-BMG – open blue circle symbols) as the applied load increases. Black scale: 5 μm, white scale: 2 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Please cite this article as: B. Sarac, et al., Micropatterning kinetics of different glass-forming systems investigated by thermoplastic net-shaping, Scripta Materialia (2017), http://dx.doi.org/10.1016/j.scriptamat.2017.02.038