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Hierarchical surface patterning of Ni- and Be-free Ti- and Zr-based bulk metallic glasses by thermoplastic net-shaping

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ABSTRACT

In order to establish a strong cell-material interaction, the surface topography of the implant material plays an important role. This contribution aims to analyze the formation kinetics of nickel and beryllium-free Ti- and Zr-based Bulk Metallic Glasses (BMGs) with potential biomedical applications. The surface patterning of the BMGs is achieved by thermoplastic net-shaping (TPN) into anisotropically etched cavities of silicon chips. The forming kinetics of the BMG alloys is assessed by thermal and mechanical measurements to determine the most suitable processing temperature and time, and load applied. Array of pyramidal micropatterns with a tip resolution down to 50 nm is achievable for the Zr-BMG, where the generated hierarchical features are crucial for surface functionalization, acting as topographic cues for cell attachment. The unique processability and intrinsic properties of this new class of amorphous alloys make them competitive with the conventional biomaterials.

1. Introduction

Bulk metallic glasses (BMGs) are a new class of non-crystalline engineering materials composed of three or more elements. These lab-made multicomponent alloy systems offer unique combinations of strength, elasticity, toughness, compressive plasticity together with good corrosion and wear resistance due to absence of grain boundaries and dislocations in the glassy state [1–4]. Apart from their favorable structural and surface properties, recent findings have postulated the feasibility of thermoplastic net-shaping (TPN) of BMGs into geometries previously unrealizable with any other metal forming technology [5–8]. Specifically, the deformation behavior of BMGs becomes significantly altered upon heating to their supercooled liquid region (SCLR), i.e., it changes from inhomogenous deformation to completely homogenous Newtonian flow [9]. However, akin to polymers the change in viscosity between the glass transition, T_g, and crystallization, T_x, temperatures is relatively gradual as opposed to conventional metallic alloys exhibiting an abrupt change in viscosity at their melting temperatures [10]. Hence, BMGs combine high mechanical strength (comparable with or higher than high-strength steels) with the processability of thermoplastics.

BMGs are relatively new in the area of biomaterials that exhibit desirable properties for osteosynthesis and fracture fixation systems (such as wires, pins, nails, rods, plates) [11–18]. In particular, restoration of the fragmented bones upon injury necessitates external fixtures or stems of customized shapes with promising mechanical and chemical properties. Recent findings suggest that Ti- and Zr-based BMGs can assist cell adhesion, differentiation and growth in-vitro, which renders them appropriate candidates for their potential use as implant materials [19]. In particular, Ni-containing BMGs and conventional crystalline alloys are known to be toxic [12,20,21], and even carcinogenic [22,23], leading to the limitation of the applications of BMG alloys in the medical field. Newly discovered Ni-free Ti- and Zr-based BMG alloys, in this respect, can revolutionize the current biomaterial performance with combinations of biological safety and enhanced material properties.

In an effort to address the TPN kinetics of different metallic glasses, in this study we have adopted two different alloy types, $Zr_{48}Cu_{36}Al_8Ag_8$ [24] and $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Ga_2$ (developed by microalloying a Ti-BMG [25] with traces of gallium) with different glass-forming ability (GFA), where GFA influences the flow kinetics of the BMGs. Furthermore, these compositions are selected because of their suitability for potential biomedical applications owing to their high corrosion resistance [26,

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27], as well as being free from other toxic elements such as V, Co and Be [27]. Al containing Ni-free Zr-based BMGs were also shown to promote cell adhesion and differentiation [17,28,29]. Moreover, Ti-BMGs have been proven an ideal substrate for biochemical interaction and cell differentiation as in the case for pre-osteoblast conversion into osteoblasts [30] as well as for hydroxyapatite formation on the surface [31,32]. The compressive strength σ_y and density ρ of Zr-BMG are 1850 MPa and 7.12 g/cm^3 which results in a specific strength (the ratio of strength to density) of 2.6×10^5 Nm/kg. For the Ti-BMG, σ_y and ρ are measured to be 2015 MPa [24], and 6.94 g/cm^3, respectively, which has a specific strength of 2.9×10^5 Nm/kg. Thus, these alloy families have significantly higher specific strength compared to many other alloys currently used in bone implantations which has been postulated to be one of the key aspects in bone-material interactions [33].

As compared to flat biomaterial surface, the functionality of different cell types was demonstrated to be better controlled and enhanced by an array of micropattern design (i.e. equally spaced grooves, square protrusions, pillars with a possibility of further surface functionalization) imprinted to the substrate material [34–39]. However, the lithography of silicon and net-shaping of conventional alloys into complex geometries have certain limitations. For example, creating features with sharp tips protruding outward which increases the surface area-to-volume ratio dramatically (i.e. from μm to nm up to three orders of magnitude) is a very challenging task. This ratio increase has been found to effectively improve the immobilization of cell proteins or biomolecules [40,41], and thereby favors cell adhesion and differentiation [42]. BMGs, in this respect, can replicate surface features down to a couple of nanometers [43,44].

Here, the micro-patterning characteristics of two distinct BMG types are investigated. Parameters such as temperature and time for optimized pressing conditions while retaining the fully glassy state are determined by thermophysical and thermomechanical measurements. The net-shaping kinetics is then examined as a function of the applied pressure and the final height of the micropatterns for both alloy types together with the surface oxidation kinetics during pressing of the Zr-BMG.

2. Materials and methods

The BMG master alloy ingot was prepared from elements with purity higher than 99.99% using an Edmund Bühler GmbH arc-melter. The obtained ingots were heated above the liquidus temperature four times to form a homogenous mixture. The master alloys were then sliced into 10–12 g pieces, and plates of 10 mm × 75 mm × 1.5 mm were produced by centrifugal casting under an Ar atmosphere of 10^{-5} mbar from around 200 K above the liquidus temperature of each alloy using a Linn High Therm-Vacutherm 3.3 Titan centrifugal casting device. Inductive melting in a cold wall crucible followed by casting at a rotation speed of 500 rpm results in a very smooth cast surface without any microporosity, as inspected by a Keyence Digital Microscope VHX 2000. The surface crystallites of around 5 μm in thickness were removed from each side of the cast plates. The samples were cut to 10 mm × 10 mm × 1.5 mm using a Struers Accutom 50. The chopped samples were ground and subsequently mirror-polished down to the desired thickness level by Buehler Metaserv 250 to eliminate any influence of possible surface crystallization and oxidation caused by heterogeneous nucleation. In addition, smaller pieces of about 20 mg were used for calorimetric measurements. Using a PerkinElmer Pyris Diamond Differential Scanning Calorimetry (DSC), each sample was heated above its crystallization temperature at a rate of 20 K/min followed by cooling at a rate of 100 K/min. The onset temperature of the first crystallization event was taken as the crystallization temperature T_x. The same device was used to obtain the isothermal heating curves for selected temperatures, which were used to estimate the incubation time for crystallization for the specific alloy type. The melting and liquidus temperatures of each alloy were obtained from the DSC traces measured with a Netzsch DSC 404 calorimeter at a heating rate of 20 K/min followed by rapid cooling (100 K/min). Samples with an initial height of 1.43 ± 0.01 mm (two samples for each alloy type) were used to estimate viscosity values during continuous heating at a rate of 20 K/min using a Perkin-Elmer thermo-mechanical analyzer (TMA 7) with 3 mm diameter flat tip parallel plate probes. The processing temperature of the corresponding BMG was determined from the DSC isotherm scan, parallel-plate rheometer viscosity measurement data and hot pressing trials at different temperatures. For the substrate material, 500 μm thick silicon chips with [100] orientation were selected. The chips were etched anisotropically in KOH solution, where the SiO_2 mask is used to prevent the excess reaction. After KOH etching, the SiO_2 mask was removed in an oxide etch step. HF etching of the Si chip generates a relatively smooth texture within the inverted pyramid features. The samples were finally ultrasonically cleaned with acetone, isopropyl alcohol, and deionized water, respectively (further details regarding the etching process can be found in [45]). The wet anisotropic etching process results in sharp-tipped pyramidal structures with a slope of 54.74° with respect to the (100) plane. The produced Si chip with an array of embedded inverted pyramidal features and the BMG situated on top were heated to the desired processing temperature at a heating rate of 20 K/min. The thermoplastic net-shaping was conducted in a custom-made hydraulic press under high vacuum (4×10^{-4} mbar) to minimize the influence of oxidation during the material flow. The height of the surface polished TPN samples varied between 1.40 and 1.45 mm, which correlates with the sample height used in the viscosity measurement. Automatic preloading was applied (10 kN) to eliminate any unwanted dynamic impact on the Si chips. Taking the area of the BMG samples perpendicular to loading into account (100 mm^2), the applied pressure is calculated to be 100 MPa. The pressure drops down even further when the material gains Newtonian flow kinetics at its SCLR. Therefore, the Silicon chip remains intact throughout the patterning process. For temperature stabilization, a waiting time of 30 s was applied. The samples were deformed at various maximum load levels at constant temperatures for ~2 min. Due to the sluggish kinetics of the BMG alloys preventing crystallite formation inside the samples, no fast cooling is required after TPN. However, for minimizing the oxide layer on the material surface, the specimens were then fast cooled down to 473 K (at a rate of 50 K/min) using Ar gas while they were kept in the enclosed chambers. The deformation process was monitored on the computer screen using the LabVIEW system design software. Scanning electron microscopy (SEM Zeiss Ultra Plus) investigations were performed to visualize the deformed surface features on the meso-scale. Second phase compositional analysis was carried out by using an energy dispersive x-ray (EDX) detector attached to the SEM. Structural characterization was performed before and after pressing by X-ray diffraction using a D3290 PANalytical X'pert PRO with Co-Kα radiation. It is noteworthy to mention that because of the uneven surface, the XRD measurement from the micro-patterned side gives inaccurate peaks and no broad diffraction maxima, which renders one to analyze the flat (unpatterned) side of the specimens. Before measuring the XRD patterns from the flat sides, the surface oxide layer formed during TPN process were grinded manually by 5 μm to ensure that the surface oxides are completely removed.

3. Results and discussion

3.1. Thermoplastic net-shaping of BMG patterns

Fig. 1a displays the etched Si chip with periodically spaced inverted pyramids, and a schematic cross section. Fig. 1b shows a sketch of the thermoplastic net-shaping process. The prepared BMG discs were situated on the patterned Si wafer, and were heated together to the processing temperature T_P. The viscosified BMG flows into the pyramidal cavities under the applied load within a certain period.