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Performance of nickel and bulk metallic glass as tool inserts for the microinjection molding of polymeric microfluidic devices

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ABSTRACT

Electroformed nickel and bulk metallic glasses (BMGs) can be designed to incorporate features with length scales ranging from millimeters to nanometers. This, combined with their good mechanical properties relative to other materials, makes them competitive candidates for manufacturing multi-scale molds to produce high volumes of polymeric microfluidics components and other micro/nano devices. Despite this attractiveness, BMGs are newly developed engineering materials and their capabilities as a mold material have not been evaluated. This paper compares the performance of nickel tools made by an electroforming process and BMG tools made by a thermoplastic forming process, specifically with regard to typical microfluidics patterns and features. Ni shows excellent capabilities for good feature replication. BMG thermoplastic forming is highly dependent on the choice of alloy composition, which restricts the achievable feature size and aspect ratio. Compared to Ni, BMG has hardness values that are close to those of stainless steel and shows the superior mechanical strength that is required for mass production applications. However, oxidation in BMG tool manufacturing process affects the tool surface finish significantly and reduces the tool's corrosion resistance. Future development of BMG tools include preventing the formation of oxidation layers or developing BMGs with an anti-oxidation composition, and further reducing their overall cost and widening its processing window parameters. Despite these challenges, however, BMGs are shown to combine excellent mechanical properties and capabilities for multi-scale forming; this makes them significantly more attractive than relatively soft Ni tools.

1. Introduction

Molded polymer microfluidic devices contain channels, the dimensions of which span hundreds of microns to hundreds of nanometers. Machining such small features is a challenge for manufacturing tooling technology. An ideal high performance tool should be strong and durable, capable of being manufactured to have features of particular size and aspect ratio, should maintain good de-molding capability with a reasonable draft angle, have an achievable appropriate surface finish and a good cost/performance ratio, and should retain its original geometry for at least 10^4 molding cycles without significant wear. Conventional mold construction uses tool steels, such as P20, which can last for 200,000–500,000 molding cycles with good tool maintenance. Stainless steel can be machined to have high aspect ratios and a user-defined draft angle using various micro-manufacturing technologies, such as micromilling, micro-EDM and laser micromachining. However, the micromilled trench features cannot be smaller than 50 μm, with a geometric tolerance of ±10 μm, which is limited by the 50 μm diameter of the smallest micromilling tools. Tool wear, when machining hard materials, influences the achievable accuracy, roughness, and generation of burrs (Uriarte et al., 2006). Micro-die EDM (electrical discharge machining) sinking has the problem of uneven wear of micro and macro features on the electrode. Micro-EDM milling has the challenge of compensating for electrode wear. When using laser micromachining, it is difficult to find an optimal process to achieve good quality outputs (Teixidor et al., 2013).

Among all of the various manufacturing technologies, electroformed nickel and bulk metallic glass are capable of integrating length scales ranging from millimeters to nanometers. Nickel electroforming is a metal deposition process whereby a nickel anode is dissolved into an electrolyte and thence deposits onto a conductive cathode upon applying a voltage, as shown schematically in Fig. 1. The deposit on to the cathode is finally separated from an inverted substrate to form a single part. Electroforming itself is an established "atom-by-atom" technique, which can create a nearly perfect copy of the master geometry at virtually all scales.

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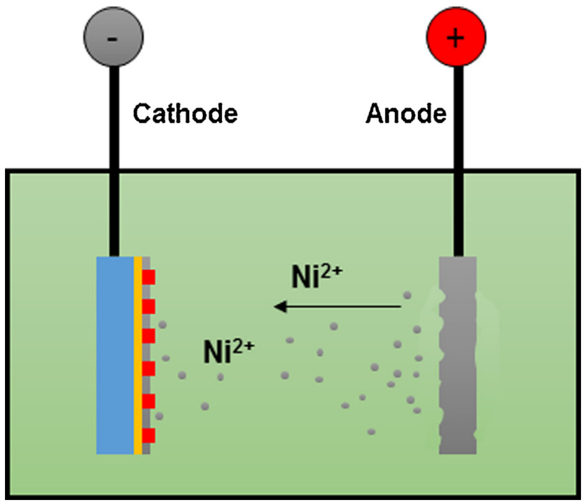

Fig. 1. Nickel electroforming process to fabricate micropatterned tool.

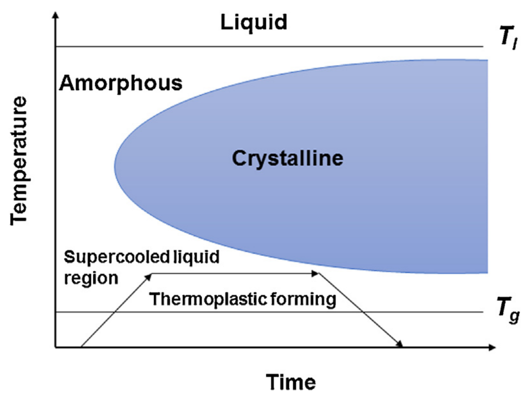

Fig. 2. A schematic time–temperature–transformation (TTT) diagram for a typical BMG, where T_l is the liquidus temperature and T_g is the glass transition temperature.

Ni tools have been used in injection compression molding to manufacture DVD and Blu-Ray Disks for mass production of low aspect ratio (<1) nanofeatures that range in size from 400 nm to 150 nm. It is the most widely used process for fabricating tools for injection molding of polymeric microfluidic devices.

Bulk metallic glass can be patterned at the nanometer scale either by using thermoplastic forming (Schroers, 2010) or Focused Ion Beam machining (Zhang et al., 2012a,b). In the thermoplastic forming process, BMG is heated into the supercooled liquid region (SCLR) above the glass transition temperature of the material and below its crystallization temperature, where it is easily deformed into a master mold and then cooled down, as shown in Fig. 2. Metallic glasses in their supercooled liquid region are metastable and these materials tend to crystallize. However, the crystallization kinetics of glass-forming alloys are sluggish, which provides an opportunity to carry out thermoplastic forming without crystallization (David et al., 2009). BMG molds created by thermoplastic forming have been used for embossing of polymer microfluidics (Browne et al., 2013). Henann et al. (2009) thermoformed a commercial BMG, Vitreloy-1 ($Zr_{41.2}$ $Ti_{13.8}$ $Be_{22.5}$ $Cu_{12.5}$ Ni_{10}), with inverted channel features of height 43.5 μm and width 55 μm. The thermoplastic forming process was simulated based on their numerical modeling and the optimal process parameters were found to be 450 °C with a holding pressure of 40 MPa and a holding time of 2 min. BMG was found to successfully reproduce features of a Si master and was used as a tool for embossing COC and PMMA. He et al. (2012) also used Zr based BMG ($Zr_{35}Ti_{30}Be_{26.75}Cu_{8.25}$) to thermoplastically form inverted microchannels 50 μm wide and 100 μm deep with a spacing of 200 μm. Patterns were well replicated without any voids or material crystallization. The inverted patterns were successfully imprinted onto PMMA substrates. Our previous work has used BMG as a tool insert for micro/nano injection molding, where the smallest feature that was reproduced is 100 nm (Zhang et al., 2012a).

Although Ni and BMG are comparable in achieving similarly sized features, the actual size of features that can be achieved using these two materials, and their respective mechanical properties, physical properties, tool life and associated costs are different. In our previous work (Zhang et al., 2015a), we have broadly discussed the performance of various tool materials, including stainless steel, Ni and BMG, but the tool features were not the same for each material tested. In the present work, we will focus on the replication of microfluidic patterns, including inverted channels and micro separation arrays and the testing of honeycomb structures and the evaluation of tool performance (cost, mechanical properties, surface finish, tool life) using large-area BMG and Ni tools based on microinjection molding using various plastic materials. Insights and key challenges regarding the development of mass production tools for polymeric microfluidic devices will also be discussed.

2. Experiments

2.1. Manufacturing processes for Ni and BMG tool inserts

2.1.1. Ni tool inserts

Standard UV-LIGA, and DRIE processes were used to transfer relatively high aspect ratio features onto a Si master, as shown in Fig. 3. A Ni layer of approximately 300 μm thickness was electrochemically deposited onto the substrate in a ready-to-use nickel bath under a well-defined recipe. Afterwards, the Si substrate was totally removed by wet etching with potassium hydroxide (KOH) at 82.8 °C. CNC milling was then used to dice the Ni wafer into the dimensions of the mold insert and the uneven back surface was polished using SiC polishing paper. The finished Ni insert is shown in Fig. 4(b).

2.1.2. BMG tool insert

Large area BMG with a composition of $Zr_{44}Cu_{40}Al_8Ag_8$ was cast using an in-house tilt-casting technique following alloying and arc melting in an argon atmosphere. The Cu–Zr–Al–Ag system was chosen, because of its good glass forming ability, lack of toxic or prohibitively expensive elements, and reasonably high glass transition and service temperatures, enabling use for molding a variety of polymers (Browne et al., 2013). The amorphous nature of the BMG was confirmed using X-ray diffraction. Thermal characterization of BMG was carried out using differential scanning calorimetry (Netzsch DSC 200F3). Constant heating rate experiments were performed at 10 K/min and isothermal experiments were performed at various temperatures between 457 °C and 480 °C to generate the time-temperature transformation diagram (Fig. 5(a)). Viscosity was measured using Dynamic Mechanical Analysis (DMA) – Netzsch 242 Artemis – at 1 Hz with a heating rate of 0.2 K/min (Fig. 5(b)). The BMG materials were then machined and polished to achieve a surface roughness of less than 10 nm. Microfluidic features were patterned on a Si wafer using standard lithography and deep reactive ion-etching (DRIE) techniques (Fig. 3(b)). The polished BMG and Si wafer were then heated to 472 °C (745 K), above the BMG's glass transition temperature (710 K). Hot embossing was performed using a custom built apparatus attached to a Hounsfield uniaxial testing machine with a compression force of 25 kN, which was held for 2 min. The selection of these process conditions was based on optimization from previous trials using the same