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Manufacturing microstructured tool inserts for the production of polymeric microfluidic devices

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Abstract: Tooling is critical in defining multi-scale patterns for mass production of polymeric microfluidic devices using the microinjection molding process. In the present work, fabrication of various microstructured tool inserts using stainless steel, nickel and Bulk Metallic Glasses (BMGs) is discussed based on die-sinking EDM (electrical discharge machining), electroforming, Focused Ion Beam milling and thermoplastic processes. Tool performance is evaluated in terms of surface roughness, hardness and tool life. Compared to stainless steel, nickel and BMGs are capable of integrating length scales from 10^0 to 10^{-8} m and are good candidates for producing polymeric microfluidics. Selection of tool materials and manufacturing technologies should consider the end-user requirements of actual applications.

1. Introduction

Microfluidics have wide applications in life sciences (pharmaceutical, personalized medicine and point of care) and other areas such as environmental, analytical and agro-food [1, 2]. However, the adoption of microfluidic technology into mainstream biology research and commercial markets has not matched the initial enthusiasm for lab on a chip technology [3, 4]. Apart from reasons of competing existing technologies, and issues of integration, finance and regulation, the incompatibility of laboratory based prototyping methods with the requirements of clinical tests and early stage scale-up is a real barrier for commercialization of microfluidic-based products. For example, soft lithography using Polydimethylsiloxane (PDMS), which is widely used in laboratory environments, can replicate very small and high aspect ratio features at room temperature because of its low viscosity, and it has fewer demolding issues because of the material's elasticity and surface treatment. Instead, replication of high aspect ratio features by rigid transparent thermal plastic for mass production, such as COC (Cyclic-Olefin-Copolymer) and PMMA (Poly(methyl methacrylate)), is very process dependent and also has possible issues of feature breakage during demolding. There are also additional differences between PDMS and thermoplastics, such as gas permeability, bonding methods, surface functionalization methods, compatibility with different assays (e.g. PDMS absorbs small molecules) and scale-up capability, etc. [3]. As a result, the direct transfer from laboratory-based microfluidics devices to clinical test and commercialization may require re-development of a chip, and the entire process then becomes a different challenge. Directly using commercial plastics as prototyping materials offers benefits of lowering the risk of development failure due to materials and process issues.

Furthermore, this makes the transition from medium to mass production feasible and shortens the time for prototyping and technology transfer for commercialization, and this approach has been used by various research institutes and industries [5, 6].

Microinjection molding is one of the most popular mass production technologies for manufacturing large thermoplastic polymer parts with small surface details, such as microfluidics and micro lens. A key issue for mass production of polymeric microfluidics is the fabrication of inverted microstructured tools. Mass production tools must be strong and durable, be manufactured with the required feature size and aspect ratio, and should maintain a good demolding capability with a feasible draft angle, appropriate surface finish and a good cost/performance ratio, and should preserve the original geometry for over 10^4 molding cycles. Table 1 summarizes the performance of various materials and manufacturing technologies for tool manufacturing for injection molding. SU8, Si and hybrid polymer inserts are mainly used for prototyping purposes.

- SU8 can be patterned on a Si substrate using X-ray/UV-lithography. It has disadvantages that the substrate can break and delaminate when used as a mold [7].
- Silicon can easily be patterned using mature semiconductor fabrication, but it is brittle and has demolding issues because of scallop from the Bosch process and possible molding flash being squeezed into the insert [8]. Although soft supports, such as Polytetrafluoroethylene (PTFE) [9] and Teflon sheets [10], increase the compliance of a Si insert, molding conditions have to be well controlled with low cavity pressure.
- Hybrid polymer inserts (e.g. Epoxy, Polyimide, Polyether-ether-ketone) can be thermally imprinted using a hard master and then coated with a metal protection to prevent chemical interaction with the work piece. However, such barrier coatings tend to delaminate soon after ~20 molding cycles [11].

Tool steels are the main tool material for conventional injection molding. Electroformed metallic tools, such as nickel (Ni), have been used in injection compression molding to manufacture DVD and Blu-Ray Disks for mass production of low aspect ratio (<1) nanofeatures as small as 400nm to 150nm. Such materials have been adapted for manufacturing tool inserts for polymer microfluidics by using micro manufacturing technologies (Table 1).

- Stainless steel and brass can be machined using various micro manufacturing technologies with high aspect ratios with a user-defined draft angle; however, the micro-machining process can only accurately produce features about 50 μ m and larger. Further, the micro-machining process usually leaves machining marks and burrs, which can result in a poor surface finish [12].
- Ni offers excellent replication capability and good surface finish. However, because of feature size limitations and the requirement for a thick support layer, a lower current density needs to be applied, which makes the process slow and time consuming. It is difficult to produce high aspect ratio features because of void formation [13]. However, it is still the most widely used process because of the lower capital equipment investment and material costs.

Bulk Metallic Glasses (BMGs) have lower structural order limited to nanometers and offer the possibility of producing submicron and nanoscale features. They have drawn attention because of their good mechanical properties, such as high strength and hardness, good corrosion resistance, lower shrinkage upon cooling to room temperature, and durability. Additionally, they can easily be processed like plastics in their super cooled liquid region (SCLR) [14, 15]. Several researchers have used BMG thermoplastic forming to fabricate tools for polymer microfluidics, as reviewed in [16]. Henann et al. [12] thermoformed a commercial BMG Vitreloy-1 ($Zr_{41.2}Ti_{13.8}Be_{22.5}Cu_{12.5}Ni_{10}$) with inverted channel features with height 43.5 μ m and width 55 μ m. The thermoplastic forming process was simulated based on their mathematical modeling and optimal process parameters were found to be 450°C with a holding pressure of 40MPa and a holding time of 2min. 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. [17] also used Zr based BMG ($\text{Zr}_{35}\text{Ti}_{30}\text{Be}_{26.75}\text{Cu}_{8.25}$) to thermoplastically form inverted microchannels 50 μm wide and 100 μm deep, spaced 200 μm apart. 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 sub 10 micron and nanoinjection molding, where the smallest feature that we reproduced was 100nm [18].

Although considerable work has been done on prototyping microfluidics using plastics, relatively little work has been reported on comparing tool material performance in terms of mass production. The present work focuses on comparing the performance of mass production tools that are manufactured from stainless steel, Ni and BMG to fabricate polymer micro devices using the microinjection molding process. We discuss microstructured tool insert manufacturing processes based on our own manufacturing facilities and prototyping experience. For stainless steel, we used micromilling and die-sinking EDM (Electrical Discharge Machining) processes, since there is a lack of information on characterising the interaction between electrode and work piece for manufacturing microfluidic patterns. For electroforming of Ni, we explored the replication of features varying in size from tens to hundreds of microns and with various aspect ratios. Processing effects on achievable aspect ratios of various features and tool hardness were also discussed. For BMG tools, examples of multi-scale tools for nanofluidic applications using FIB milling have been demonstrated; the ability to thermoplastically form various inverted channel features on the micro scale was also studied using our own cast BMG. Tool performance (surface finish, hardness, tool life, pattern transfer) and issues regarding manufacturing processes were also discussed.

2. Experiments

2.1 Manufacturing processes for tool inserts

2.1.1 Stainless steel inserts

In the present work, micromilling and die-sinking EDM (electrical discharge machining) were combined to manufacture Stavax stainless steel inserts with protruding inverted microfluidic patterns, as shown in Figure 1 (a). In die-sinking EDM process, the microfluidic pattern was firstly milled on a graphite/copper electrode; then a thermal erosion process takes place between the tool and workpiece under a controlled electric spark, which has the effect of eroding the workpiece to form a replica of the electrode on a stainless workpiece. This process offers force free machining independently from the mechanical properties of the processed material and allows batch production of micro dies and molds for injection molding and hot embossing. Seco 0.6mm and 0.3mm solid carbide end milling tools (MEGA-T) were used to machine the electrode with a HURCO VM3 CNC milling machine, where the spindle rotation speed was 8000RPM (here and throughout the rest of this paper).

In addition, we also provide a case of using ultra-precision machining to directly manufacturing a Stavax stainless steel insert for microinjection molding of spherical lenses. For optical elements, the requirements of complex form, higher surface finish and better geometrical accuracy are challenging for machining processes [19, 20]. Figure 1 (b) shows the geometrical model of a typical element of lens arrays with 110 spherical lenses, each with a radius of 0.6 mm on a 10 $\times$ 6 mm² area.

Figure 1. Manufacturing of Stavax stainless steel tools: (a) Micromilling of graphite/copper electrode, die-sinking EDM of stainless steel workpiece, (b) geometric model of spherical lenses on a $10 \times 6 \text{ mm}^2$ area.

2.1.2 Ni tool inserts

Electroforming is a metal forming process that causes metal to grow through the electroplating process, where an anode, such as Ni, electrolyzes and metal ions travel and deposit onto a patterned conductive cathode surface. The electroformed part (cathode) can be stripped off its mandrel, once the desired thickness has been reached. Two Ni insert fabrication processes were proposed using either a micro milled Aluminum master (Figure 2 (a)) or Si master (Figure 2 (b)) with a wide range of feature sizes from tens to hundreds of microns. A series of trench arrays with a nominal aspect ratio of 2 and widths of 200, 250, 300, 400, 500 and $600 \mu\text{m}$ were machined on an Al substrate via the micromilling process. An electroforming process was then carried out with current densities of $\sim 1.2 \text{ A/dm}^2$, $\sim 0.6 \text{ A/dm}^2$, and $\sim 0.4 \text{ A/dm}^2$ in a Nickel sulfamate bath. A 10% sodium hydroxide solution was prepared to dissolve the aluminum and expose the nickel features. Meanwhile, standard UV-LIGA and DRIE processes were used to transfer features onto a Si master, as shown in Figure 2 (b) [21]. A Ni layer of $300 \mu\text{m}$ nominal thickness was electrochemically coated 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 backface surface was polished using SiC polishing paper.

Figure 2. Process chains for manufacturing Ni tool inserts: (a) Aluminium master was machined with trenches using micromilling process; a Ni insert was created with inverted trench patterns by electroforming and Al dissolving; (b) UV-LIGA process: (1) Si oxidation, (2) Spin coating photoresist, (3) UV lithography with chrome mask, (4) Development, (5)

Removing photoresist, (6) DRIE etching of Si, (7) etching away of SiO₂, (8) PVD Coating Ti and Ni, (9) electroplating, (10) Si dissolving and Ni wafer dicing & polishing.

2.1.3 BMG tool insert

BMG tooling was fabricated from a ternary BMG, with composition Zr₄₇Cu₄₅Al₈, via a drop-casting technique in an argon atmosphere. A BMG rod (5mm diameter, 40 mm long) was machined into a flat dog-bone shape, polished and mounted as an insert into a steel die, as indicated in our previous work [22]. A FEI Quanta 3D FEG Dual Beam FIB was used to machine the sub-micron and nano scale features on the surface of the BMG insert, as shown in Figure 3 (a).

For thermoplastic forming (TPF) in the supercooled liquid region, BMG with a composition of Zr₄₄Cu₄₀Al₈Ag₈, in the form of a square bar (dimension 6×6×40mm), was cast using the same drop casting technique. The BMG was then machined to form a disc of dimensions 6×6×3mm and polished to achieve a surface roughness of less than 10nm. Thermal characterization of BMG was carried out using differential scanning calorimeter NETZSCH DSC 200F3. Constant heating rate experiments were performed at 10 K/min in the temperature range 100 to 550°C and some isothermal experiments were performed at various temperatures between 445°C and 480°C. Figure 3 (b) shows the thermoplastic forming process of protruding micro features from a Si wafer using UV lithography and the DRIE process (Figure 2 (1-6)) to BMG. A customized thermal forming tool was first pre-heated to the selected processing temperature. The polished BMG and the Si wafer were then stacked and left in the center of the embossing platen after the temperature was stabilized. Hot embossing was performed using a custom built apparatus attached to a Hounsfield uniaxial testing machining. The Si master was then dissolved in a KOH bath to expose the inverted BMG features.

Figure 3. Process chains for manufacturing BMG tool inserts: (a) direct Focused Ion Beam milling on BMG workpiece, (b) BMG insert manufactured by thermoplastic forming using Si master and wet etching Si away.

2.2 Feature measurement and material characterization

A Keyence 3D microscope was used to measure the large micromilled features. A Veeco optical profilometer was used to measure surface roughness and features smaller than 100µm. In order to study the effect of current density on the microstructure of the Ni tool, the two electroplated Ni shims under currents of ~0.6A/dm² and ~1.2A/dm² were mounted in epoxy and polished using 3µm and 1µm diamond polishing suspension. The exposed nickel surface was then submerged into a shallow dish containing Marble's reagent for ~10 seconds, and cleaned to observe its microstructure. Vicker's hardness tests were performed to evaluate tool

mechanical performance. A 5kg load was applied using a standard Vicker's indenter in order to determine the hardness of the tools. Since the tools have micro patterns, we directly indented the tool surface without mounting and polishing the surface. In this case, tool surface roughness may induce certain variations. However, such variations could be ignored because of the large difference between the various materials.

3. Results and Discussion

3.1 Stainless steel inserts

Figure 4 (a) and (c) show the graphite/copper electrodes and the corresponding stainless steel inserts (Figure 4 (b) and (d)) with protruding inverted serpentine microfluidic mixer patterns and cross channels fabricated by the combined process of micromilling and die-sinking EDM. Firstly, a relatively high discharge energy $\sim 10\text{kJ}$ was used to roughly machine the stainless steel, and then the electrodes were re-machined (sharpened) again to finish the pre-machined pattern with a lower energy $\sim 0.1\text{kJ}$. As indicated in Figure 5, the overview and “T” junction indicate that all channels are very well defined by die-sinking EDM using a graphite electrode. The top width of the inverted channel on stainless steel is $481\pm 19\mu\text{m}$, which indicates a possible discharging gap of $\sim 43\mu\text{m}$, when compared to the counterpart of the graphite electrode. A copper electrode was used to spark cross-channel microfluidics with nominal $200\mu\text{m}$ width and $50\mu\text{m}$ channel depth (Figures 4 (c) and (d)). The average channel width in the stainless steel is $204\pm 11\mu\text{m}$. This means the dielectric discharge gap is $\sim 48\mu\text{m}$, which is smaller than if using a graphite electrode, when the channel width is assumed to be the same as the tool diameter. Additionally, compared to the graphite electrode, the wear resistance of the copper electrode is better than the graphite one. However, as indicated in Figure 6, although the crater size is similar (Figure 6 (b) and (d)), the graphite electrode gives much better shape definition, while the copper electrode gives a non-uniform edge finish along the channels and worse pattern transfer at the cross-junction. This is possibly because copper is malleable and any micro-machined finish after milling will be transferred to the tool by the EDM process. From this perspective, using high-speed micromilling would require an optimised milling strategy and subsequent cleaning of any burr from a copper electrode would improve the pattern transfer using die-sinking EDM. Figure 7 displays the profile of electrodes and corresponding patterns on stainless steel. The profile of the graphite electrode closely matches the counterpart of the stainless steel with a draft angle $\sim 15^\circ$. Meanwhile, the trench of the copper electrode does not fit with the corresponding protruding steel features with the draft angle being as large as $40\sim 55^\circ$, which is mainly because of electrode deformation and wear during milling and rough sparking.

Figure 4. Micromilling and die-sinking EDM process: graphite electrode (a) and finished stainless tools (b); copper electrode (c) and finished tools (d) (width of square insert is 25mm).

Figure 8 (a) shows the Stavax stainless steel tool directly machined by ultra-precision machining with a fast tool servo system, based on the requirement that the P-V value (peak-to-valley value) of lens should be smaller than $2.0\mu\text{m}$ and the surface finish be smaller than $0.2\mu\text{m}$ in Ra. The lenses shape on the mold insert was made according to the lens array geometry (Figure 1 (b)). However, the molded parts had a large form error of $12\mu\text{m}$ in P-V value. Error compensation had to be conducted to improve the form accuracy of the molded parts. Figure 9 shows that the P-V value of the molded parts after compensation was reduced down to $1.7\mu\text{m}$, where the surface roughness of $0.15\mu\text{m}$ in Ra was achieved.

Figure 5. SEM images of stainless steel tool insert: an overview (a) and an inverted “T” junction channel (b).

Figure 6. Comparison of Stavax stainless steel insert manufactured by die-sinking EDM: the graphite electrode give better geometry definition on micro patterns (a), while copper electrode gives a non-uniform edge finish along the channels and worse pattern transfer at the cross-junction (c), although the crater size of using both electrode are similar ((c) and (d)).

Figure 7. Comparison of graphite (a) and copper (b) electrodes with corresponding finished stainless steel patterns.

Figure 8. Mold insert manufactured on Stavax using ultra-precision machining (a) and replicated PMMA lens using injection molding process (b) over $10 \times 6 \text{ mm}^2$ area.

Figure 9. Form error of the lens molded, vertical axis is form error (μm) and horizontal axis is lens dimension (mm).

3.2 Ni tool insert

Electroforming itself is established “atom-by-atom”, which can create a nearly perfect copy of the master geometry at virtually all scales [23]. Ni inserts fabricated by the electroforming process are highly dependent on the precision of masters. As shown in Figure 10 (a), the profile of the Ni tool is copied very well from its Si master. It is also seen that the etching depth of the Si wafer after the DRIE process is not uniform and the high aspect ratio trenches have lower depths, which are transferred to the Ni tool by the electroforming process. This phenomenon is the so called “aspect ratio dependent etching” of the Bosch process, where the silicon etching rate decreases as the depth or aspect ratio increases. This is attributed to ion flux loss at the bottom of the etched structure, depletion of reactive neutral species due to neutral shadowing and Knudsen transport [24]. Figure 10 (b) shows an electroplated Ni tool with hexagonal pillars and periodic ridge patterns, where the nominal pillar diameters are 80, 60, 40 and 20 μm with nominal height 50 μm (corresponding aspect ratios 0.625, 0.833, 1.25 and 2.5). The corresponding pillar heights are 47.1, 45.9, 44.5 and 40.4 μm , respectively, with the maximum relative dimensional error 19%, which is because of aspect ratio dependent etching of the Si master. Except for Si, photoresists such as PMMA and SU8 were also used as masters for electroforming. However, thermal expansion and water absorption of photoresist in the electroplating bath affected the precision of the counterpart Ni. For example, for an aspect ratio of 10, the relative error can be as much as 28% from water absorption for PMMA photoresist in the X-ray LIGA process [25]. SU8 photoresist in the UV-LIGA process typically has 14%~17% relative dimensional error in electroforming, depending on plating time, because of swelling at high temperature and the effects of the acidic electrolyte [26]. Such swelling behavior of SU8 is associated with soft baking and SU8 can absorb water and saturate in several tens of seconds, depending on the initial thickness [27]. Ultrasonic treatment for less than 15min can, however, increase SU-8 surface hydrophilicity and reduce SU8 swelling, leading to improved dimensional accuracy of electroplated counterparts [28].

Figure 10. Ni insert with hexagonal pillars and ridge periodic patterns with aspect ratios 0.625, 0.833, 1.25 and 2.5.

Figure 11 shows trenches that were milled on an Al master using micromilling and the corresponding protruded features on the Ni tool. The remaining tool tracks on the Al master were clearly copied to Ni, which will influence the surface finish of the corresponding polymer part. The protruding features were cross-sectioned to study the influence of current on microstructure and mechanical properties. Voids were found and became more severe when feature width increased (Figure 12). Void size decreased when current density reduced from $\sim 1.2 \text{ A/dm}^2$ to $\sim 0.4 \text{ A/dm}^2$, as indicated by the feature with the minimum width of $200 \mu\text{m}$ (Figure 12). Void formation can be explained by the “edge effect”. Regarding direct current electroplating, a high current is concentrated on the edge, leading to relatively fast growth of the electroformed layer; at the same time, the limited diffusion of ions to the bottom of high aspect ratio features results in faster growth of layers at the top corner than at the bottom and side [29]. Such phenomena become more significant under high current density conditions for the relatively wider features (Figure 12, top). Although a lower current density eliminates or reduces the size of voids, electroforming time increases significantly. Pulse reverse current electroplating has been successfully used to eliminate voids in high aspect ratio (~ 4.5) submicron features by dissolving the deposited metal material according to the anodic reaction [30-32].

The effect of current on the microstructure of a feature is shown in Figure 13. The columnar grains extend perpendicularly from the edge to the core of features. For protruding features, the columnar crystals grow from three adjacent edges and finally meet at the feature’s entrance, because of the “edge” effect (Figure 13 (a) and (c)). The columnar grain size becomes thinner when current density decreases from $\sim 1.2 \text{ A/dm}^2$ to 0.6 A/dm^2 , as indicated by both the feature and supporting layer. The hardness of Ni shim formed at a lower current is $257 \pm 10 \text{ HV5}$, which is much higher compared to that formed at a high current ($160 \pm 7 \text{ HV5}$). This observation is consistent with reports on the effect of current on microstructure and hardness [30, 33, 34]. Overall, the Ni insert is composed of features and a bottom supporting layer. Using lower current densities to electroform the features and high current densities to form the supporting layer can prevent voids from forming and increase manufacturing efficiency, where required mechanical properties can also be tuned.

Figure 11. Al master machined by micromilling (a) and Ni counterpart by electroforming (b) and the detail view of milling tracks from Al master and Ni tool.

Figure 12. Cross-section of Ni rectangular pillar features under various current densities: $\sim 1.2 \text{ A/dm}^2$ (top), $\sim 0.6 \text{ A/dm}^2$ (middle) and $\sim 0.4 \text{ A/dm}^2$ (bottom); the size of void increases with the increase of current density and feature width, because of the “edge” effect.

Figure 13. Microstructures of Ni tool from figure 12, where electroplating direction is from bottom to top: $\sim 0.6 \text{ A/dm}^2$ (a, c and e) and $\sim 1.2 \text{ A/dm}^2$ (b, d and f): (a), (b), (c) and (d) are features; (e) and (f) are supporting layer.

3.3 BMG insert

Direct machining can provide a controlled method for fabrication of BMGs with high dimensional accuracy. However, conventional machining of certain BMGs is difficult, due to the brittleness of many alloys, and great care must be exercised to avoid workpiece damage. For example, BMGs experience high strain rates and high temperatures in conventional machining, such as lathe turning, which will create risks of crystallization and oxidation [35]. Micromilling and micro-EDM were also used in attempts to machine BMGs [36]. Significant burrs can form even when spindle speeds are higher than 22,000 RPM. Although micro-EDM avoids burr formation, the roughness of overlapping surface craters can be a practical limit to the minimum surface roughness. Laser machining of BMGs has the same risk of losing amorphous structures, because of heat effects during ablation [37]. The surface morphology, such as ring structure with multilevel structure, after laser ablation depends on the incident beam energy, and the surface finish is rather poor [38]. Micro-scale and nano-scale machining

of BMGs using the techniques of focused ion beam (FIB) milling and thermoplastic forming are promising technologies for multi-scale patterning, which have been successfully demonstrated for various BMG compositions [18, 39-41]. Here, we demonstrated some efforts of machining of multi-scale features from 10^0 to 10^{-7} m using FIB milling and thermoplastic forming.

Figure 14 shows the patterned UCD crest in positive and negative forms, where features on the scale of 10^{-2} to 10^{-7} m were machined using FIB milling. The smallest feature can reach 85nm and was well replicated by the microinjection molding process using HDPE. Such patterns present aspect ratio dependent replication and lower aspect ratio regions have better filling than high aspect ratio regions, which is related to polymer flow resistant and local heat transfer [22].

Figure 14. Microstructured BMG insert (left) and replicated patterns on HDPE (middle and right): (a) positive pattern and (b) negative pattern.

Here we demonstrate a multi-scale mold fabricated by using FIB milling and FIB deposition, which provides an efficient method to fabricate nano-scale testing channels for DNA operations. For example, sieve-type separation with a regular pillar array has been proposed as a substitute for polymer gels in electrophoresis for separation of DNA molecules by length [42]. In addition, research on isolation and manipulation of single biomolecules used nanochannel based nanofluidic devices [43]. Currently, these aforementioned chips with micro/nano structures are fabricated mainly using Electron beam lithography, FIB milling, nanoimprinting lithography etc, or by utilizing various nanomaterials, as discussed in a recent review by Duan et al. [44]. These fabrication methods used either silicon or silicon nitride (SiN) as chip material or nanoimprinting lithography for the formation of nanochannels on an imprinting resist using a Si master, which is associated with low manufacturing efficiency and high material cost. From a production perspective, using a BMG tool insert integrates multi-scale features and represents a promising technology to bridge the gap between current state-of-the-art prototyping and production technologies for polymer nanofluidic devices.

Based on the separation principle using electrophoresis proposed by Baba et al. [42], a demonstration chip was designed, as shown in Figure 15. The mixed sizes of DNA molecules are injected into the top two square chambers (Figure 15 (a)). Once the voltage is applied to DNA, the charged DNA molecules move to the other end chamber. During this process, the proposed micro pillar array (Figure 15 (a) middle) will separate the DNA according to size: the narrow gaps are constructed of nano-obstacle arrays, which are separated from each other

by wide gaps. Molecules smaller than the narrow gap will enter the narrow gaps due to Brownian motion while moving smoothly through the wide gaps. Once a molecule enters a narrow gap, the velocity of its motion is significantly suppressed by collisions with the nano-obstacles. On the other hand, molecules larger than the narrow gap cannot enter the narrow gaps, but they can move smoothly through the wide gaps. Consequently, the large molecules tend to move much faster than the small ones. The larger DNA strands could be separated for the next step and pass through the nanochannels. FIB milling was used to machine the 10 μm wide channels and micro pillar arrays based on a bitmap design (Figure 15 (b)). We used two ways to fabricate the inverted nanochannel patterns (Figure 15 (a) right): FIB deposition technology and FIB milling. Firstly, the nanochannel region was reduced to the bottom of the 10 μm channel and arrays of platinum patterns were then deposited using FIB deposition (Figure 15 (b) right). Otherwise, the adjacent region was firstly reduced to the designed height of the inverted nanochannels using FIB milling, and further milling was used to subtract relatively large areas of material and leave inverted nanochannel features (Figure 15 (b) right). Microinjection molding replicated the micro pillar arrays and defined the nanochannels very well (Figure 15 (c)). Based on current tests on inverted nanochannel arrays, they could preserve their shape even after more than 1000 molding cycles. Although FIB milling is a material subtractive method, a proper design could mean that FIB milling of BMGs is a useful method for fabricating positive nanostructured tools for proof of concept and production of polymer biomedical devices, such as nanofluidics, micro/nano wells for cell or bacterial culture etc.

Figure 15. A demonstration nanofluidic design using FIB milling BMG insert (left) and feature replication using microinjection moulding: (a) bitmap design of chip and micro arrays; the nanochannel is formed by either two-step FIB milling or FIB deposition; (b) BMG insert with detail view of micro arrays and nanochannels; (c) replicated patterns on high density Polyethylene.

Apart from the FIB milling of features smaller than 10 microns on BMG, thermoplastic forming has been widely used as a key micro/nano fabrication technology for BMGs. However, there are several challenges associated with thermoplastic forming (TPF). Viscosity of the BMG at any temperature controls how easily plastic flow of BMG occurs, and it can be understood using the Hagen–Poiseuille-equation,

$$P = 16\eta v \frac{L}{d^2} + 4 \frac{\gamma}{d} \quad (1)$$

where γ is the surface tension of the alloy melt and P is the pressure required to fill a liquid of viscosity η with velocity v into a channel of width d and depth L . The equation has been modified to take into account the capillary effect at small length scales that decides the filling of the supercooled metallic melt into the small feature size. In the SCLR, the viscosity of the BMG is known to decrease with an increase in temperature. Therefore, a higher temperature would make the flow process easier. However, one has to consider the time-temperature-transformation (TTT) diagram of the alloy to determine how much processing time is available at any temperature before crystallization takes place. Therefore, the kinetics of crystallization indirectly guides the selection of an operational temperature for the TPF process. In addition to time and temperature constraints, there is also a limitation on the strain rate that can be used. A higher strain rate leads to non-Newtonian flow (inhomogeneous flow), which is undesirable in thermoplastic forming [41, 45-47].

For the alloy composition under this study, the TTT diagram and the viscosity measured in SCLR are shown in Figure 16. Micro channels of varying widths were selected to study the limits of the BMG composition to embossing the smallest feature sizes. Figure 17 (a) shows SEM image of micro channels with varying width from 300µm to 1µm and the same depth of 100µm patterned on a Si wafer. Figure 17 (b) shows the SEM image of BMG embossing with the Si master. Figures 17 (c) and (d) show these images at higher magnification from the same BMG. It can be seen clearly that the channels are successfully replicated on BMG until the spacing is smaller than ~10µm. It is worthwhile noting that surface oxidation of about 1~2µm thick occurred on ridge features when thermoforming BMG. Additionally, patterns near the ends were not fully filled as much as near the middle, due to increased flow resistance by the geometry constriction. The profile was not as fully rectangular near the edges as on the counterpart Si master, which is because of insufficient filling and increased flow resistance. The depth of filling was found to be 100µm when the spacing was 100µm wide. However, when spacing was reduced to 50µm, the BMG did not fully fill into the Si master and showed a rounded flow front, because of flow resistant from sidewall, as shown in Figure 18. Therefore, process selection and optimization should consider not only the size of

a feature itself, but also the feature density and spacing. For example, by using the operational parameters of $P=50\text{MPa}$, $T=472\text{ }^{\circ}\text{C}$, $t=120\text{s}$, $d=10\mu\text{m}$ and $\eta=3000\text{ MPa}\cdot\text{s}$, one can estimate the length of filling using equation (1) and it was found to be $\sim 5.5\mu\text{m}$. Figure 17 (g) also shows successful hot embossing of a $10\times 10\times 10\mu\text{m}$ micro well from Si wafer (Figure 17 (h)). The scallops due to the DRIE process were also clearly replicated in BMG.

Figure 16. T-T-T curve showing transformation from glassy state to crystalline state in BMG (a) and viscosity measured using DMA at 1 Hz and heating rate of 0.2 K/min (b).

Figure 17. Thermoplastic forming of BMG using Si master: (a) Si master with varying spacing from 100µm to 1µm, (b) embossed BMG counterpart, (c) and (d) enlarged view of features on BMG, (e) oxidation on end of rectangular ridge patterns of BMG, (f) rounding at top edge of rectangular ridge patterns, (g) 10×10×10µm micro well on Si master and corresponding pillar replicated on BMG (h).

Figure 18. Comparison of profile of BMG patterns and corresponding Si master.

3.4 Tool performance evaluation

The production of polymer micro devices, such as microfluidics, places quite strict requirements on tool materials. A prospective material must have mechanical properties (high mechanical strength, stiffness and fracture toughness) and wear and corrosion resistance characteristics that are as good as conventional mold tool steels [40]. Meanwhile, it must be amenable to various manufacturing methods for machining multi-scale features as per product requirements. For microfluidics applications, a reasonable surface finish is also required for optical detection, such as integrated micro lens for flow cytometry, and detection using UV detectors and optical microscopy. Additionally, possible contamination from tools may also be toxic for living cells. Of course, manufacturing quantities, lead-time and cost are also essential considerations. Selection of tool materials and manufacturing methods should be based on the actual application. In this section, we discuss the surface finish, hardness and tool life of stainless steel, Ni, and BMG for use as production tool materials. Particular emphasis is given to Ni and BMG, since they have competing capabilities for fabrication of multi-scale features. The performance of various complementary tools for prototyping and the production of polymer micro devices is also summarized.

3.4.1 Surface finish

The surface of stainless steel tools machined by die sinking EDM shows overlapped spark craters, as shown in Figures 6 (b) and (d). Although the crater diameters look similar, the average surface roughness sparked by a graphite electrode is $\sim 1.2\mu\text{m}$ on the bottom tool and $\sim 0.52\mu\text{m}$ on the circular protruded pattern (c.f. Figure 5 (a)), while the copper electrode gives better surface roughness at the bottom tool $\sim 0.53\mu\text{m}$ and at the top of the pattern $\sim 0.27\mu\text{m}$. This is related to crater depth. The corresponding surface roughness replicated on the COC mixer chip is $\sim 1.89\mu\text{m}$ at the part surface, which is of the same magnitude as that of the stainless steel tool.

The comparison of the average surface roughness between the master and tool is shown in Figure 19. For the electroforming process, the surface roughness of the Ni insert relies on the Si/Al master. The raw Si wafer is polished by a chemical mechanical polishing process with an average roughness of 3nm (standard deviation 0.4nm). The etched surface by the DRIE process induces surface unevenness because of chemical etching of the Bosch process with an average surface roughness of 11.5nm (standard deviation of 0.9nm), although process optimization may reduce surface roughness. The Ni insert achieved good reproduction of the master surface with the roughness of the corresponding polished Si surface being 3.8nm (standard deviation 0.7nm) and the etched Si surface being 24.5nm (standard deviation 9.4nm). When thermoplastically forming BMG using a Si master, the surface roughness increased significantly with a high standard deviation, where the BMG surface replicated from the polished Si was 111nm (standard deviation 56.3nm) and from the etched Si surface was 115.8nm (standard deviation 40nm). This was mainly because of surface oxidation during the thermoforming process and the oxidation layer was more easily broken (Figure 17 (e) & (f)). In addition, uneven compression from the embossing process and KOH etching are possible reasons for this high standard deviation. However, such process related issues can be optimized and a good surface finish close to that of the master may possibly be obtained.

Figure 19. Comparison of tool average surface roughness and their corresponding master.

3.4.2 Hardness

Hardness is the property of a material that enables it to resist plastic deformation, usually by penetration. Figure 20 compares the hardness of the tool materials in the present work. The unhardened Stavax stainless steel tool used had a hardness of 223.2HV with standard deviation 5.9HV. After hardening, it can reach 649HV depending on the austenitising temperature and holding time. The mechanical properties of the electroplated Ni tool is sensitive to electroforming conditions, such as bath chemistry, current density, agitation and additives [34]. For example, in the present work, electroplating at the lower current density of $\sim 0.6\text{A/dm}^2$ produced smaller grains with a hardness of 257.4 HV (standard deviation 10.36HV). A Ni tool electroformed at the higher current density of $\sim 1.2\text{A/dm}^2$ increases the size of columnar grains (Figure 13), with a corresponding hardness of 166.2HV (standard deviation 7.85HV). It was also reported by Torre et al. [48] that nano-crystalline Ni had a strength of up to 1100MPa under room temperature, although it can reduce from $\sim 800\text{MPa}$ to $\sim 400\text{MPa}$ when the temperature increases from 210°C to 265°C , which spans a broad range of processing temperatures for most plastics. The BMG that was used in this work had a hardness of 509HV with standard deviation 6.44HV. In addition, we also used directly milled brass for prototyping tools for polymer microfluidics. However, the hardness of brass is 125HV (standard deviation 7.85HV), which is much lower than stainless steel or BMG. From the perspective of hardness, Ni and BMG are comparable to stainless steel and are promising tool materials for mass production of polymeric micro devices.

Figure 20. Comparison of tool hardness.

3.4.3 Tool life

The tool inserts were examined using SEM in order to evaluate any surface wear and feature integrity arising from the number of injection molding cycles. Here we only focused on Ni and BMG tools, since they offer similar length scales ranging from millimeters to nanometers. Figures 21 (a) and (b) compared FIB-milled features smaller than 10 micron on BMG before and after ~20,000 molding cycles. The ridge features were worn away after ~20,000 cycles. It appears that the integrity of the large feature exceeded that of the small features, because of size-dependent mechanical properties. Compared to the original insert, a number of new surface scratches were found on the tool surface and they became much deeper. Apart from scratches caused by occasional breakage of polymer parts and tool handling, wear is the main reason for feature failure. In our previous work [22], wear of a tool surface was explained by thermal fatigue when subjected to repeated or cyclic loading and temperature. The mold materials will experience temperature fluctuations ranging from high (melt temperature) to relatively low (mold temperature) during the molding cycle. Meanwhile, the features will endure high shear stress up to ~0.8MPa [49]. Although the polymer melt temperature is below the glass transition temperature of our BMG, repeated thermal cycling can induce annealing effects on BMG, which could result in embrittlement. This, in turn, might reduce the wear resistance of the BMG insert [50].

Some pitting defects were observed on the BMG surface after ~300 molding cycles along with some scratches. Such pitting defects did not proliferate across the tool surface but only accumulated in certain areas. After ~5000 cycles, the pitting became dense and the size became larger. Similar pitting defects were also found on the Ni insert. Figure 22 shows an inverted channel with negative holes in it. After ~130 molding cycles, the micro hole features had become quite distinct. However, some Ni fragments peeled off from the bulk inverted channels and different size pitting defects had appeared.

It is known that pits initiate at some chemical or physical heterogeneity of the surface, such as inclusions, second phase particles, solute-segregated grain boundaries, flaws and mechanical damage or dislocations [51]. Pitting is influenced by many environmental and material parameters, such as electrochemical potential, alloy composition, electrolyte concentration, and temperature [52]. To the authors' knowledge, most corrosion research has been carried out in aqueous environments and there is little in the published literature on the pitting behavior of tool inserts with polymer melts in the injection molding process. Regarding BMGs, it was reported that zirconium has the highest pitting susceptibility and Zr-based alloys are not favorable materials for achieving high corrosion resistance [53]. Except for alloy composition, heterogeneities, such as small crystallites formed from cooling of the melt and local segregation from thermal fluctuations [54], can work as pit initiation sites. During our experimental molding processing, acetone was used to remove plastic residue from micro cavities caused by demolding failure, which may have resulted in possible pits. In addition, mechanical grinding can also cause some surface scratches, which could be potential pitting initiation sites. Since polymer melt temperature in the injection molding process can reach ~280°C, it reduces the breakage potential of passive films and a mold tool insert has to endure significant shear stresses. Mechanical stresses at weak sites and flaws result in electrostriction, and surface tension effects cause local breakdown events. Such phenomena were observed directly from the Ni insert, when injection molding COC, where the mold temperature was close to the glass transition temperature of COC. Some peeled off Ni fragments were observed sticking to plastic surfaces (Figures 22 (c) and (d)). But such behavior is mainly limited to the first 10-20 molding cycles and gradually reduces, because of possible rapid healing and repair. From Figure 22 (b), in addition to small pits, large fragments were broken from the Ni surface, which was directly related to surface tension, especially when high temperature and high pressure were applied in the molding process. Regarding the electroformed Ni tool, corrosion resistance was influenced by microstructure (grain size, surface morphology) and related electroforming parameters, such as current

density, pH, plating bath composition, agitation and additives [55]. For micro/nano molding, although Ni inserts have been used for ~10,000 cycles in the CD and DVD industries, the associated pits and lands are small with low aspect ratio and coatings, such as diamond like carbon, are coated on to Ni molds when producing CDs and DVDs [56]. Additional coatings, such as TiN, have been shown to be effective in protecting tools for ~20000 cycles without significant wear [57].

Figure 21. Performance of BMG tool insert: sub-10 micron features before (a) and after 20000 moulding cycles (b); pitting on surface of BMG tool after ~300 moulding cycles (c) and ~5000 moulding cycles (d).

Figure 22. Ni insert has good surface conditions before moulding (a) and shows surface significant surface fracture and pitting defects after ~130 moulding cycles when high temperature and high pressure were applied in the molding process (b); such Ni fragments stick to plastic surface features (such as Polypropylene) (c) and are visible under an optical microscope when enlarged (white regions in (d)).

3.4.4 Challenges and opportunities

Stainless steel, Ni and BMG are all good candidates as tool materials for mass production of polymer micro devices. Because of grain size limitations, stainless steel cannot be patterned to the submicron scale and the smallest size of patterns are limited to tens of microns. Surface finish also restricts applications of stainless steel for optical elements and microfluidic devices requiring high transparency. In addition, machine tool dimensions and wear issues pose constraints on manufacturing high density small spacing features using stainless steels. This is a limitation for some microfluidic operations, such the capture, separation and mixing of biological cells, where micro patterned arrays are required to have dimensions similar in size to the biological scale. However, stainless steel does have reasonable mechanical properties and the associated manufacturing technologies are versatile, well-developed and accessible.

Electroformed Ni, based on Si, SU8, and PMMA masters etc. fabricated using semiconductor fabrication technologies, is the most commonly used tool for prototyping and the production of polymer microfluidics [58]. Electroforming has almost no size limitation because of its intrinsic atom-to-atom deposition. Although pitting defects were found in the present work, the use of coatings has been proven to extend tool life [57]. However, Ni is a relatively soft material compared to hardened stainless steel and BMG, which limits the number of moulding cycles for which it can be used as a single tool. Additionally, the toxicity of Ni may contaminate polymer devices by sticking to chip surfaces for the first 10-20 cycles, as discussed in Section 3.4.3. Care must be taken to ensure chips are not contaminated because of Ni pitting and fracture during the molding process, which may make chips unsuitable for biological applications, particularly those involving living cells. Improving the performance of a Ni tool relates to many factors including composition, agitation, surface treatment and coatings. Void formation limits the achievement of high aspect ratio features and new techniques still need to be developed. Although many studies have used Ni inserts for prototyping microfluidics, none of them have yet evaluated tool performance with respect to micro scale features. Understanding the interaction between molten polymer and a tool, and optimising tool performance (e.g. nanocrystalline Ni) are necessary for successful commercialization of this technology.

As a new engineering material, BMGs combine the benefits of steel and Ni tools. BMG can integrate length scales from $10^0 \sim 10^{-8}$ meters, because of its amorphous nature. Zr-based metallic glasses have strengths that are as high as hardened stainless steel without any surface coatings and they can preserve this strength over the processing temperature of most plastics. It is prone to much less wear and pitting defects compared to Ni tools. It offers non-toxic

elements and can be deformed into high aspect ratio cavities without any voids. However, this does not mean that BMGs are the perfect replacement for stainless steel and Ni. Because rapid cooling is a characteristic of creating BMGs, casting of large area BMGs is still challenging. It is also difficult to find one BMG composition that offers good mechanical properties, a large thermoplastic forming window for embossing millimetre to nanometer sized features, low cost and toxicity, and a lack of porosity, etc. Pattern replication via thermoplastic forming is constrained by relatively small processing windows with possible problems including surface oxidation, risk of crystallization, non-uniform filling around large areas, and aspect ratio related filling. Tailoring an alloy composition and optimisation of casting/thermoplastic processes for tool applications are critical. Cost may also be problematic for BMG microstructured tools, because of the expense of elemental metals and the investment required for expensive casting equipment, when compared to a Ni insert. For various compositions, BMGs need to be fully characterized to identify an appropriate process window. However, any cost/performance evaluation needs to be averaged to a single part, since a low-cost, short-lived tool may have a similar per-part cost as a more expensive and more durable tool [58]. Tool wear must also to be considered in order to produce suitably qualified parts.

4. Conclusion

This work focused on the manufacturing of tool inserts and the evaluation of tool performance for producing polymeric microfluidics. Stainless steel microfluidic inserts were demonstrated using micromilling and die-sinking EDM. Graphite electrodes exhibit good machinability and provide more accurate feature definition than copper electrodes. However, although die-sinking EDM is good for batch production, electrode wear is significant for machining stainless steel and the precision with which features are defined is low.

Ni tools were electroformed using a micromilled aluminium master and a Si master. These tools exhibited excellent feature and surface roughness replication, although aspect ratio dependent etching from the DRIE process affects the precision of a Si master. In addition, the Ni deposition rate around an edge was much faster, resulting in void defects, which became smaller when the feature size reduced. Reducing the current density minimized edge effects for the same aspect ratio, leading to smaller columnar grains and high hardness. Pitting defects and surface cracking occurred on Ni tools after ~130 cycles, due to surface weakness and high adhesion forces during demolding. However, Ni is a relatively soft material compared to stainless steel. Exploring nanocrystalline Ni and functional coating are potential ways to improve Ni tool performance.

BMG tools with multi-scale patterns ranging in size from tens of microns to tens of nanometres were manufactured for a UCD crest pattern and a demonstrator nanofluidic pattern using Focused Ion Beam milling. Meanwhile, features sized from tens of microns to one hundred microns were fabricated using thermoplastic forming BMG in its supercooled liquid region. Ridges ($100 \times 100 \mu\text{m}$), with reduced spacing varying from $100 \mu\text{m}$ to $10 \mu\text{m}$, were successfully achieved. Surface oxidation was found to influence tool finish. Although some pitting defects and scratches occurred on the BMG tool during the moulding process, it still exhibited good wear resistance and preserved features smaller than $10 \mu\text{m}$ for ~20,000 molding cycles. Proper design to combine FIB milling and thermoplastic forming is potentially useful to integrate multi-scale features on a single tool insert.

Although stainless steel has versatile and well-developed manufacturing technologies and good mechanical properties, its application in microfluidics is limited by the achievable feature size. Ni and BMG have the capability of integrating length scales ranging from $10^0 \sim 10^{-8}$ meters. However, Ni applications are limited by its achievable aspect ratio, toxicity, and relatively lower mechanical properties. Although appropriate design could allow the integration of micro/nano scale features using FIB milling and thermoplastic forming, it is still difficult to have a BMG composition which can satisfy all tool requirements, such as low cost, large area, free of pores, good thermoplastic ability over the micro to nanoscale. Consequently, the selection of appropriate tool materials and manufacturing processes needs

to be made with regard to actual applications.

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Tool material	Tool manufacturing method	Minimum feasible feature (Theretical minimum feature) [μm]	Achieved maximum AR (Theretical maximum AR)	Draft angle (geometry) [$^\circ$]	Surface finish [μm]	Tool life regarding molding cycles	Mechanical properties and tool failure (strength, durability, brittleness)	Manufacturing time	Notes	Reference
SU8	UV lithogrpahy	25 (5)	3.6 (20)	1-6 (2.5D)	1~6	8-100	Si substrate breakage and SU8 delamination	~30minutes	500nm(e-beam lithography)	[7, 59]
Si	UV lithography +DRIE	25 (5)	4 (20)	1-10(2.5D)	0.01	NA	Si is brittle and easy to break during demolding	4.5 hours (design, UV-LIGA, DRIE)		[60], this work
Epoxy (10% Al powder)	Casting with SU8, Si, SU8 mold	0.5	1.06 (20)	1-10 (2.5D)	0.27	~200	Relatively low wear risistance	<5 days		[61]
Hybrid tool (Polymer with metal protection coating)	Laser, embossing	8	10	NA	<0.1	20~50	Low wear reisistace, chemical reation with molding plastics, fast delimiation of metal coatings	~2 days	Polyimide, PEEK, PSU	[11]
Stainless steel (Protuding patterns)	Micromilling	25 (20)	4(7.5)	0-90 (3D)	0.15-0.2	>50,000 It may depend on feature size	Tool steel, good wear resistance, high strength, hardness>500HV,	~5 days	burr, tool wear	[62, 63], this work
	MicroEDM milling	20	30	0-90 (3D)	~0.2			~5 days,	Tool wear	[64]
	Die-EDM sinking	100 (20)	1 (20)	0-90 (3D)	0.6-1.2			~5 days,	Tool wear compensation	[64], this work
	Laser machining	20	4(10)	0-90(3D)	0.2-0.3			Relatively slow process		[11]
Ni	Si master	5	2.25 (20)	1-10(2.5D)	0.024	NA	Possible voids defects limits eletroplating efficiency and aspect ratio; SU8 adhesion to Ni, removal problems	1~2 weeks		[29, 65]
	Micromachined Master	20	4	(3D)	0.2~1.2			1~2 weeks		This work
	SU8 Master	30	5.8	2(2.5D)	1-6			~5 days		[66]
BMG	MicroEDM, micromilling	NA	NA	0-90 (3D)	0.7~1.4	NA	Risk of crystallization from heat affacted zone	NA		[36]
	Laser machining	NA	NA	0-90 (3D)	0.26~0.90	NA	Risk of crystallization from heat affacted zone	NA		[67]
	FIB	~50~100nm	2	NA		~20,000		Several hours for submicron patterns in 50×50 μm areas		This work and our previous work [22]

	Thermoplastic forming using Si master	45	~1	1-10(2.5D)	0.12	NA	Surface oxidation and risk of crystallization	~ 5 days (embossing, Si etching, post finish)		[12] and this work
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Table 1. Summary of performance of tools for prototyping and production of polymer micro devices using microinjection moulding

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