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Polymer Micro Hot Embossing with Bulk Metallic Glass Mold Insert

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Abstract. Polymer microstructures are used more and more in many fields. Hot embossing is one of molding processing to achieve micro polymer components. In this paper, bulk metallic glass was selected as mold material to fabricate mold insert of micro hot embossing. Traditional UV-lithography and ICP-etching were used to achieve micro features on silicon wafer. And then, micro features were transferred from silicon wafer to bulk metallic glass mold insert above its glass transition temperature. Finally, applied bulk metallic glass mold insert to replicate polymer microstructure with hot embossing. Three commonly used thermoplastic polymers: high-density polyethylene (HDPE), polypropylene (PP) and polycarbonate (PC) were selected in this study. Experiments show that microstructures can have a good replication from bulk metallic glass mold insert to the thermoplastic polymer using hot embossing.

Introduction

Molding of micro components from thermoplastic polymers has become a routinely used industrial production process. Polymers are cheap and are available in different modifications with a wide range of properties. Therefore, microstructures with a large bandwidth of properties can be replicated, suitable for the application they for which they are needed. Polymeric microstructures show more and more important and used in many fields such as MEMS, microfluidic, biochip, etc [1,2]. Hot embossing [1,3] is one of micro molding process mainly for replication of surface structures on thermoplastic substrates.

Bulk metallic glasses (BMGs) are a new emerging field of materials with many desirable and unique properties, such as high strength, good hardness, good wear resistance, and high corrosion resistance that can be produced in near net shape components [4]. Tremendous research effort has been dedicated in the last two decades to developing BMGs with larger critical casting sizes, however it is still difficult to obtain BMG which is larger than 80mm. The prospect of BMGs being used as engineering materials is still not fully clear [5]. Ironically, the present results imply that metallic glass exhibits a new feature, that is, “smaller is safer.” Therefore, BMGs can be potential candidates as materials in smallscale applications [6,7].

In theory every microstructured surface can be used as a mold insert [1]. Mold insert of polymer micro hot embossing usually made of metal, brass and steel, Ni or PDMS. Two kind of methods are generally used in fabricating micro mold insert, one is direct structuring methods, like mechanical machining, electric discharge machining (EDM) or laser structuring; and the other is the field of lithographic methods, like E-beam lithography, UV-lithography, and for structures with high aspect ratio, X-ray lithography. All lithographic processes require the step of electroforming to obtain a metal mold insert. Each structuring method has different characteristics and is therefore suited for different kinds of applications. Direct structuring processes are well suited for large microstructured areas. However, the surface of quality does not achieve the quality of lithographic processes. Independent of the lithographic process, the post-process step of electroforming is required to obtain a mold insert of metal. However, electroforming for microstructure has some disadvantages, such as non-uniformity, time-consuming, etc.

As an alternative to traditional metal processing techniques, thermoplastic forming (TPF)-based microfabrication methods have been developed which can process some BMGs like plastics [8]. Therefore, it's easy to replicate microstructures from silicon mold to BMGs with TPF not need use other additional process. The purpose of the present study is to fabricate mold insert of polymer micro hot embossing by thermoplastic forming of metallic glasses.

Bulk metallic glasses

The unique crystallization behavior of BMGs enables to process these high strength metals in a similar manner than plastics. BMGs are also characterized by a large supercooled liquid region, defined as the temperature interval between the glass transition, Tg, and crystallization, Tx, temperatures, that is, $\Delta Tx = Tx - Tg$. The supercooled liquid region is a manifestation of the extraordinary metastability against crystallization of BMG alloys and thermoplastic forming of BMG takes place in this temperature region. Some authors also call thermoplastic forming as "superplastic forming" [11-12].

Pd-based BMGs were firstly found having large supercooled liquid region and good glass-forming ability. $Pd_{40}Cu_{30}Ni_{10}P_{20}$ amorphous alloy exhibits an obvious glass transition phenomenon at 577 K (Tg) and a supercooled liquid state over a wide temperature range of 96 K [9]. The viscosity of the BMG is very low in this temperature regime and, therefore, it is very easy for the BMG to be conveniently fabricated into complex shapes. In fact, TPF of BMGs in this temperature interval has been achieved [10-13]. It has been frequently pointed out that the TPF of BMGs is very similar to the processing of plastics [15]. Since TPF is an established commercial practice, this should prove extremely beneficial and economical in the processing of BMGs. The only point that needs to be kept in mind during TPF of BMGs is that the time available for processing of the BMGs is limited, since they tend to crystallize. The time for crystallization is short at high temperatures and is reasonably long at lower temperatures. Of course, the actual values are different for different types of BMG alloys. In the case of TPF operations, the time for processing has to be shorter than the time required for crystallization.

As a mold material, selected BMG should have two characteristic: firstly, BMG must have a good formability of TPF; secondly the Tg of BMG is higher than the polymer processing temperature. In fact, many BMGs can meet the two requirements such as Pd-based and Zr-based BMGs etc.[16] In this study $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG was selected as mold material.

Experimental procedures

The alloy ingots were prepared by arc melting a mixture of pure elements with purity above 99.9% or better in a titanium-gettered argon atmosphere. To achieve compositional homogeneity, the master alloys were remelted at least six times, followed by casting into a copper mold to form piece shaped specimen with a size of 5mm×80mm×1mm.

The specimens for TPF with a size of 5mm×10mm×1mm were cut from the as-cast samples. The thermal properties of the alloy were measured using differential scanning calorimetry (Perkin-Elmer DSC 7) with a heating rate 10 K/min in an argon atmosphere.

A backward forging process was carried out on an Instron-3384 universal materials testing machine to replicate micro features from silicon mold (stamp) to the BMG surface. Heating temperature above Tg of BMG, forge the silicon mold on BMG specimen with specific pressure. The load limit of the testing machine was 150 kN. The accuracy of loading was controlled to be within ±0.1 kN. Fig. 1 shows the schematic illustration of the experimental set-up used for the thermoplastic forming of BMG alloys.

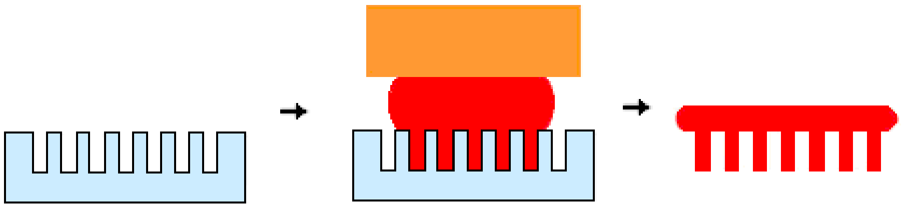


Fig. 1 Illustration of thermoplastic forming micromolding process

For every replication process a mold or master is necessary to copy the structures of the mold into a molding material. For example, silicon mold is master for forming BMGs and BMG with microstructure is master for polymer hot embossing. Because of the different structuring methods of classical mechanical mold fabrication in the macroscopic range and the structuring methods of microstructures, the mold has to be split into the tool and the mold insert with a microstructured surface. The parts using BMG alloys have complex shapes, and the sizes of these parts are much smaller than what have been achieved using conventional crystalline alloys. And then, BMG with microstructured surface will be mold insert of polymer hot embossing.

The procedures of hot embossing polymer microstructure just like below four steps. Firstly, heating of the semifinished product to molding temperature; secondly, isothermal molding by embossing; then, cooling of the molded part to demolding temperature, with the force being maintained; demolding of the component by opening the tool at last.

Results and discussion

Fig. 2 presents the DSC thermogram obtained from the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG specimen made by suction casting method. The glass transition temperature (Tg) and crystallization temperature (Tx) of this alloy were determined to be 570 and 660 K, respectively.

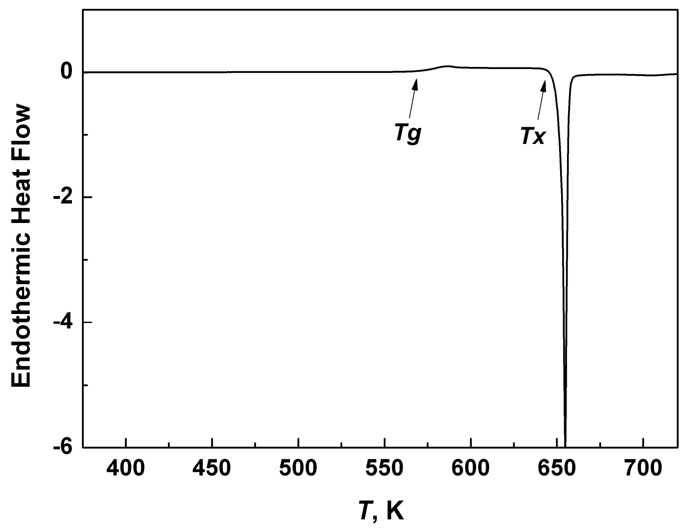
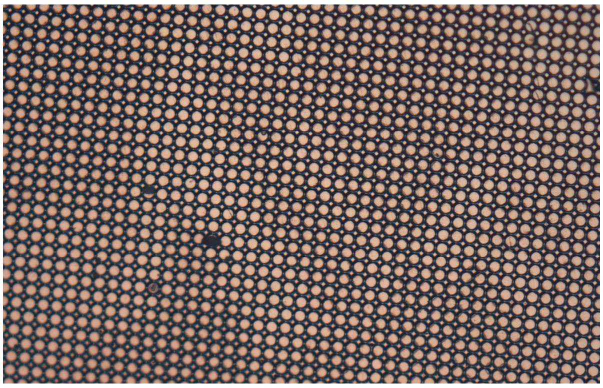


Fig. 2 DSC curve of the as-cast $Pd_{40}Cu_{30}Ni_{10}P_{20}$ bulk metallic glass.

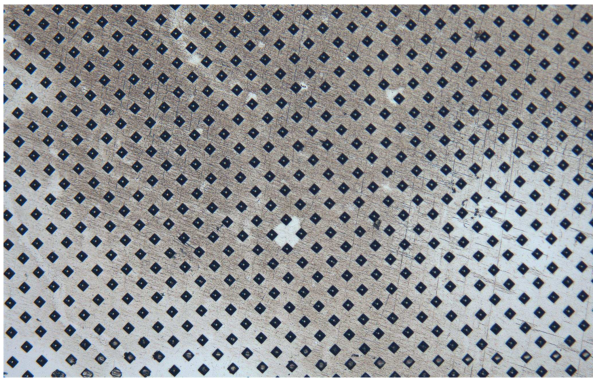
Superplastic deformation of BMG should ideally occur near or above Tg, to significantly decrease the material's flow stress, yet below Tx, to avoid crystallization. Accordingly, five test temperatures, 603, 613, 623, 633, 643 K, were thus chosen for superplastic deformation of the alloy.

Traditional UV-lithography and ICP-etching were used to achieve micro pattern on silicon wafer. Then perform the silicon mold to hot emboss $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG specimen above setting temperature, micro features were replicated from silicon mold to BMG mold insert.

Micro mold insert was successful fabricated with $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG using TPF. Fig.3 (a) presents the molded sunken cylinders array on an area of 10×5 mm^2 of BMG on which the micro cylinder diameter is 20μm and the pitch is 5μm. Fig. 3 (b) presents the molded raised cubes array on an area of 10×5 mm^2 of BMG on which the micro cube size is 20μm×20μm and the pitch is 25μm.



(a) Sunken micro cylinders array



(b) Raised micro cubes array

Fig. 3 Replicate microstructures on $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG

The amorphous structure of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG mold insert with embossed micro pattern was identified by X-ray diffraction (XRD) using Ultima IV powder X-ray diffraction machine. Fig.4 represents only broad diffraction maximum characteristics of amorphous structure is seen in the alloy, indicating that the alloy is composed of single amorphous phase after thermoplastic forming.

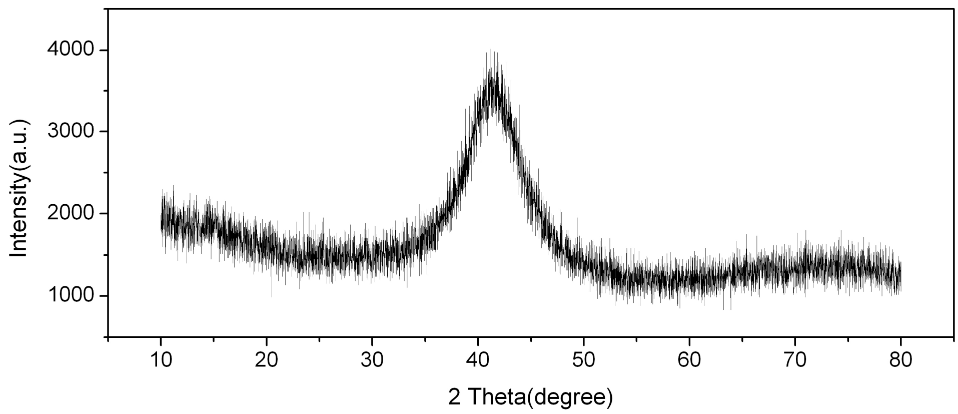


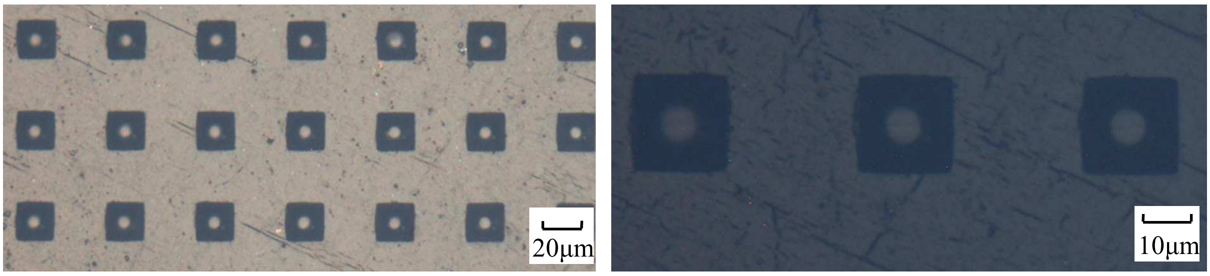
Fig. 4 XRD patterns of cast $Pd_{40}Cu_{30}Ni_{10}P_{20}$ showing broad diffraction maximum characteristics of amorphous structure

And then, the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG with microstructures was assembled to the polymer micro hot embossing tool as a mold insert. Three commonly used polymers were selected in this study: HDPE (SABIC HDPE M30054), PP (Samsung TOTAL BJ730) and PC (Bayer Makrolon 2805) respectively and processing parameters are listed in Tab.1.

Table1. Processing parameters of polymer micro hot embossing

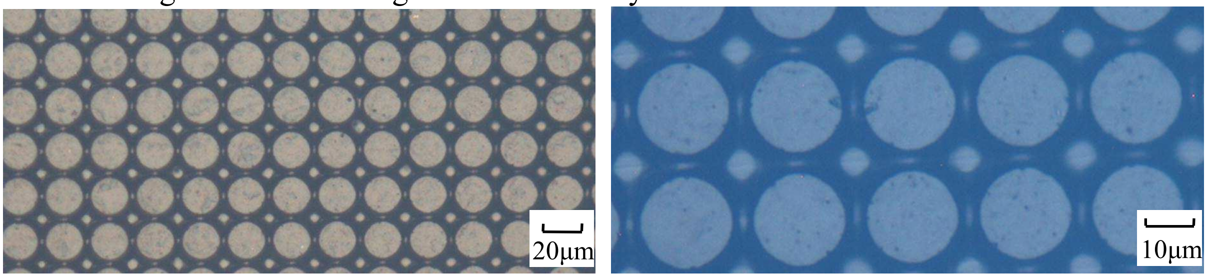
Polymers	Pressure[MPa]	Temperature[K]
HDPE	4.0	403.0
PP	4.0	443.0
PC	5.0	453.0

Olympus BX51-P polarizing microscope was used to observe the embossed polymer micro structures. Fig. 5 presents the micro cubes array on HDPE with BMG mold insert on which the micro cube size is 20μm×20μm and the pitch is 25μm. Fig. 6 to Fig. 8 present the micro cylinders array on HDPE, PP and PC respectively with BMG mold insert on which cylinder diameter is 20μm and pitch is 5μm.



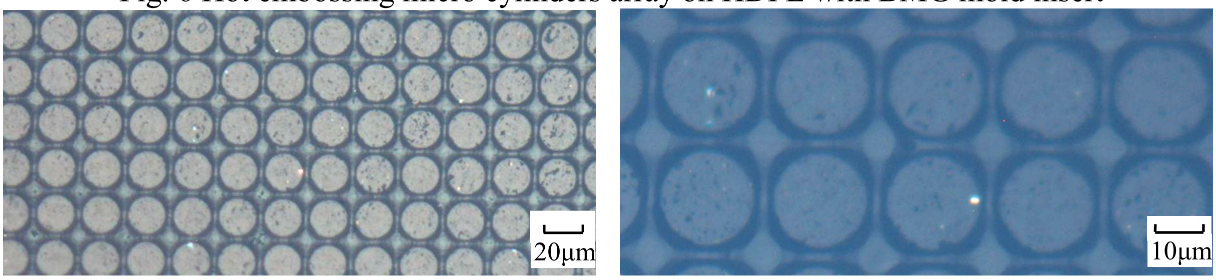
(a) Magnification 200 times (b) Magnification 500 times

Fig. 5 Hot embossing micro cubes array on HDPE with BMG mold insert



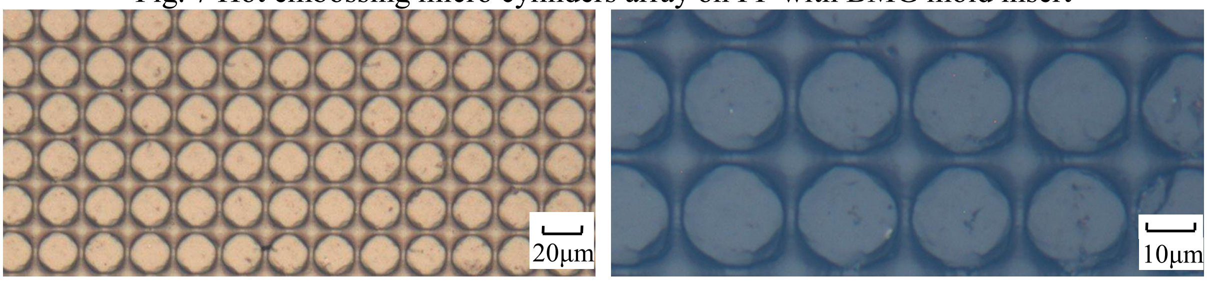
(a) Magnification 200 times (b) Magnification 500 times

Fig. 6 Hot embossing micro cylinders array on HDPE with BMG mold insert



(a) Magnification 200 times (b) Magnification 500 times

Fig. 7 Hot embossing micro cylinders array on PP with BMG mold insert



(a) Magnification 200 times (b) Magnification 500 times

Fig. 8 Hot embossing micro cylinders array on PC with BMG mold insert

From Fig. 5 to Fig. 8, we can find all three kinds of polymers can achieve micro pattern with $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG mold inserts. According to different embossing temperature, the viscosity of each polymer is different, micro cavity filling show different condition, PC melt filling is not good as HDPE and PP. Increasing embossing temperature is an approach to improve replication quality of micro pattern on polymer. Improving embossing pressure also can achieve the same results but lead to a difficulty when demolding. In the future, investigating how to optimize hot embossing process parameters and the size effects on replication of micro structures are the next research contents.

Summary

Bulk metallic glasses are a new emerging field of materials with many desirable and unique properties, such as high strength, good hardness, good wear resistance, and high corrosion resistance that can be produced in near net shape components. These amorphous materials have many diverse applications from structural applications to microcomponents. Use BMG as mold insert of hot embossing tool to replicate microstructure on polymer surface is a potential application. In this investigation, micro pattern was transferred from silicon mold to $Pd_{40}Cu_{30}Ni_{10}P_{20}$ BMG, and then we replicate microstructure form BMG to polymer substrates such as PP, HDPE and PC. As an example, use a BMG mold insert with micro cylinders array which diameter is 20μm and pitch is 5μm to hot emboss polymer substrates, and the experimental results present BMGs are potential and promising material to fabricate micro mold for polymer micro even nano-scale molding instead of conventional crystalline alloys.

Acknowledgements

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