An Investigation of the precision hot embossing process for micro-nano structured surfaces on chalcogenide glass

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To fabricate high precision chalcogenide glass (ChG) nanostructure array, hot embossing process (HEP) experiments are carried out to analyze the element diffusion mechanism between ChG and the mold. Micro-nano structured surface is fabricated on the ChG by HEP. First, the ChG embossing experiment is carried out with nickel phosphorus (Ni-P) plating mold. The diffusion of atoms between the ChG and Ni-P plating in high temperature and high-pressure is analyzed. Optical glass used as the intermediate mold for ChG embossing is also put forward. Second, fly cutting is used for ultra-precision machining the mold with large area structural color, and structural color surface on optical glass is then fabricated by HEP. Finally, micro-nano structure array is embossed on ChG by optical glass mold, the structural color characteristic of workpiece is evaluated.

1. Introduction

Infrared materials are receiving increasing attention in advanced optical systems such as thermal imaging, night visions, and laser-based sensing [1,2]. Infrared chalcogenide glass (ChG) is gradually replacing crystalline infrared materials such as single-crystal germanium (Ge) and zinc selenide (ZnSe) due to their wide infrared transmission band and excellent athermalization properties [3-5]. ChG micro-nano structure array is an arrangement of micro-nano scale lenses or prisms distributed in a certain regular pattern on the surface, which can realize a variety of optical functions due to its special geometrical characteristics. ChG micro-nano structures become an important component in modern infrared optical systems. Many manufacturing techniques, including single-point diamond cutting, photolithography, laser processing, and hot embossing process (HEP), have been intensively investigated [6-8]. Among them, HEP is an ideal method to achieve precise and efficient mass production of large-area micro-nano structure array on the surface of ChG [9-12].

Nickel-phosphorus (Ni-P) is a commonly used mold material in the HEP process of silicate glass due to its high-temperature inoxidizability, thermal corrosion resistance and excellent machinability for diamond cutting [13,14]. However, the Ni atoms of Ni-P will react with the ChG at high temperatures, leading to adhesion between the ChG and the mold [15]. While applying a protective coating onto the mold surface can prevent atomic diffusion during the HEP process, it should be noted that the thickness of coating typically ranges from tens to hundreds of nanometers [10,16]. This thickness can have an impact on the accuracy of the formed structures, especially when the period of micro-nano structures is in the range of hundreds of nanometers.

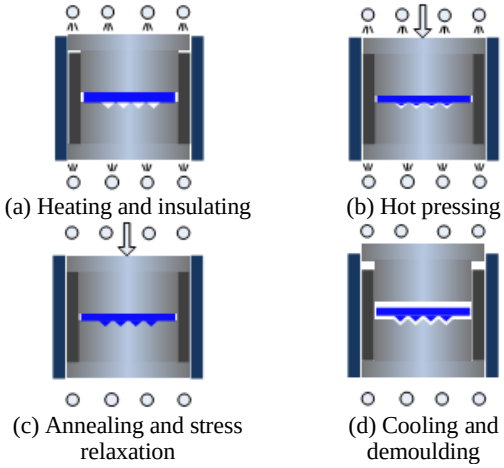
In this study, a novel method is presented for sustainable fabrication of micro-nano structure arrays on ChG using two-step HEP with a silicate glass mold. First, the atoms diffusion between ChG and mold is analyzed. Secondly, to overcome the reaction between Ni-P mold and ChG, a glass to glass HEP strategy is proposed to fabricate the ChG micro-nano structure array. The axial-feed fly cutting (AFC) technology is conducted for machining large-area micro-nano structure array Ni-P mold. Silicate glass mold replicates the surface structures on the Ni-P mold by HEP. Finally, micro-nano structure array is embossed on ChG by using the silicate glass mold. This proposed HEP strategy is non-destructive and low-cost, and can realize the multi-scale and flexible fabrication for the mold.

2. Mechanism of element diffusion at chalcogenide glass-mold interface

According to the thermal cycle, the ChG hot embossing process for micro-nano structure array is divided into 4 stages: i.e. heating, pressing, annealing and cooling. First, the glass preform is placed into the mold assembly and heated by the heating devices on the surface of the upper and lower molds. After a period of time, the glass preform is heated to the glass softening temperature. Second, the upper mold is

driven down to compress the glass preform, so that the profile of mold surface is duplicated onto the glass surface. Third, the formed glass piece is annealed under lower pressing force at a decreasing temperature. Finally, the pressing load is released, and the formed glass piece is released from the molds after cooling to the room temperature.

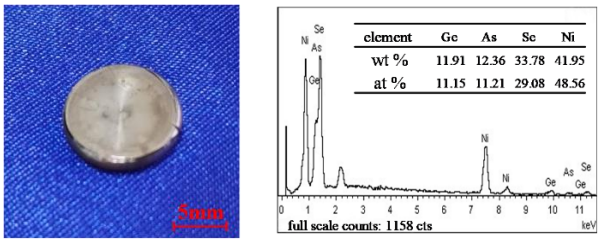
The ChG Ge22Se58As20 preform (NHG Co., Ltd., China) of height 2.8 mm and diameter Φ7.8 mm is designed for the cylindrical compression experiments. Ni-P material is chosen as the mold material in this experiment, which has high hardness, outstanding corrosion resistance and abrasive resistance applied as a usual mold material in the HEP [17,18]. By the ultrasonic-assisted electroless plating method, Ni-P plating is deposited on the surface of heat-resistant stainless steel (06Cr25Ni20). Then, a smooth surface is generated on the Ni-P mold with single point diamond cutting. The cylindrical embossing condition is performed at a embossing temperature of 392°C under a embossing force of 1362 N. Fig. 2(a) shows the embossed ChG by Ni-P mold.



(a) Heating and insulating (b) Hot pressing

(c) Annealing and stress relaxation (d) Cooling and demoulding

Fig. 1 Hot embossing process for micro-nano structure array



(a) Photograph of ChG (b) EDS of the ChG surface

Fig. 2 The ChG embossed by Ni-P mold

The EDS (Hitachi S4800, Japan) results of ChG are shown in Fig. 2(b), and it can be found that the surface of the ChG contains much nickel Ni element. There are three kinds of chemical bonds in the electroless plated Ni-P, including Ni-Ni, Ni-P and P-P. Considering that the percentage of Ni-Ni in the plating is about 90%, the Ni-Ni chemical bond dissociation energy is considered as the average bond dissociation energy of Ni-P plating. The Ni-Ni chemical bond dissociation energy is low, and the Ni element is easily reacted with the selenium Se element and arsenic As element. Therefore, the Ni elements diffuse to the surface of ChG under high temperature, affecting the surface quality and optical properties of ChG optical components.

It is proposed to use Ni-P plating mold to carry out optical silicate glass embossing, and then use silicate glass as intermediate mold to process ChG micro-nano structure array. Fig. 3 shows the embossing process of ChG micro-nano structure array using optical silicate glass as the intermediate mold.

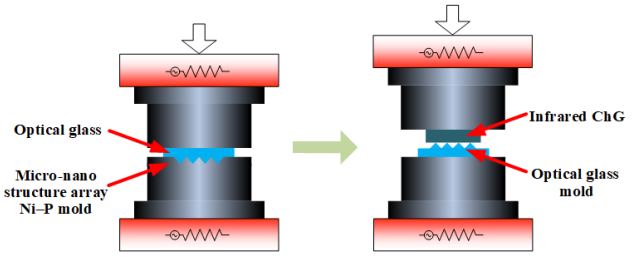


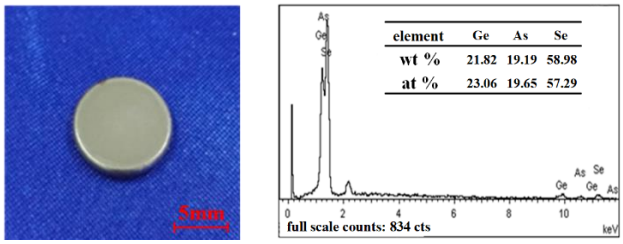
Fig. 3 The schematic of ChG micro-nano structure HEP using optical silicate glass mold

The silicate glass used as the intermediate mold material in this study is D-ZK2N (CDGM Co., Ltd, China), and its thermos-mechanical properties are shown in Table 1. The strain point temperature StP of the D-ZK2N optical glass is 448°C. The ChG used in the test is ChG Ge22Se58As20 with the Ts of 347°C. Obviously, the StP of D-ZK2N is much higher than the embossing temperature of ChG. Meanwhile, compared with Ni-P material, D-ZK2N optical silicate glass has nearly equal hardness and thermal expansion coefficient, as shown in Table 1. Hence, the optical silicate glass is an appropriate mold material used for the fabrication of intermediate mold with the method of HEP.

TABLE I. Thermo-mechanical properties of the Ni-P material, the silicate glass and ChG

Item	Ni-P	Silicate glass	ChG
Knoop hardness (20°C, kgf/mm2)	542	581	152
Elastic modulus (GPa)	150.1	83.6	18.2
Shear modulus (GPa)	5.3	33.4	6.8
Linear expansion coefficient (10^{-6}/ºC)	11.29	7.2 (20~120ºC) 9.2 (100~300ºC)	16.5 (20~120ºC) 17.0 (100~300ºC)
Strain point temperature (°C)		448	252
Annealing point temperature (°C)		485	277
Transition temperature (°C)		495	292
Softening point temperature (°C)		548	347

The formed ChG by silicate glass mold is shown in Fig. 4, and no nickel element is observed on the surface, which ensures the stability of the optical properties of ChG. In addition, because the optical silicate glass can be repeatedly embossed, the manufacturing cost of the mold can be greatly reduced. Besides, the service life of the initial machined Ni-P mold also could be extended to realize the low-cost mass manufacture of the molds used for infrared ChG embossing.

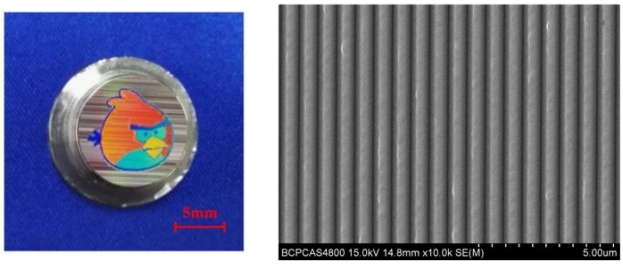


(a) Photograph of ChG (b) EDS of the ChG surface

Fig. 4 The ChG embossed by silicate glass mold

3. Experiments of the hot embossing process for micro-nano structure array

Firstly, micro-nano structured surface is fabricated on Ni-P mold. Fly cutting technology has the advantages of simple operation, high efficiency, and high processing quality for micro-nano structure mold manufacturing. To efficiently produce the micro-nano structured surface on Ni-P mold, the feeding of the workpiece in the spindle-axis direction during fly-cutting is introduced on ultra-precision machine Nanoform X (produced by Precitech Corporation, USA). The period of micro-nano structures are hundreds of nanometers, in which scale the incident light is diffracted to display a specific structural color [19]. The period can be precisely controlled by the feed rate, and the wavelength of the diffracted light is related to the feature size of the groove structure unit. Therefore, the arrangement and combination of grooves of the same size can form pixel and then form a pattern with structural color. The processed micro-nano structured surface on Ni-P mold is shown in the Fig. 5(a). Iridescence is observed on the groove surface under natural light with the incident light from a mobile flashlight. A cartoon image of Angry Bird is displayed under the white light with an incident angle of zero. The structural color images have high color saturation. Fig. 5(b) is the scanning electron microscope (SEM, Hitachi S4800, Japan) photograph of submicron-scale micro-nano groove structure fabricated on the surface of the Ni-P mold. The grooves exhibit good consistency and high surface quality. The micro-nano grooves are all high-regularly arranged and have high parallelism. No defects of serious burrs or cracks are observed, which provides a basis for ensuring the machining accuracy of HEP.

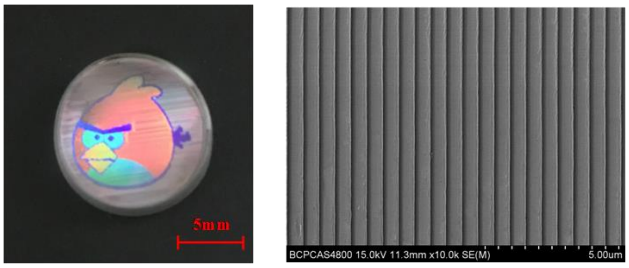


(a) Photograph of Ni-P mold (b) SEM photograph of periodic micro-nano grooves

Fig. 5 The fabricated micro-nano structure array on Ni-P mold

The embossing experiments are carried out to fabricate the silicate glass intermediate mold on an ultraprecision glass molding machine (designed and assembled by Beijing Institute of Technology, China). The embossing temperature is kept at 580ºC with the pressing force at 1362N. The embossed silicate glass component is depicted in Fig. 6(a).

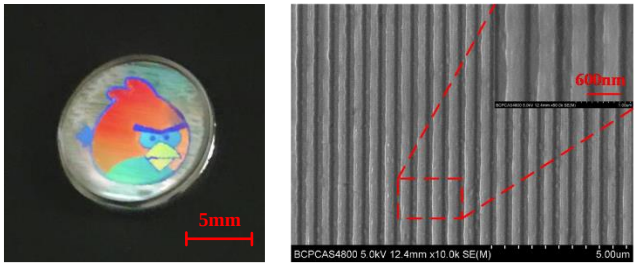
A distinct pattern of micro-nano structure array is replicated on the formed mold surface. The structural color pattern is consistent with that of the machined mold, indicating that the scale of micro-nano structure array on the silicate glass is the same as that of the machined Ni-P mold. The SEM photograph in Fig. 6(b) shows the periodic micro-nano grooves on the embossed glass. There are no obvious forming defects, and the embossed periodic grooves maintain good regularity and uniformity. The silicate glass with micro-nano structure array mold can be used as an intermediate mold for the embossing of ChG with micro-nano structure array.



(a) Photograph of the formed mold (b) SEM photograph of periodic micro-nano grooves

Fig. 6 The formed optical silicate glass micro-nano structure array mold

Based on the above experiments, an optical silicate glass micro-nano structured mold is obtained for ChG embossing process. ChG preform with a height of 2.5 mm and a diameter of 12.5 mm is subjected to compression. The embossing temperature is kept at 390ºC with embossing time of 200 s and a pressing force of 1362 N. At this embossing temperature, D-ZK2N glass mold has high hardness and will not soften, which can ensure the forming quality of infrared ChG. Fig. 7(a) shows the formed ChG piece. It is demonstrated that the micro-nano structure array shown structural color is replicated on the ChG surface. The micro-nano structure pattern is therefore successfully transferred from the mold to the ChG via twice HEP. The structural color of the pattern is completely consistent with the formed mold and the machined mold, indicating that the micro-nano groove array on the ChG surface is consistent with the mold surface. The SEM photograph of the micro-nano structure array on the ChG surface is shown in Fig. 7(b). The ChG micro-nano structured array is uniform overall, and there are no surface defects as observed from the SEM image.

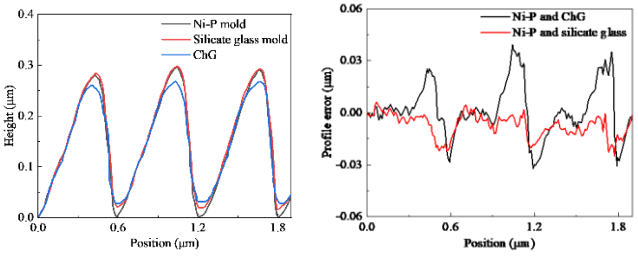


(a) Photograph of the ChG piece (b) SEM photograph of periodic micro-nano grooves

Fig. 7 The embossed ChG micro-nano structure array

The profiles of the embossed micro-nano structured array are measured by atomic force microscopy. The contour curves of the

micro-nano groove on ChG surface and the molds surfaces are shown in Fig. 8(a). Compared to the forming error of the optical glass mold, partially incomplete filling occurs at the top and bottom of the ChG micro-nano structured array, but the overall micro-nano structured array has good consistency. From Fig. 8(b), the largest forming error occurs at the top and bottom of the micro-nano structured array, and the largest forming height error is 39.2 nm. It can be seen that the overall forming quality is good. Hence, ChG micro-nano structured array could be efficiently and precisely manufactured by HEP using the silicate glass as the intermediate mold.



(a) Micro-nano structures on the molds and the ChG

(b) Profile error of mold and glass

Fig. 8 The profile curves of micro-nano structures.

4. Conclusions

In this paper, a novel HEP strategy is proposed to fabricate the ChG micro-nano structured array, which could be also applied for micro-fabrication of other amorphous materials. The surface of micro-nano structures has been manufactured by our strategy. Firstly, the diffusion mechanism on the interface between ChG and Ni-P mold is analyzed through cylindrical compression test. The silicate glass is proved to be an appropriate mold material for ChG embossing process and can used as the intermediate mold to suppress the atomics diffusion and the chemical reaction between the ChG and Ni-P mold. The axial-feed fly cutting technology is used for machining large-area micro-nano structure array Ni–P mold, and the micro-nano structured array is formed on ChG by using the optical silicate glass as intermediate mold with twice HEP. The obtained micro-nano structures on the surface of ChG has good consistency and forming quality. These results could shed light on promoting functional surface structures to broad applications in optical and optoelectronic industry.

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