Precision Molding of Microstructures on Chalcogenide Glass for Infrared Optics

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Contents

1 Introduction ................................................................................... 2
  1.1 The Application of Chalcogenide Glass in Infrared Optics .................. 2
  1.2 Methods to Fabricate Microstructures on Chalcogenide Glass .............. 4
  1.3 Precision Molding Technique ................................................... 5
2 Modeling and Simulation of Chalcogenide Glass Microstructure Molding ............... 7
  2.1 Modeling of Viscoelastic Constitutive of Chalcogenide Glass ................. 8
  2.2 Simulation of Microstructure Molding Process ................................ 9
3 Molding Process of Microstructures on ChG ........................................ 13
  3.1 Chalcogenide Glass Molding Machine ....................................... 13
  3.2 Chalcogenide Glass Molding Condition and Quality Control .............. 15
4 Summary ...................................................................................... 24
References ...................................................................................... 25

Abstract

Chalcogenide glass (ChG), as an alternative material in place of single-crystal germanium, is increasingly used in thermal imaging, night vision, and infrared guidance systems, etc., and microstructure array on the infrared component is widely used in micro-optical systems owing to their excellent formability through precision glass molding (PGM), which can achieve low cost and high efficiency compared with other microstructural manufacturing technologies. To describe the thermomechanical properties of ChG, the viscoelastic constitutive of ChG is modeled and used in finite element simulation to study the influence of process parameters on the forming stress. The processing parameters are studied...
to reduce the occurrence of microdimples and optimize the molding conditions. Finally, microstructure arrays are molded using spherical ChG preform and the optimal molding materials are identified.

**Keywords**

Chalcogenide glass · Microstructure array · Precision glass molding · Finite element simulation · Microdimples

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**1 Introduction**

Infrared materials are gaining growing attention for their wide applications, such as thermal imaging and night vision (Tang et al. 2010; Bureau et al. 2004). In the past decades, single-crystal germanium has been used exclusively in infrared optical systems though it is rare and expensive (Zhang et al. 2003a). Chalcogenide glass (ChG), which is a kind of artificial material made of mainly chalcogens (S, Se, and Te) and some other elements, shows a wide transmission wave band from near to far infrared wavelength. In comparison, oxide glasses are limited to near and intermediate infrared wave band because of the strong infrared absorption of metal-oxygen bond vibrations. Compared with single-crystal germanium, ChG is much more economic and has more excellent properties of athermalization and achromatism (Yu 2007), and it is deemed as an alternative for single-crystal germanium in various infrared systems (Cha et al. 2010). Microstructure as well as microstructure array on the optical component is widely used in micro-optical systems due to its excellent optical properties and robust thermomechanical performance. The surface microstructures of the infrared optical elements can improve the infrared thermal imaging quality and eliminate the aberration, and the microstructure array is widely used to simplify and improve the optical system, achieving special requirements. ChG lenses, including spherical lens, aspherical lens, and free-form curved surface, are mainly fabricated by single-point diamond turning. Due to the limitations of the current processing technology and materials, the research of microstructures for infrared optical components is still in the initial stage.

ChG is not only an excellent infrared material but also has similar properties as optical glass, especially the high-temperature viscoelasticity and deformation characteristics. Therefore, precision glass molding (PGM) is able to form microstructures on ChG glass. It is of great significance to promote the development of processing microstructures on ChG infrared components through precision molding.

**1.1 The Application of Chalcogenide Glass in Infrared Optics**

Infrared transmittance of infrared glass is above 50%, and it can block visible light. According to the basic composition of infrared glass, it can be divided into oxide glass and ChG. Ordinary oxide glass cannot transmit the infrared radiation when the wavelength is greater than 7 μm, due to the strong infrared absorption of metal-
oxygen bond vibrations. ChG extends the infrared transmission band from near to far infrared wavelength and has a preferable infrared transmittance. In addition, ChG has low-temperature coefficient and dispersion coefficient and unique photosensitive properties. ChG has been widely used in the infrared optical fiber sensors, infrared imaging lens, energy transmission, nonlinear optics, optical information processing, frequency multiplier, inorganic optical lithography, and other modern integrated optical systems and electronic device fields (Xue et al. 2003; Gai et al. 2010; Luo et al. 2010). ChG is considered to be the core material of the new generation of infrared optical systems.

1.1.1 Thermal Imaging System
Infrared thermal imaging technology is a sophisticated technology integrating optics, mechanics, electronics, and other advanced technologies (Eisenberg et al. 2000). Figure 1 shows the infrared thermal imaging system. The infrared detector and infrared lens are used to accept the infrared radiation energy distribution of measured target, which reflects in the photosensitive element of infrared detector to obtain infrared thermography. Generally speaking, the infrared thermal imaging system transforms the invisible infrared radiation of the object into the visible thermal image. The different colors of the thermal image represent the different temperatures corresponding with the heat distribution of the measured object.

Infrared detector is a very important component of infrared thermal imaging system. The detection capability of infrared detector can be improved by coupling ChG microlens array with infrared detector. Then, the incident beam of infrared radiation can be effectively converged on the photosensitive surface, which has a gathering energy effect and can improve the utilization rate of light energy. At the same time, ChG microlens array has the cold shield effect. The incident angle of infrared radiation is limited to ensure that each photosensitive element of the infrared detector has the same incident angle. In addition, each photosensitive element has the same background radiation that is greatly reduced, and the noise is dropped.
1.1.2 Night Vision System

The infrared night vision apparatus consists of an infrared optical imaging system and a photoelectric conversion system. It can be divided into two types: active and passive. The former one uses infrared searchlight to irradiate the target and receives the reflected infrared radiation to form image. The latter one, which is also known as thermal imager, does not emit infrared radiation. This means that the thermal image is formed based on infrared radiation of the target itself (Lu et al. 2013).

As shown in Fig. 2, the general structure of the night vision system mainly includes four parts. The photoelectric conversion device converts the infrared radiation into the image visible to human eyes, and then the image is showed on the display screen after denoising, reshaping, and amplifying. Infrared lens is an important part of night vision system, which is responsible for transmitting infrared radiation of the target. At present, the material of infrared lens is generally germanium, silicon, and zinc selenide. These materials have a large temperature coefficient of refractive index. When the temperature changes, the behaviors of thermal difference and performance degradation will occur. The increase of system volume caused by temperature change needs to be compensated. The night vision system designed with ChG and diffractive optical elements can realize the temperature adaptation control system and make the system image well even in a large temperature range.

1.1.3 Infrared Window

With the establishment of aerospace integration, infrared guidance and other infrared optical system are becoming more and more important in the modern society. Infrared window is the key component to ensure these systems work properly. Large diameter, high infrared transmittance, high optical uniformity, and good thermal mechanical properties are the common requirements of infrared windows for the next generation of infrared systems (Xie et al. 2012).

The lack of infrared windows with large size and high performance has become an important factor restricting the development of the photoelectric system, as well as one of the factors to decide the price of some important system in many cases (Zhang et al. 2011). ChG material has obvious advantages in large-size preparation and the molding process, which costs lower than the machining process. Therefore, it is an important material for the new generation of infrared window.

1.2 Methods to Fabricate Microstructures on Chalcogenide Glass

In order to meet the application requirements of microstructures on infrared optical components, various microstructure fabrication techniques have been developed.
For example, based on energy-assisted machining, the focused ion beam machining and laser processing can fabricate surface microstructures directly in optical components. However, these two methods are complex in processing, high in cost, and poor in microstructure uniformity (Naessens et al. 2003; Hisakuni and Tanaka 1995; Chiu and Lee 2011). The surface microstructures on infrared glass can also be processed by photolithography, but the shape and size of the microstructures are limited (Manevich et al. 2008). Using traditional machining techniques such as single-point diamond turning or CNC grinding and polishing, complex surface microstructures can be fabricated. The surface microstructures have ultrahigh shape accuracy. However, these methods still have many problems such as high cost and poor efficiency. They are not able to meet the needs of the market (Davies et al. 2002). Precision molding can solve the problems of the above processing technology, and it is the most promising technology to form surface microstructures on ChG (Fig. 3).

### 1.3 Precision Molding Technique

Compared with single-crystal germanium, ChG is an amorphous material without fixed melting point. The viscosity of ChG gradually decreases during heating until it is suitable for the precision molding to process surface microstructures (Zhang et al. 2003b). The precision molding has high processing efficiency and can achieve mass production to reduce the processing cost with a good forming accuracy of surface microstructures. Therefore, it has a broad prospect for development and application.
1.3.1 Fundamental of Chalcogenide Glass Molding Process

In a precision molding cycle, the molds and ChG are heated simultaneously. The ChG is heated above softening point and fully softened. Then the upper mold is moved down to compress the ChG preform, and the stress is relaxed by holding the pressing load without further deformation for a short time. After that, the ChG is annealed at a slow cooling rate. Finally, the formed ChG is cooled to ambient temperature rapidly and released from the molds, and the surface microstructures of the molds are replicated to the ChG surface. Hence, ChG molding process can be divided into four stages, heating, pressing, annealing, and cooling, as shown in Fig. 4.

Fig. 4 Four stages of a precision molding cycle: (a) heating, (b) pressing, (c) annealing, and (d) cooling

The surface microstructures with different shapes can be processed by changing the shape of the mold’s surface microstructures. A set of molds can be used to form large quantities of ChG, so the precision molding has great advantages in the mass production of surface microstructures on ChG. The precision molding process is simple and the production efficiency can be greatly improved. It has been corroborated that the molding process would not deteriorate the infrared transmittance of ChG (Liu et al. 2012). Therefore, this technology has received extensive attention from various research institutions and enterprises in the world.

1.3.2 Chalcogenide Glass Materials for Microstructure Molding

ChG can be divided into sulfide glass, selenide glass, and telluride glass according to the elemental composition. The As-S and Ge-S glass are the earliest studies of sulfide glasses. As-S glass has the advantages of good infrared transmittance, high refractive index, low sound speed, and high quality factor. However, there are also some shortcomings such as high intrinsic loss, low mechanical strength, and poor chemical stability. In order to improve the comprehensive properties of As-S glass, the preparation and properties of Ge-As-S glass have been studied. The results show that the density, hardness, softening temperature, and chemical stability of glass increase and the expansion coefficient decrease with the content increase of element Ge. The transmittance region of Ge-As-S glass is 0.6 μm ~ 11 μm (Zhang et al. 2003a, b).
Selenide glass is easier than sulfide glass to prepare due to the higher rate of chemical reaction between Se and other elements, as well as the lower pressure when Se melts. The Ge-As-Se and Ge-Sb-Se glass in selenide glasses are most suitable for infrared optical system. Ge-As-Se glass is of intrinsic optical stability and has a wide glass forming range. The Ge-As-Se glass has a great transmittance of long wave infrared, the transmittance range of which is 0.8 μm ~ 15 μm.

1.3.3 Mold Materials for Chalcogenide Glass Molding
The molds are the key items for forming high-precision optical components, the quality of which directly affects the quality of the final component. The differences of mold materials will lead to great differences in the internal stress distribution, the surface roughness, and the surface shape of the formed ChG. In order to obtain high-quality molded component, the selection of ChG mold material is of great importance. The molds are under the conditions of high temperature and high pressure during the forming process for a long time, so the material selection of the molds is mainly considered from the aspects of high-temperature stability, heat-shock resistance, stress release property, hardness and strength, mechanical performance, etc. In addition, in order to avoid deterioration of infrared optical properties, the mold material cannot react with oxygen or ChG. The thermal expansion coefficient of the mold material needs to be small to reduce the shape error of the formed glass, making the mold and glass easier to separate, avoiding the adhesion between the mold and the formed glass after annealing and cooling. The mold materials, including cemented carbide, cermet, and heat-resisting stainless steel with Ni-P plating, are available for molding.

1.3.4 Mold Coating
As a result of the adhesion between the mold and the formed glass, the shape error and surface roughness of the formed glass will increase, and the surface of the mold will be damaged leading to the decrease of the mold’s service life. In order to ensure the forming quality and extend the life of the mold, it is an efficient way to have a release film on the mold surface. The film material is closely related to the mold material and can prevent chemical reactions between the mold and the glass. For example, the surface of cemented carbide substrate can be plated with precious metal alloy, titanium nitride coating, hard carbon, diamond-like carbon, and other carbon coating.

2 Modeling and Simulation of Chalcogenide Glass Microstructure Molding
ChG is a typical amorphous material, and its material properties are affected by temperature. When the temperature increases gradually, the ChG is gradually softened from hard brittle state to viscoelastic state. It is important to learn the thermal deformations during glass molding process by figuring out the material properties and processing properties of ChG under high temperatures.
2.1 Modeling of Viscoelastic Constitutive of Chalcogenide Glass

Viscoelasticity is a time-dependent response of a material to stress or strain. At a constant load, the ChG strain is made up of instantaneous strain (elastic effect) and a continual strain as a function of time (viscous effect). This time-dependent deformation under a constant load is termed creep. On the other hand, when a constant strain is applied, the stress relaxes with the increase of time, which is termed stress relaxation. Creep and stress relaxation are the two main characteristics of deformation behavior during molding process.

Viscoelastic constitutive models are necessary to analyze the time-dependent creep behavior and stress relaxation of ChG at high temperatures. The simple Maxwell model, the Kelvin model, the Burgers model, and the generalized Maxwell model are four typical constitutive models (Pipkin 1972), which allow the rate of the inelastic strain change to be a function of the total stress and previous strain. These models can be expressed by a series of springs and dashpots. The simple Maxwell model can fit stress relaxation but is not suitable for modeling creep. The Kelvin model is unable to describe the time-dependent change of stress during creep. The Burgers model can simulate creep perfectly. It can be used to simulate stress relaxation too, but it was found that a deviation always happens at the beginning of the stress relaxation (Zhou et al. 2009). Therefore, among the four kinds of models, the generalized Maxwell model might be the best one to describe creep and stress relaxation in the viscoelastic deformation of glass at high temperatures (Zhou et al. 2011). The generalized Maxwell model is based on a single Maxwell model, formed by a spring and multiple Maxwell models in parallel as shown in Fig. 5.

According to the Boltzmann superposition principle, the time-dependent response of the generalized Maxwell model can be described by Eq. 1:

\[
\sigma(t) = \int_0^t G(t - \tau) \frac{d\varepsilon}{d\tau} d\tau
\]  

(1)

where the integral is evaluated for current time \( t \) based on past time \( \tau \). \( G(t-\tau) \) is not a constant value, which can be described by the Prony series:

\[
G(t) = G_0 \sum_{i=1}^{n} \omega_i e^{-\frac{t}{t_i}}
\]  

(2)

where \( G(t) \) is the relaxation modulus, \( G_0 \) is the elasticity modulus of the spring, \( \omega_i \) is the weight coefficient of single Maxwell model, and \( t_i \) is the relaxation time. The weight coefficients and the relaxation time can be described by the following two equations:
\[ n_i = \frac{\omega_i}{C_2 \eta_i} (3) \]

where \( \eta_i \) is the viscosity of each dashpot.

2.2 Simulation of Microstructure Molding Process

Finite element method (FEM) is a well-known and widely applied method, so its fundamentals need not be reviewed here. In order to give an example to demonstrate the simulation of microstructure molding, a commercial nonlinear FEM software ABAQUS/Explicit is used, and the ChG Ge\textsubscript{22}Se\textsubscript{58}As\textsubscript{20} is chosen to be preform material with its thermal and mechanical properties listed in Table 1. The program is capable of simulating large deformation of material flow under isothermal or non-isothermal conditions. It is able to analyze complex models such as mechanics and thermal field coupling problems. It can be used to visualize the glass molding process and monitor some difficult-to-measure variables including strain/stress distribution and internal temperature variation.

It will take a larger workload and need more computation time when three-dimensional model is used for the finite element simulation analysis, and the simulation process is prone to errors. It is much easier to simplify the microstructure molding into a two-dimensional simulation model as shown in Fig. 6.

The flat upper mold can be moved downward to press the softened ChG. The lower mold with microstructures is fixed. In order to avoid the stress convergence in the contact region and save remeshing time at the sharp corners during the molding simulation, the sharp corners of the microstructures are rounded with a small radius of 0.5 \( \mu \)m. As the ChG preform is pressed at a uniform temperature, as the same as the molds, the pressing stage can be treated as isothermal process without heat transfer.
In the molding process, the stress distribution of the ChG can reflect its forming feasibility. It can be shown where forming defects are easy to occur because of the stress concentration. The magnitude of the stress can be used to determine the magnitude of the residual stress, the annealing scheme, and the annealing time. Therefore, studying the stress distribution is helpful to plan the experiment scheme and get the optimized formed microstructure glass. Furthermore, molding temperature and other technological parameters seriously affect the forming stress distribution and magnitude of the ChG. Hence, it is essential to study the molding parameters’ affection and optimize the technological parameters.

In order to study the effect of the technological parameters on the internal stress distribution of ChG, two representative special points are selected in the simulation model of the ChG, as shown in Fig. 7. The point A is in the contact area between the ChG and the top of the mold microstructure. The point B is in the contact area of the ChG and the mold surface without microstructure.

### 2.2.1 Effect of Molding Temperature on Forming Stress of Microstructure

It is crucial to choosing the appropriate molding temperature to guarantee the forming quality of the ChG microstructure. If the molding temperature is too low, the ChG cannot be fully softened, and it cannot fill the cavities of microstructure on the mold. Then a greater pressure is needed to achieve better filling effects, and the residual stress of ChG will increase, which leads to a greater shrinkage in the annealing stage. If the molding temperature is too high, it may cause the interface

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $\rho$ (g/cm$^3$)</td>
<td>4.41</td>
</tr>
<tr>
<td>Young’s modulus $E$ (GPa)</td>
<td>18.2</td>
</tr>
<tr>
<td>Poisson’s ratio $\nu$</td>
<td>0.28</td>
</tr>
<tr>
<td>Transition temperature $T_g$ (°C)</td>
<td>282</td>
</tr>
<tr>
<td>Softening temperature $T_s$ (°C)</td>
<td>352</td>
</tr>
<tr>
<td>Thermal expansion coefficient($10^{-6}$/K)</td>
<td>17</td>
</tr>
</tbody>
</table>

**Table 1** Thermomechanical properties of ChG Ge22Se58As20

![Fig. 6 The two-dimensional simulation model of microstructure molding](image-url)
adhesion between the mold and the ChG (Monfared et al. 2017). In addition, high temperature leads the cooling temperature range to increase, and the ChG shrinks more serious during the cooling stage of molding process. All in all, excessive temperature results in difficulties in guaranteeing the shape and surface accuracy of the microstructure and even reduces the mold life. Previous research findings show that the ChG can better duplicate the surface morphology of the mold when the temperature is above the softening temperature (Monfared et al. 2017).

The effects of molding temperature are studied by FEM at 382 °C, 392 °C, 402 °C, and 412 °C, respectively. The pressing velocity is set to 0.001 mm/s, and the molding time is set to 20 s. The friction coefficient is specified to 0.1. Figure 8 shows the changes in the equivalent stresses of point A and point B at different temperatures from 382 °C to 412 °C. When the temperature of the ChG rises continuously, the internal stress of ChG decreases gradually. According to the simulation results, considering the longer service life of the mold and the shorter heating time, the molding temperature is chosen as 392 °C for the later demonstration.
2.2.2 Effect of Pressing Velocity on Forming Stress of Microstructure

In order to study the influence of the pressing velocity on the internal stress of ChG after precision molding, the pressing velocities are set to three levels, 0.001 mm/s, 0.005 mm/s, and 0.01 mm/s, respectively. Changing the length of the analysis step ensures that the displacement is 0.02 mm. The molding temperature is fixed at 392 °C and the coefficient of friction is set to 0.1. The simulation results of these three groups are shown in Fig. 9.

The stresses of point A and point B increase gradually with the increase of pressing velocity. The ChG preform is in a stable equilibrium state, and the internal molecular structure is relatively stable before the precision molding. After the pressure is applied, the ChG begins to flow passively and fill the cavities of the mold microstructures. The greater the pressing velocity is, the faster the strain rate of the ChG is. A shorter time is needed to fill the mold cavities, and the relaxation time is also shorter. The stress is released less, and the internal stress of ChG is greater. Therefore, under the premise of ensuring the production efficiency and filling quality, the lower pressing velocity is preferred. According to the simulation results, 0.001 mm/s is chosen as the pressing velocity in this later demonstration.

2.2.3 Effect of Friction Coefficient on Forming Stress of Microstructure

In the molding process, the friction force will significantly affect the forming stress of the microstructure and service performance of the molded components. According to the previous simulation results, the molding temperature is set as 392 °C, and the pressing velocity is set to 0.001 mm/s. The molding time is 20 s. In the simulation model, three groups of friction coefficient are set to 0.1, 0.3, and 0.5, respectively. The variation of the internal stresses of the ChG with the friction coefficient is shown in Fig. 10.
The internal stresses of ChG rise with the increase of friction coefficient, which means the residual stress rises with the increase of the friction force. After the friction coefficient is increased to 0.3, the stress increasing rate decreases. When the friction coefficient is larger, the flow deformation of ChG on the mold surface is poorer, and the filling in the microstructure cavities is hindered. The above forming defects will all affect the optical performance of the molded infrared optical components. Therefore, the friction coefficient between the mold and the ChG should be reduced as much as possible to reduce the internal stress in the forming process of the ChG, which sets demands for ultraprecision molds.

3 Molding Process of Microstructures on ChG

The ChG technological parameters of the molding process can be optimized base on the above FEM simulation results. In order to introduce the molding process of microstructure on ChG, precision glass molding experiment is carried out with an ultraprecision glass molding machine. Then the forming quality of the microstructures is analyzed by comparing the microstructures on the ChG and the mold.

3.1 Chalcogenide Glass Molding Machine

The ChG molding machine used in this experiment consists of two parts, the main equipment and the peripheral devices. It mainly includes multistation molding
machine, water cooler, air compressor, and nitrogen container. The multistation molding machine is the main equipment for precision molding experiment. It contains seven station controllers, temperature and pressure control system, cooling system, and automatic conveying devices, as shown in Fig. 11. The peripheral devices include a water cooler, an air compressor, and a liquid nitrogen container.

Multistation molding machine consists of seven stations. From right to left, there are three preheating stations heating the ChG preform and the molds to the molding temperature. Then, a molding station presses the ChG to copy the surfaces of the mold to the surfaces of the ChG. Next, two annealing stations are used to anneal the ChG and eliminate the residual stress. Finally, a cooling station cools the formed glass rapidly to room temperature. The microstructures on ChG can be processed through the seven stations. The water cooler provides cooling water circulation for the cooling of the mold, the ChG, and the machine body. The air compressor provides compressed air to drive the up and down motion of cylinders in these seven stations and motion of automatic conveying devices in the molding process. The liquid nitrogen container continuously delivers nitrogen to avoid the ChG, the mold, and the interior of the machine body being oxidized by air.
3.2 Chalcogenide Glass Molding Condition and Quality Control

### 3.2.1 Chalcogenide Glass Molding Condition and Optimization

The ChG molding conditions can be partly confirmed by the FEM simulation results. Before the microstructure molding experiments, the cylindrical molding tests can be conducted to explore the other microstructure molding conditions. The cylindrical molding experiments were conducted using molding temperatures at 382 °C and 392 °C under a pressing force of 1362 N. Many microdimples were observed on the ChG pillars, as shown in Fig. 12. The same observations were made using confocal laser scanning microscopy. The scratch-like surface defects were actually caused by coalesced dimples. The maximum peak-to-valley height difference was 1.562 μm, which is within the infrared transmission waveband of Ge22Se58As20 and reduces the infrared transmittance. To guarantee infrared transmittance, microdimples must be suppressed.

To reduce the microdimples, gas generation should be reduced, and gas escape should be improved. For gas generation, the solubility of gas has been studied, and it can be expressed using A. Sieverts’ square root law (Gupta 2006):

\[
S = k \sqrt{P} e^{-\Delta H/(RT)}
\]

where \(S\) is the dissolved concentration, \(k\) is a constant, \(P\) is the gas partial pressure, \(\Delta H\) is the dissolution heat, \(R\) is the gas constant, and \(T\) is temperature. The movements of the molecules become more intense as the temperature increases, leading to more reactions, smaller gas solubility, and more gas generation. Pressure is another contributor that affects the gas solubility, in addition to the temperature. The gas density is greater with the increasing pressure, so the free molecular motion decreases, and the gas increasingly dissolves, as expressed by Eq. 5. According to Dalton’s law of partial pressure, the total pressure is equal to the sum of the partial pressures of the mixed gas (Silberberg 2000). Meanwhile, based on Newton’s third
law (Kelley and Leventhal 2017), the total pressure increases with the increase in the pressing force. This law indicates that the gas solubility increases with the increase in the pressing force.

To quantify the effect of the temperature, the area ratios of the microdimples were evaluated. Avoiding the obvious molding defects, five measuring points are equidistantly chosen in the direction of diameter on the upper surface of a formed pillar, of which the third point is in the center, and the average area ratio values are obtained. In order to make the results more vivid, the central measurement point images are shown in data maps. The area ratio of the latter is also measured by this method. The area ratios of the microdimple areas increased almost logarithmically with the molding temperature, as shown in Fig. 13. By extrapolating the trend line in Fig. 13, we could estimate that the temperature for preventing microdimple was approximately 379.8 °C. However, this temperature is too low and could lead to surface scratching. In our experiment, surface scratches remained even after molding at 380 °C. Therefore, it was inferred that the optimum temperature would be between 380 °C and 382 °C. In the subsequent study, we fixed the molding temperature at 382 °C and focused on other parameters that could minimize the effects of gas release when gas release was inevitable.

Meanwhile, the area ratios of the microdimples with different pressing forces were also evaluated. As shown in Fig. 14, the area ratios of the microdimples decrease with the increase in the pressing force at a molding temperature of 382 °C. They decrease slowly from 1362 N to 2723 N and then decrease rapidly from 2723 N to 4085 N. Therefore, it can be assumed that if the contact pressure is larger than the saturated vapor pressure of the ChG, the gas will no longer be generated.

To decrease the occurrence of microdimples on the glass surface, the effect of the contact surface roughness was studied. Due to the surface microstructures of the mold and glass, the enclosed spaces resulted in a lower local pressure, as shown in Fig. 15. The pressure of the enclosed spaces was lower than the saturated vapor
pressure of ChG, which intensified the evaporation of selenide gases and led to the morphology that exhibited incomplete reproduction and microdimples. However, the pressure of the joined surfaces was much higher than the saturated vapor pressure of ChG, and hence, these surfaces were reproduced in full. When the contact surfaces were smoother, the number of enclosed spaces was lower, and the gas generation decreased. In contrast, the enclosed spaces resulted in enclosed gas, which impeded gas escape. When the contact surfaces were smoother, the gas escaped more completely, as shown in Fig. 16, which also led to a better surface quality.

To verify the contact surface roughness effect, three groups of molds were prepared with surface roughness (Ra) values of 7 nm, 62 nm, and 835 nm,
respectively. The surface roughness (Ra) of the glass preform was 10 nm. The glass molding experiments were carried out under the pressing force of 4085 N at the molding temperature of 382 °C. Figure 17 shows the area ratios of the microdimples under different mold surface roughness values. It can be concluded that smoother mold surfaces led to fewer microdimples, which verified the notion of the effect of the contact surface roughness, as shown in Figs. 15 and 16. When the mold surface roughness (Ra) was 7 nm, the area ratio of the microdimples reached its minimum value. Moreover, 7 nm meets the precision requirement of infrared optical applications, so it was chosen for the next study.

When the glass surface is more curved with a smaller radius, the gas escape becomes easier as shown in Fig. 18, and the area of contact surface is smaller when the displacement is the same, which means the pressure is larger under the same force at the same displacement. Both of these two reasons can reduce microdimples as mentioned above. The effect of the surface curvature of the glass preforms was also studied. The mold surfaces were planar with a roughness (Ra) of 7 nm. The glass preforms had spherical surfaces with different curvature radii. It is impracticable to control a uniform pressure between contact surfaces. Therefore, in our experimental study of the effect of surface curvature, we can only guarantee external force to be the same. It can be seen from Fig. 19 that the area ratios of the
microdimples of the formed pillars decreased or were even completely eliminated, with the decrease in the glass curvature radius. The surface roughness (Ra) of a formed pillar without microdimple can reach 20 nm.

Another experimental scheme to study the contact surface curvature effect included reducing the curvature radius of the mold surface, as shown in Fig. 20a. The glass surface was plain with a roughness (Ra) of 10 nm. The upper mold had a spherical surface with a curvature radius of 2.5 mm. After the experiment, the formed pillar had a convex surface, a flat surface, and a concave surface as shown in Fig. 20d, e, f respectively. Moreover, microdimples were not present on these

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**Fig. 19** Area ratios of the microdimples of the formed lenses with different glass surface curvature radii under 4085 N with a molding temperature of 382 °C

**Fig. 20** Glass molding experiments with spherical molds: (a) experimental scheme, (b) the lower surface of a formed pillar, (c) the upper surface of a formed pillar, (d) the micromorphology of the convex surface, (e) the micromorphology of the flat surface, and (f) the micromorphology of the concave surface.
surfaces, which means that the microdimples could be eliminated by reducing the curvature radius of the mold. It was also concluded that the gas generation and escape could be improved by enlarging the curvature difference between the glass surface and the mold surface, either by reducing the curvature radius of the glass or the molds.

3.2.2 Microstructure Shape and Morphology Control

The microstructure molding experiment is conducted by using spherical preform glass, and the microstructures include microgrooves and microlens arrays. The lower mold with some microgrooves on its surface based on above research is shown in Fig. 21.

According to the optimum technological parameters, the molding temperature is set to 382 °C, and molding time is set to 20 s. Microscopic observations of the ChG surface and the mold surface are performed using a confocal laser scanning microscope, and the microscopic observations of the microstructures are shown in Fig. 22. It can be found that there is no interfacial adhesion occurring in the edges of ChG, and the forming quality of microgrooves is excellent.

The contour curves of the microgrooves of the ChG surface and mold surface are extracted to analyze the forming quality of the microgrooves, as shown in Fig. 23. The filling rate is 97.43%, and the filling error is 2.57%. It can be seen from the contour curve that the top of the microgroove is sharp, although the forming quality of bottom is a little worse. Therefore, the molding process can better ensure the replication accuracy of the microgroove.

In the microlens arrays mold preparation, the upper and lower molds are generated on the Ni-P plating layer by diamond cutting, using a round diamond tool. Then, microlens arrays are generated by feeding the diamond tool with three-axle linkage and using a high-speed diamond-ball nose-end milling tool with an included fillet radius of 500 μm and shank diameter of 6 mm. Figure 24a is the microscopic image of microlens arrays on the Ni-P mold. The diameter of the microlens is 80 μm, and the height of the microlens is 1 μm. The microlens array was fabricated by the
Fig. 22 Micrograph of microgrooves: (a) microgrooves of ChG, (b) 3D morphology of ChG microgrooves, (c) microgrooves of mold, (d) 3D morphology of mold microgrooves

Fig. 23 Microgroove profile of mold and ChG after experiment
precision glass molding. Figure 24b is the microscopic image of microlens arrays on the chalcogenide glass.

Figure 25 shows the microlens arrays profile of mold and molded chalcogenide glass. The average error of the height is 0.034 μm. We can see that the forming quality is high and it is suitable for the fabrication of microstructure infrared optical components.

3.2.3 Molding Defect and Minimization
Although the ChG microstructure molding has high replication accuracy, there are still some defects. Most ChGs have a greater saturated vapor pressure, which enables the release of trace gases during the molding process. When these gases cannot escape, the lens shape and surface quality (Hilton 2010) are severely impaired. Also, interface adhesion exists in the molding process which reduces the forming quality
of the optical components. It deteriorates the surface quality of the mold and has an important influence on the forming process (Saiz et al. 2008; Rieser et al. 2008).

Atomic diffusion will come up between the surfaces of the ChG and the mold in the molding process. The motion of atoms is violent, and the diffusion phenomenon is serious at high temperature (Wang et al. 2014), which will lead to the change of optical property of ChG and thermomechanical property of mold material. Then the interface adhesion will be more serious (Suryanarayana and Bulk 2013). The diffusion degree of atoms is related to the material properties of the contact surface. Therefore, it is necessary to study the influence of the mold materials on interface adhesion. Three kinds of mold materials which are widely used in molding process are selected. They are cemented carbide, Ni-P coating mold, and heat-resisting stainless steel.

Experiments are carried out using these three kinds of mold materials. The surfaces of the ChG and the mold are analyzed by scanning electron microscope (SEM) and energy spectrum analysis (EDS). The atomic diffusion is studied by comparing the atomic composition of ChG preform with the mold.

The atomic percentage of formed ChG is shown in Table 2. It can be seen that there is no atomic percentage change in ChG after forming by using cemented carbide mold which is of the stable chemical property and high chemical bond dissociation energy (Cottrell 1958). So there is no atoms diffusion between the ChG and the mold even at high temperature.

The surface of ChG formed by using heat-resisting stainless steel mold contains small amounts of nickel Ni and iron Fe. It can be seen that some atoms of the heat-resistant stainless steel mold diffuse to the ChG surface, and the interface adhesion between the mold and the ChG is slight. The interface adhesion between ChG and the mold is most serious when using Ni-P coating mold. X-ray diffraction (XRD) is used to analyze the composition of ChG formed by using Ni-P coating mold. The diffraction pattern is shown in Fig. 26.

There are obvious diffraction peaks in the diffraction pattern. Compared with the standard diffraction pattern, the diffraction peak can be determined as crystal As10Ni8.8Pd1.2. Hence in the molding process, the ChG react with Ni-P coating mold. Therefore, the adhesion of the ChG is more serious when the Ni-P coating mold is used. Cemented carbide mold can avoid the phenomenon of interfacial adhesion and is the suitable mold material for ChG forming process through comparative analysis.

Table 2 Atomic percentage of ChG formed by using different mold materials

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Mg</th>
<th>Fe</th>
<th>Ge</th>
<th>As</th>
<th>Se</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>ChG preform</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formed ChG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cemented carbide</td>
<td>6.94</td>
<td>22.73</td>
<td>16.89</td>
<td>53.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat-resistant stainless steel</td>
<td>4.45</td>
<td>21.19</td>
<td>19.49</td>
<td>54.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-P coating mold</td>
<td>8.21</td>
<td>4.24</td>
<td>21.81</td>
<td>13.91</td>
<td>47.23</td>
<td>4.6</td>
</tr>
<tr>
<td>Ni-P coating mold</td>
<td>1.45</td>
<td>11.96</td>
<td>11.91</td>
<td>32.31</td>
<td>42.36</td>
<td></td>
</tr>
</tbody>
</table>
4 Summary

The precision molding of microstructures on ChG can fabricate the microstructure infrared optical elements with excellent surface morphology. Compared with other microstructural manufacturing technologies, the molding process can achieve low cost and high efficiency machining of microstructures. The following conclusions are obtained:

1. The application of ChG in infrared optics and the advantages of ChG materials are introduced. The precision molding technology is compared with other microstructure processing methods, and the advantages and practical value of it are expounded.
2. The viscoelastic constitutive of ChG is modeled. A two-dimensional simulation model of ChG microstructure is established, and the influence of process parameters on the forming stress of ChG microstructures is studied.
3. To reduce the occurrence of microdimples, the processing parameters, including the temperature, pressure, surface roughness, and curvature difference, are studied to decrease the gas generation and increase the gas escape. Based on the optimization of ChG molding conditions, microstructure arrays are fabricated by molding process using spherical ChG preform. The optimal molding materials are identified.

However, the elements of sulfur (S), selenium (Se), and tellurium (Te) in ChG are easily influenced by environment. Meanwhile, the ChG has high refractive index and large reflection loss. In order to improve the infrared optical performance of the ChG, antireflective film technology needs to be further explored which will effectively reduce the infrared reflection loss of ChG and improve the infrared optical transmittance. Hence, we should apply an antireflective coating on the ChG microstructures after molding, and the maximum utility of ChG microstructures in the infrared optical systems can be achieved.
References


Pipkin A (1972) Lectures on viscoelasticity theory. Springer, Berlin


