Precision Engineering 39 (2015) 25–30

Contents lists available at ScienceDirect

Precision Engineering

journal homepage: www.elsevier.com/locate/precision

Development of polycrystalline Ni–P mold by heat treatment for glass microgroove forming

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ARTICLE INFO

Article history:
Received 20 November 2012
Received in revised form
25 November 2013
Accepted 5 July 2014
Available online 15 July 2014

Keywords:
Glass molding press
Nickel phosphorus
Crystallization
Microgroove manufacturing
Mold material

ABSTRACT

This paper aims at developing electroless plated nickel phosphorus (Ni–P) as a mold material for glass microgroove forming by glass molding press (GMP) method. A kind of Ni–P with excellent machinability is investigated for the mold fabrication. The mechanical characteristics and the performance of amorphous nickel phosphorus (a-Ni–P) plating layer were experimentally tested. In order to increase the shape consistency and prolong the service life of the mold, polycrystalline nickel phosphorus (c-Ni–P) was developed by heat treatment. With the increase of the hardness after crystallization, the plating layer shape changes due to the heat treatment, and the strategy to deal with the deformation and the techniques to produce c-Ni–P mold are generalized. Finally, the performance of c-Ni–P mold was experimentally tested, which confirmed that c-Ni–P is a workable mold material for glass microgroove forming.

1. Introduction

Microgrooves can be used as backlight panels in the LCD monitor to improve the imaging quality and brightness. Microgrooves with feature size and periodic size less than the optical wavelength are a kind of typical binary micro optical elements, which provide excellent imaging characteristics as well as high diffractive efficiency [1,2]. Microgrooves can also be used as micro fluid channels or fluid switches in the biochips [3,4]. For these advantages, microgrooves are widely used in the optical system, biology equipment and so on. As the increasing needs of the glass microgrooves, how to fabricate the microgrooves efficiently and precisely in a wide size range becomes a challenging research task recently.

Usually, the microgrooves with *U*-shape in the range from 500 nm to 10 μm are made by the MEMS techniques, but sharp angle microgrooves with V-shape are not easy to be fabricated and large area patterns are unavailable. Micro cutting can produce trans-scale sharp microgrooves on large surface, but this method is time-consuming and not suitable for mass production. Though micro injection molding and sheet nano imprinting can replicate the microgroove shape of the mold efficiently, it is only suitable for plastic material [5].

As everyone knows, the glass material is brittle and hard at room temperature, and not easy to be machined directly [6,7]. According to the reports [8–12], glass molding press (GMP) process has successfully applied to glass lens fabrication by using the tungsten carbide (WC) mold. WC with high hardness at the molding temperature is relatively easy to achieve smooth surface by precise grinding, but it is difficult to create microgrooves on the surface [13,14]. In order to extend the GMP method to generate microgrooves on the glass surface, the microgroove mold should be machined firstly. Therefore, one of the key techniques is to develop a kind of material with high hardness to achieve a durable mold, at the same time, this kind of material should has excellent machinability for microgroove fabrication.

The electroless deposition of nickel in bath containing hypophosphite was first noted by Wurtz in 1844 [15], and promoted to industrial application by Brenner and Riddell in 1946 [16,17]. Since then, electroless nickel phosphorus (Ni–P) has been attracting much interest and widespread uses as a hard coating, due to its excellent hardness, corrosion resistance and antiwear property. The mechanical properties of Ni–P change greatly with

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http://dx.doi.org/10.1016/j.precisioneng.2014.07.002

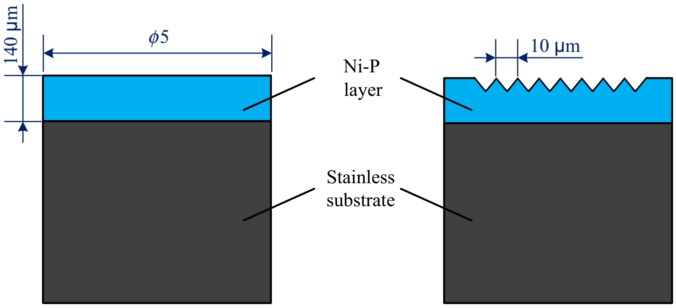

Fig. 1. Ni–P mold for microgroove glass molding press.

different phosphorus content, and most researches concentrate on the effect of the phosphorus content on the thermal phase transformation or microstructure evolution during heating, but very few research has been carried out on other mechanical properties of layer shape deformation and machinability [18,19].

This paper aims at making Ni–P coating material attainable in high performance mold development. As shown in Fig. 1, first, Ni–P layer was coated on the stainless substrate by electroless plating method; then, microgrooves with a pitch of 10 μm and a height of 5 μm in the area of a 5 mm diameter circle were created on the Ni–P surface by single diamond point cutting; finally, the shape of the microgrooves were replicated to the glass surface by GMP.

In the authors' previous work [9,12], 2D and 3D numerical simulations were used to illustrate the details of the GMP process for microgrooves, and the molding condition has been optimized according to the simulation results. Additionally, experimental research on GMP for microgrooves was also carried out to study the forming accuracy, mold life and so on. The as-deposited Ni–P is in a glassy state, and this solid phase is termed amorphous. As the hardness of the amorphous nickel–phosphorus (a-Ni–P) decreases rapidly with the increase of temperature, the microgrooves on the a-Ni–P layer were easily deformed under the repeated pressing load at the glass molding temperature. At the same time, the amorphous Ni–P alloy undergoes a self-crystalline transformation to Ni and Ni_3P at temperature above 300 °C [20,21], which increases the uncertain factors during the molding process. In this research, polycrystalline nickel–phosphorus (c-Ni–P) mold was developed to apply to the molding process directly. As the hardness of c-Ni–P is increased and no phase transformation occurs, the mold life is expected to be prolonged and the forming consistency would be improved in glass microgroove forming. Experiments were carried out to test the mechanical property and the performance of the c-Ni–P in GMP. Finally, polycrystalline Ni–P mold was confirmed as a workable material for glass microgroove forming.

2. Experiments on a-Ni–P mold

2.1. Performance test of a-Ni–P mold in microgroove forming

In glass molding press, a glass preform is pressed at a temperature of tens of degrees centigrade above its transition temperature (T_g) to replicate the shape of the mold to the glass surface. At the molding temperature, glass is at a state between plastic solid and viscous fluid, which is termed viscoelasticity, so that the forming accuracy can be precisely controlled. However, the compressing stress of glass forming is still much higher than that of the resin forming. Therefore, the Ni–P mold should be hard enough to endure the compressing stress during the pressing.

First, the performance of a-Ni–P mold in GMP is evaluated. A kind of a-Ni–P with a phosphorous content of 10 wt% (17.4 at%), which has an excellent machinability [1], is selected in the experiments. The a-Ni–P layer with a thickness of 140 μm was coated on the stainless substrate by electroless plating method. Then, the plated rough flat surface was machined to a fine mirror surface by diamond cutting using a round diamond tool with a corner diameter of 10 mm; moreover, the a-Ni–P mirror surface was machined to microgrooves using a triangle diamond tool with an included angle of 90°, so that the height is half of the pitch of the microgrooves. The microgroove was generated by feeding the diamond tool from right to left in horizontal direction. After finishing one microgroove, the diamond tool was shifted in the vertical direction with a distance of the pitch of the microgrooves to generate the next microgroove. By repeating these processes, parallel microgrooves will be created on the Ni–P plating layer. The microgroove cutting experiments are carried out on the ultraprecision machine Toyoda AHN-05 (JTEKT Corp., Japan), and cooled by oil mist. The cutting speed is specified at 3000 mm/min in straight feeding, and it costs about 30 min to complete the 500 parallel microgrooves in the area of a 5 mm diameter circle on the mold surface.

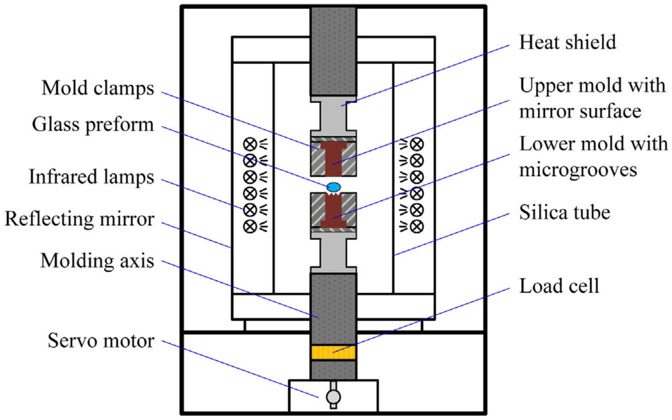

Fig. 2. Schematic diagram of the structure of the glass molding press machine.

Table 1
Optical and thermal properties of the glass.

	K-PG325 (Sumitomo optical glass)	K-PG375 (Sumitomo optical glass)
Refractive index (*nd*)	1.5067	1.5425
Abbe number (*νd*)	70.5	62.9
Transition temperature (*Tg*)	288 °C	344 °C
Yield temperature (*At*)	317 °C	367 °C

All the test glass pieces were molded on the ultraprecision glass molding machine, GMP211 produced by Toshiba Machine Corporation (Shizuoka, Japan), and the structure is schematically shown in Fig. 2. The glass preform is heated by infrared rays. After the glass preform reaches the molding temperature, the lower mold will be driven upward to close the molds, while the upper mold is fixed on the upper axis. In this way, the shape of microgrooves on the mold is replicated to the glass surface. Then, annealing is conducted by controlling the cooling rate to release the internal stress. Finally, the molded microgrooves are cooled to room temperature naturally.

Two kinds of glass preform with different transition temperature as listed in Table 1 were molded in their corresponding molding condition as shown in Table 2. After molding, the spherical glass preform was compressed into a cylindrical shape with a

Table 2
Molding conditions in glass molding press.

Glass type	K-PG325 K-PG375
Glass preform shape	Sphere ϕ3.66 mm
Pressing load	1000 N
Molding temperature	330 °C (K-PG325) 380 °C (K-PG375)

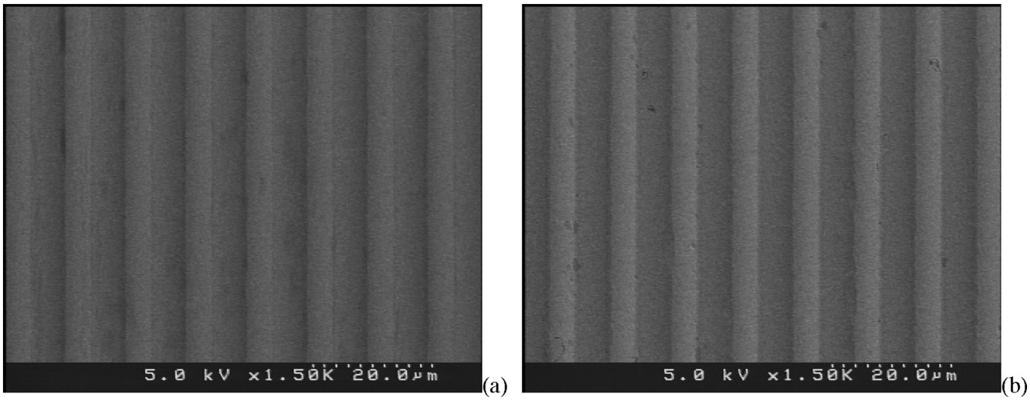

Fig. 3. Microgrooves on the glass surface made by GMP: (a) K-PG325 and (b) K-PG375.

cross-section diameter of ϕ5 mm and a thickness of 3.3 mm, and the microgrooves on the whole surface of the mold were replicated onto the glass surface by GMP. The molded microgrooves on the glass surface were tested by scanning electron microscope (SEM). From Fig. 3, it can be observed that the microgrooves with a pitch of 10 µm and a height of 5 µm are formed precisely on the both surfaces of the two kinds of glass. It seemed good news of this method for the experimental result. However, later we found that the microgrooves are formed precisely in the partial area, but lack of homogeneity on the whole surface, which means that the large area microgroove forming is limited by this technique. Additionally, the mold surface begins to turn rougher when the pressing cycle repeated for tens to hundred times, which will lead to a cloudy surface of the transparent glass.

2.2. Mechanical test of a-Ni–P mold

In order to find the reason of the inhomogeneity of the microgroove forming, the mechanical properties and resistance to deformation of the a-Ni–P mold were tested by the designed experiment as shown in Fig. 4. The lower mold with microgrooves was replaced by an a-Ni–P mold with mirror surface in the GMP, after pressing, the surface profile of the a-Ni–P mold across the mold center was measured by a Laser Probe 3D Measuring Instrument (NH-3SP), produced by Mitaka Kohki Corporation (Tokyo, Japan), to confirm the plating layer deformation.

As shown in Fig. 5, when pressing the glass at the molding temperature of 330 °C, a negligible tiny deformation occurred on the mold surface; but at 380 °C, the deformation is about 360 nm and the surface profile has changed into a convex shape. The shape change is considered a major contributor to the above-mentioned inhomogeneity of the microgroove forming.

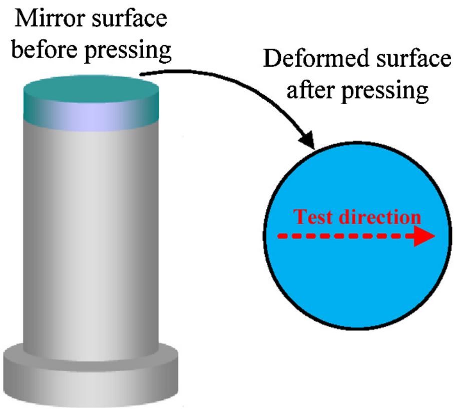

Fig. 4. Method to test the surface deformation in glass molding press.

In order to reveal the cause of the mold deformation, the Vickers hardness of the a-Ni–P is tested by a dynamic ultra micro hardness tester, DUH-W201, produced by Shimadzu Corporation (Kyoto, Japan). As shown in Fig. 6, the hardness is decreased sharply with the increase of temperature. As hardness of the mold is one of the most important parameters in glass molding press process, to

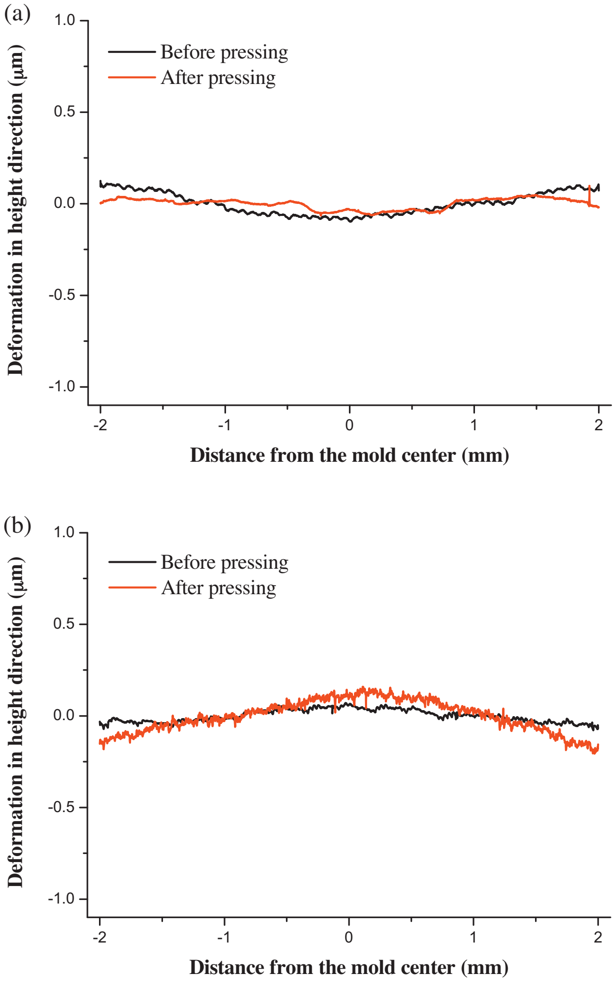

Fig. 5. Mold deformation at different glass molding temperature: (a) 330 °C for K-PG325) and (b) 380 °C for K-PG375.

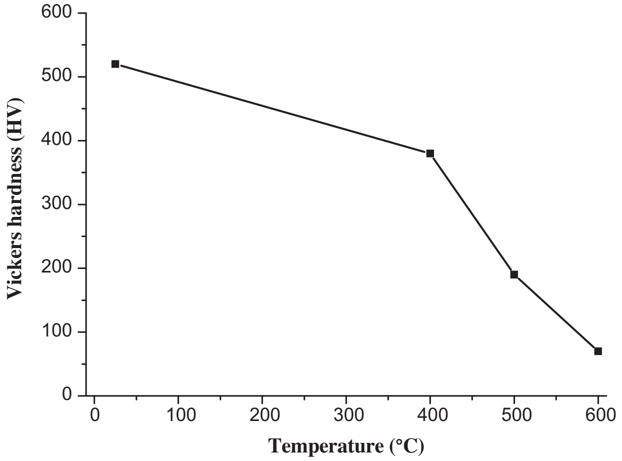

Fig. 6. Hardness decrease at elevated temperature.

improve the high temperature hardness is necessary in the mold development.

3. Experiments on c-Ni–P mold

3.1. Ni–P crystallization

As the a-Ni–P mold is subject to deformation at high temperature molding, c-Ni–P which has a higher density is considered to be capable of resisting the deformation in GMP. Therefore, as shown in Fig. 7, the a-Ni–P is crystallized by heat treatment. The heat treatment condition is shown in Table 3. In this crystallization process, the a-Ni–P is heated to the annealing temperature (600 °C) in the nitrogen gas atmosphere, and the temperature is maintained for 1 h to make sure that the crystallization process progresses completely. According to the reported literature the as-deposited amorphous Ni–P changes to crystalline Ni and crystalline Ni_3P under this heat treatment process [22,23].

The state of Ni–P after heat treatment is tested by a laser micro-Raman spectroscope, NRS-3100, produced by JASCO Corporation

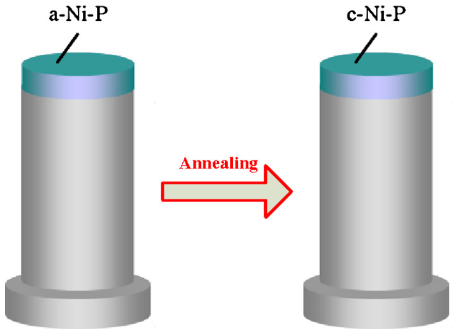

Fig. 7. Crystallization of Ni–P by heat treatment.

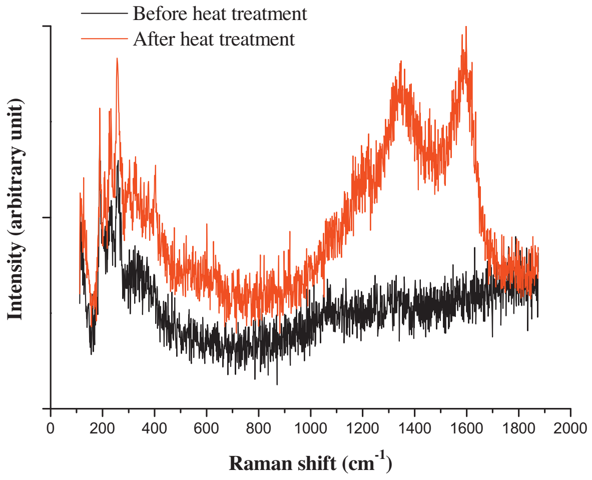

Fig. 8. Raman spectrum of Ni–P before and after the crystallization.

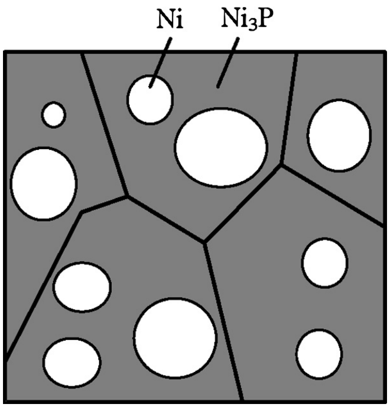

Fig. 9. Microstructures of the polycrystalline Ni–P after heat treatment.

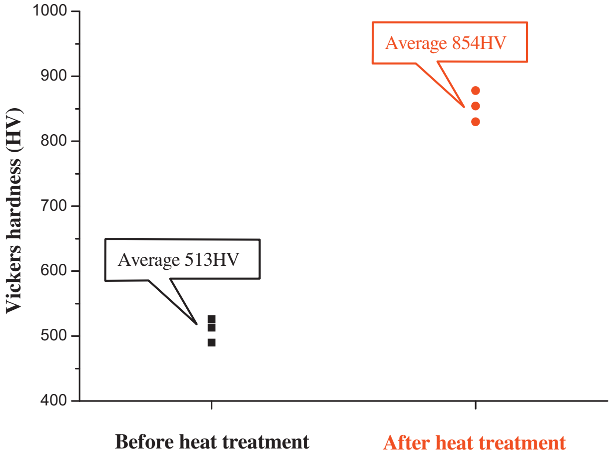

Fig. 10. Hardness improvement of Ni–P by crystallization.

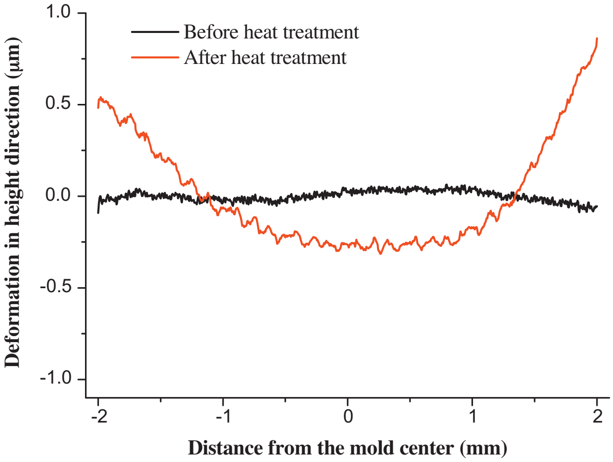

Fig. 11. Deformation of Ni–P layer due to crystallization.

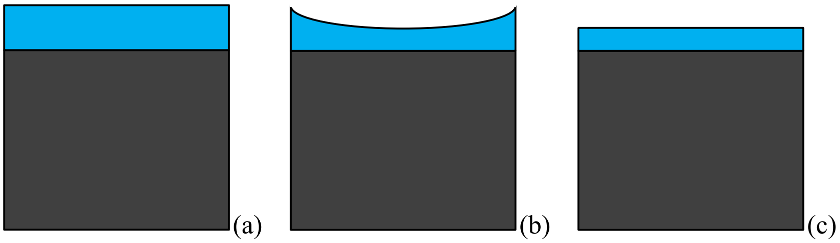

Fig. 12. Shape reconstruction of the c-Ni–P mold: (a) shape of a-Ni–P mold, (b) deformation induced by crystallization, and (c) shape reconstruction by diamond cutting.

Table 3
Heat treatment condition of Ni–P.

Atmosphere	N_2
Annealing temperature	600 °C
Annealing time	1 h

(Tokyo, Japan). As shown in Fig. 8, the laser diffraction pattern with a single broad peak characteristic of an amorphous material was observed for the as-deposited coating, and the reflection peaks emerged indicating the presence of another phase. Two sharp and strong peaks at 1340 cm^{-1} and 1580 cm^{-1} that corresponds to the crystalline grains of Ni and Ni_3P, respectively. Therefore, the Raman spectra results confirm that the a-Ni–P has transformed into c-Ni–P by the heat treatment.

With continued heating, the plating layer begins to crystallize and lose their amorphous character, and finally, nickel phosphide particles conglomerate and a two-phase alloy forms with coatings [24]. As shown in Fig. 9, c-Ni–P alloy is a bi phase material composed of nickel grain and nickel phosphide Ni_3P matrix phases. These changes significantly increase their hardness. The hardness was experimentally measured. As shown in Fig. 10, the average value of hardness at room temperature has been elevated from 513 HV at a-Ni–P state to 854 HV at c-Ni–P state.

3.2. Shape amend of crystallization induced deformation

After the heat treatment, the hardness of Ni–P plating layer is increased due to the crystallization. As the heat expansion coefficient of a-Ni–P is different from that of c-Ni–P, thermal stress occurred during the phase transformation and the layer shape changed. As shown in Fig. 11, the plat Ni–P plating layer changes into a concave shape, and the concave depth surface is about 800 nm. The curvature of the Ni–P layer after heat treatment can be either convex or concave depending on whether the plating layer is under compressive stress or tensile stress. The internal stress is accumulated due to the difference in the thermal expansion coefficients of the Ni–P plating material and the stainless steel substrate in the heating process. The different diffusing rate of the surface and substrate atoms may lead to a rougher surface, while the internal stress results in a deformed surface shape.

In order to make the c-Ni–P mold workable, as shown in Fig. 12, the plating layer was reconstructed by cutting the concave surface into a plane mirror surface by a round shape diamond tool. As the thickness of about 90 μm is removed, the remained layer thickness is about 50 μm by a simple calculation, which is thick enough for the later grooving process.

3.3. Performance test of c-Ni–P mold

In order to compare with a-Ni–P, the performance of c-Ni–P is tested at the same molding condition shown in Table 1. From Fig. 13, it can be found that the no obvious deformation occurred under the high temperature pressure after 10 shots of the GMP process. Therefore, we can deduce that c-Ni–P has a higher hardness, which is able to resist the surface deformation in GMP.

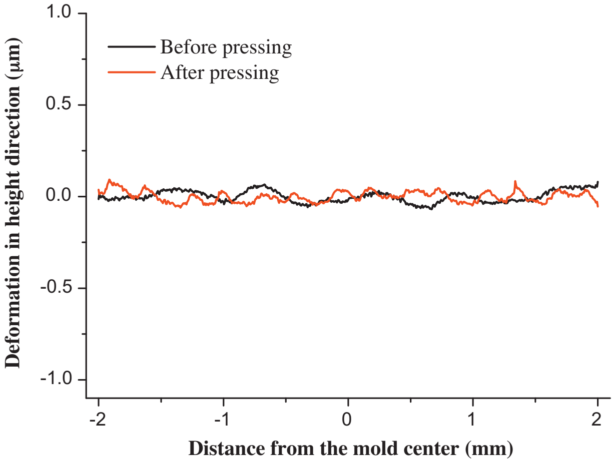

Fig. 13. Deformation resistance of the c-Ni–P Mold.

In fact, the c-Ni–P is at a steady bi-phase state below the heat treatment temperature, so the surface roughness is also sustained during the molding process. We have carried the experiments to cut microgrooves on the c-Ni–P layer, and then, uniform microgrooves were formed by using this mold in the GMP.

4. Conclusions

From the experiments of crystallization of electroless plating Ni–P, the phase transformation process has been confirmed and c-Ni–P with a harder surface is availed. Through this research we have established a way to create microgrooves on the glass surface uniformly by using Ni–P mold in GMP. In this paper, the following conclusions are obtained.

1. Amorphous Ni–P mold has been confirmed to be workable for microgroove forming in the glass molding pressing at 330 °C, but its whole shape changes when the molding temperature is at 380 °C.
2. Polycrystalline Ni–P mold was proposed to press glass at 380 °C, and the shape changes during the crystallization and the method to reconstruct the flat surface is developed.
3. Polycrystalline Ni–P mold has been confirmed to be capable of pressing glass at 380 °C without whole shape deformation, which shows a bright application prospect of c-Ni–P mold in precise microgroove forming.

The future work will concentrate on developing a mold for glass pressing process at even higher molding temperature. Furthermore, the substrate material and its roughness will be studied to improve the adhesion strength of the plating layer, which may prolong the mold life.

Acknowledgments

This work has been supported by Japan Society for the Promotion of Science, Grant-in-Aid for JSPS Fellows, project number 203234 and Grant-in-Aid for Research Activity Start-up, project number 22860003. The authors would also like to thank Toshiba Machine Corporation for the technical supports during the experiments.

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