Study of the Influence of pH on NiP Ultra-Precision Polishing

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Abstract: The nickel-phosphorus (NiP) coating has corrosion resistance, high hardness, wear resistance, and good machinability, which is a widely used surface layer in optical molds. However, cutting marks appear on the NiP coating surfaces after single point diamond turning (SPDT), leading to diffraction and stray light, which affects the quality of workpieces. Based on chemical mechanical polishing (CMP) approach, this article investigates the effect of citric acid, an environment-friendly pH regulator, on the CMP of NiP coating, and then identify the best pH value of the polishing solution on the self-developed polishing device, to effectively remove the cutting marks. The single factor variable experiment is conducted to determine the optimal pH value of the polishing solution. A surface roughness of 0.28 nm in Sa are successfully achieved on the NiP coating, and the influence of pH on the surface roughness is discussed. This work provides a theoretical basis and technical support for the ultra-precision polishing of NiP coating.

1. Introduction

With an increasing application of optical molds in the manufacturing field, the requirements for the accuracy and surface quality are becoming high, and the corresponding processing difficulty is also increasing, mainly reflected in the requirement for roughness to reach ultra-smooth surfaces. At the same time, to prevent the surface of the mold from being damaged during use, a layer of wear-resistant and corrosion-resistant nickel-phosphorus (NiP) layer is usually coated on the surface. However, the NiP coating after single point diamond turning (SPDT) will generate cutting marks, leading to diffraction and stray light, affecting the quality of the mold. Therefore, ultra-precision polishing is needed to solve this issue, in order to obtain a high-precision NiP coating surface and ensure the quality of mold pressing.

Chemical mechanical polishing (CMP) is a method that combines the mechanical removal effect of nano particles and the corrosive effect of polishing solution to achieve ultra-smooth surface, improve material removal rate, and reduce defects. In the chemical reaction process of CMP, the reaction environment has a significant impact on both the reaction rate and the reaction result [1-3]. Among the factors affecting the reaction environment, pH value of the polishing solution is the most important factor. A suitable pH value for the polishing environment can accelerate the polishing rate and achieve good polishing surface quality, while an inappropriate one may cause the decomposition of oxidants in the polishing solution, leading to the failure or increased oxidation, resulting in excessive corrosion of the workpiece surface and affecting surface quality. Therefore, it is necessary to study the acid-base environment of CMP. This article utilized citric acid, an environment-friendly pH regulator, on the CMP of NiP coating, and then identify the best pH value of the polishing solution on the self-developed polishing device, to effectively remove the cutting marks. The single factor variable experiment is conducted to determine the optimal pH value of the polishing solution. A surface roughness of less than 0.3nm in Sa is successfully achieved on the NiP coating, and the influence of pH on the surface roughness is discussed. This work provides a theoretical basis and technical support for the ultra-precision polishing of NiP coating.

2. CMP Mechanism of NiP Coating

2.1 CMP Mechanism of NiP Coating

In the CMP process, the polishing solution composed of polishing particles and hydrogen peroxide solution is transported between the polishing pad and the NiP coating surface, evenly distributed under the action of centrifugal force. Under the action of hydrogen peroxide in the polishing solution, a part of the surface of the NiP coating is oxidized, and the oxide film is a mixture of nickel oxide, nickelous oxide, and phosphorus oxide. In polishing solution, phosphorus oxide will be hydrolyzed, and nickel oxide and nickelous oxide will react with water to form nickel hydroxide. The reaction equation is formula (2-1) (2-2) (2-3):

$$Ni + H_2O_2 \rightarrow NiO + H_2O \quad (2\text{-}1)$$
$$NiO + H_2O_2 \rightarrow Ni_2O_3 + H_2O \quad (2\text{-}2)$$
$$P + H_2O_2 \rightarrow P_2O_3 + H_2O \quad (2\text{-}3)$$

Nickel hydroxide has a weak ionization equilibrium in water, and nickel oxide can be converted into $Ni^{2+}$and Ni^{3+} into the solution, making the reaction move to the right and accelerate the oxidation reaction, achieving the dissolution of polishing products. The reaction equation is formal (2-4) (2-5) (2-6):

$$P_2O_3 + H_2O \rightarrow H_3PO_4 \quad (2\text{-}4)$$
$$NiO + H_2O \rightleftarrows Ni(OH)_2 \rightleftarrows Ni^{2+} + OH^- \quad (2\text{-}5)$$
$$Ni_2O_3 + H_2O \rightleftarrows Ni(OH)_3 \rightleftarrows Ni^{3+} + OH^- \quad (2\text{-}6)$$

On the other hand, due to the lower bonding force between the oxide film and the substrate compared to the bonding force between the internal molecular layers of the substrate, it is easy to remove. Then, the oxide film is removed from the surface through the mechanical action of abrasive particles and polishing pads, and the flowing solution takes it away, exposing a new surface. The alternating process of oxide film formation and mechanical removal achieves ultra-precision polishing of the workpiece surface. The schematic of the CMP process is shown in Fig. 1. The abrasive particles in chemical mechanical polishing are generally soft and have a hardness equivalent to the surface material. At the same time, due to the complex micro morphology of the workpiece surface with peaks and valleys, the material removal rate is not completely the same at different positions. The oxide film at the slow removal speed position can form a certain protective effect on the surface, avoiding excessive scratches. Therefore, the reasonable use of oxidants can improve polishing efficiency and help to obtain ultra-smooth workpiece surfaces. According to the mechanism, SiO_2 is chosen as the abrasive particle, with the same hardness of about 7 as NiP.

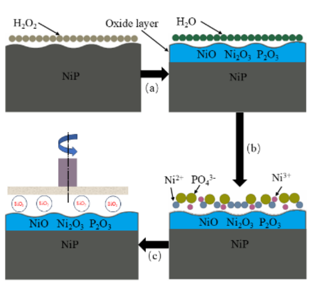

Fig. 1 Schematic diagram of NiP CMP：(a) the hydrogen peroxide oxidizes part of the NiP coating surface, and the oxide layer of nickel oxide, nickelous oxide, and phosphorus oxide generates, (b) the oxide layer undergoes a hydrolysis process, (c) the oxide layer is mechanical removed.

2.2 Polishing Device

The design of the polishing device is based on the principle of adjustable parameters, such as polishing pressure and speed. The three-dimensional structure diagram is shown in Fig. 2. The polishing device mainly consists of a stepper motor, a lever, a spindle, a disc connected with workpiece and a polishing disc with a stepper motor at the bottom. The device has a simple structure, moderate overall size, and is easy to install. From Fig. 2, it can be seen that the motor transmits the rotational motion to the spline through the transmission belt, driving the spindle to rotate. At the same time, due to the spline connection structure of the main shaft, the rotating main shaft is connected to the synchronous belt driven wheel through splines. This not only ensures that the rotating main shaft can follow the driven wheel to rotate, but also allows the main shaft to move freely in the vertical direction. The main shaft speed can be precisely adjusted from 0 to 200 rpm. The load is added through the lever of the counterweight, and the position of the counterweight on the right side of the lever is adjusted. In the absence of weights, the left and right ends of the lever are balanced. Then, weights are added to the weight table to achieve precise control of the load, with a minimum load control of 20 g. The vertical displacement table motors, the two stepper motors and the overall polishing device are all controlled by a unified control card. The NiP coating workpiece is installed on the upper disc and the polishing pad is pasted on the lower disc. The upper and lower discs should be placed eccentrically.

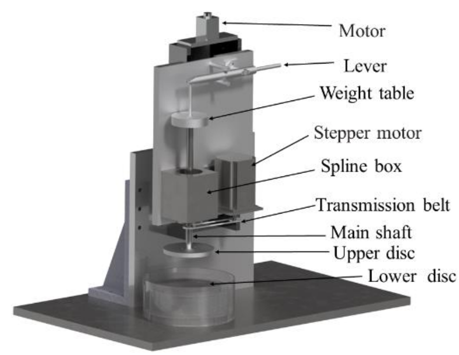

Fig. 2 Three-dimensional structure diagram

3. Experiment Setup

3.1. Single-point Diamond Turning

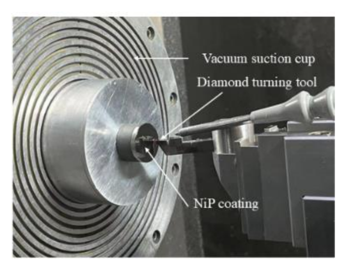

Fig. 3 SPDT process of NiP coating

The SPDT process for NiP coating is conducted using a Nanotech 250 ultra-precision single-point diamond lathe. The process is illustrated in Fig. 3, with the NiP coating deposited on the S136 surface being about 200 μm thick, held in place by stable suction from a vacuum suction cup. The process parameters are detailed in Table 1, and the nose radius of the single-point diamond tool used in SPDT is 0.5 mm [4]. The SPDT process is divided into three steps: rough turning, semi-precision turning, and precision turning. Rough turning primarily removes most of the machining allowance on the NiP coating surface, bringing the shape and size of the workpiece closer to the final product. It also flattens the full diameter surface to ensure effective and reliable cutting depth in subsequent steps, thereby improving production efficiency. After rough turning, the surface exhibits significant tool marks, necessitating semi-precision machining to prepare for the final precision machining step.

Table 1 SPDT process parameters

Processing Steps	Spindle speed/rpm	Feed Speed/(mm/min)	Cutting depth/μm
Rough turning	1000	25	10
Semi precision turning	1000	10	5
Precision turning	1000	1.5	1.5

3.2 Polishing Solution

The polishing pad chosen for this study is IC1000. IC1000 polyurethane polishing pads are frequently used in CMP processing due to their stable performance and long service life. The IC1000 polyurethane polishing pad features dense pores of varying sizes on its surface for storing polishing solution, and many micro convex peaks to support the mechanical removal of oxide particles on the chip surface, as illustrated in Fig. 4. The polishing solution chosen for this study is the silicon solution, with hydrogen peroxide as the oxidant. The ratio of silica solution to hydrogen peroxide is 40:1.

In the experiment, two polishing solution environments were set up: acidic (pH ≈ 4), and alkaline (pH ≈ 10) to polish NiP coating, in order to determine the appropriate pH of the polishing solution. Reagents for regulating pH is NaOH and citric acid, and pH test paper is used to detect acidity and alkalinity.

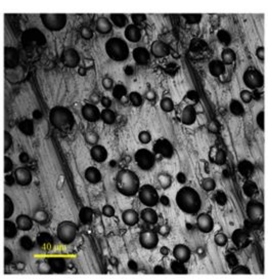

Fig 4 Surface microstructure of IC1000 polishing pad

3.3 Optimal pH Value

The actual chemical mechanical polishing process is a very complex process, and there are many process parameters that affect polishing efficiency and surface quality. This article only considers the influence of pH on the CMP polishing results of NiP coatings. In order to obtain the optimal pH value for CMP polishing environment and study the influence of pH value, this study adopts the single factor variable experiment to analyze the effect of pH value on polishing surface quality. The experimental index of this experiment is the surface roughness of the polished workpiece.

According to the previous experiment, the pH value of acidic is better than that of alkaline. Therefore, the pH value is set 3, 4, 5, 6, 7. The other experiment factors are all the same. The polishing pressure is 0.5kg, the upper- and lower-disc velocity are both 30 rpm.

4. Results and Discussion

4.1 SPDT Process

The surface morphology of the NiP coating after SPDT is shown in Figure 5. It was measured by a white light interferometer (Vecco NT9300) with a 20× objective lens and a 1× eyepiece. The measurement area is set to 315 μm × 236 μm. The roughness value is the average roughness value of five points along a line through the center. From Fig. 5, it can be seen that the surface presents an obvious periodic structure, which would enhance the surface scattering effect, and the rainbow is formed on the NiP coating surface. Therefore, subsequent polishing must be carried out to improve the surface quality from SPDT.

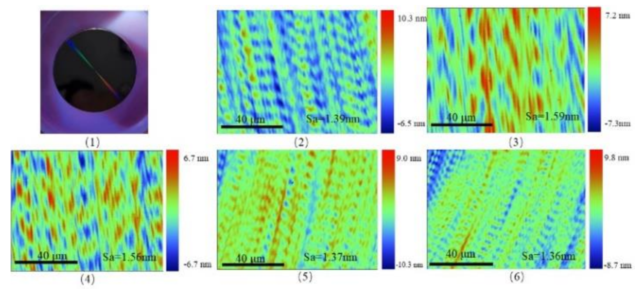

Fig. 5 (1) The surface morphology of the NiP coating after SPDT, (2) to (6) the WL measurements of the NiP coating after SPDT

4.2 Influence of pH on Polishing Surface

As shown in Fig. 6 (1), under alkaline conditions, dense pits appeared on the surface of the workpiece, with varying sizes and irregular shapes, accompanied by irregular scratches on the surface. In acidic environments, there are no obvious pits on the surface, as shown in Fig. 6 (2), indicating a significant improvement in surface quality compared to alkaline environments.

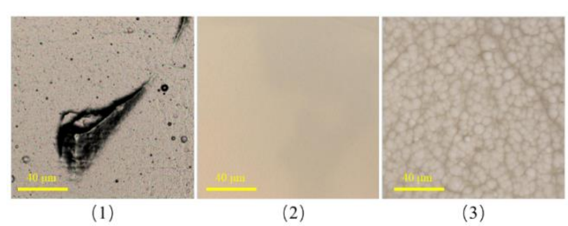

Fig 6 The NiP coating surface topography after CMP under (1) alkaline and (2) acidic condition, and the NiP coating cell structure via the laser confocal microscope observation images (Olympus, OLS 4000)

Regarding the coating cell structure of NiP, the reason for the peeling and pit formation of NiP coating is the alkaline brittleness of the NiP, which means brittle fracture occurs in alkaline medium, leading to layered peeling. The main reason for alkali embrittlement is the residual tensile stress inside the coating. In alkaline environments, due to the presence of tensile stress within the coating, surface microcracks will continue to propagate until the cracks merge, causing the coating surface material to detach and form pits at the detachment site. Considering the current status of NiP coating technology, pits appear on the surface of the workpiece in alkaline environments, which affects the polishing effect and is not conducive to obtaining a super smooth surface. On the other hand, acidic environments can effectively avoid this problem. Under alkaline conditions, hydrogen peroxide will also decompose, leading to a decrease in the rate of oxide film formation on the surface, which is prone to scratches and pitting corrosion. Therefore, the environment for polishing is determined as acidic environment.

4.3 Verification of the Optimal pH Value

The effect of pH value of polishing solution on the surface quality of nickel phosphorus coating CMP is shown in Fig. 7. As the pH decreases, the surface roughness of the workpiece first decreases and then increases. The best surface roughness is obtained at pH = 5, which is 0.28nm in Sa. The surface quality obtained under neutral conditions (pH = 7) is relatively poor, only around 0.60nm in Sa. When the pH value is 7, the polishing solution has a weak corrosion effect on the surface of the NiP coating. At this time, the chemical effect is very small, and the material is mainly removed by mechanical removal. The surface removal is very uneven, and the surface roughness is relatively poor. As the pH gradually decreases, chemical and mechanical interactions reach an approximate equilibrium, and the surface gradually becomes smooth with a decrease in roughness. When pH =5, the optimal surface roughness is achieved, which is 0.28 nm in Sa. When the pH further decreases, the chemical reaction is further enhanced, and the chemical reaction is greater than the mechanical reaction, resulting in an increase in surface roughness.

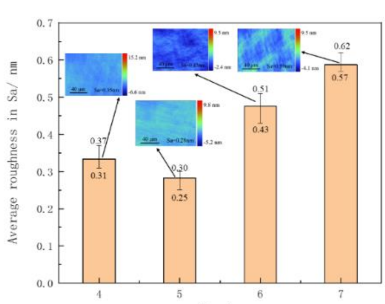

Fig 7 The average roughness values of different pH values from 4 to 7 for NiP coating CMP polishing

Citric acid has weak acidity and causes less corrosion to the surface of nickel phosphorus coatings. After polishing, the NiP coating surface quality is good. Citric acid, as a commonly used food additive, can be consumed in small amounts without harming the environment and human health. And it is weakly acidic, with a certain buffering capacity for polishing pH. Therefore, citric acid is determined as a pH regulator。

When the pH of the polishing solution is low, hydrogen peroxide has good stability and is not easily decomposed into water and oxygen [5]. H_2O_2 has good stability and strong oxidation effect at low pH values. During the polishing process, it will undergo chemical reactions on the surface of the NiP coating, forming an oxide layer. The oxide layer will be removed under the mechanical action of SiO_2, resulting in a better surface roughness. As the pH value of the polishing solution increases, the number of H^+ ions in the polishing solution decreases, and the chemical reaction gradually weakens. The weakly acidic environment also deteriorates the stability of H_2O_2, and some H_2O_2 decomposes into water and oxygen, weakening the oxidation effect of H_2O_2. In addition, nickel and other elements on the surface of the NiP coating will react with the dissolved oxygen in the polishing solution to form dense oxides, which affects the chemical reaction of the polishing solution on the surface of the NiP coating, resulting in an imbalance between chemical and mechanical reactions and affecting the polishing result.

5. Conclusion

This article investigates the influence of polishing solution parameters (pH value) on the CMP effect of NiP coatings through single factor variable experiments, and draws the following conclusions:

(1) Due to the alkaline brittleness of NiP coatings, acidic CMP polishing solution for NiP coatings is more effective than alkaline polishing solution.

(2) As the pH value of the polishing solution decreases (7-4), the surface roughness of the nickel phosphorus coating shows a trend of first decreasing and then increasing. At pH = 5, the surface roughness is the best of 0.28 nm in Sa. When the pH value is low, hydrogen peroxide is stable and has strong oxidation, promoting a gradual balance between chemical reaction and mechanical removal, resulting in better surface roughness. When the pH value is high, hydrogen peroxide will hydrolyze, and some parts of the workpiece surface will react with dissolved oxygen, resulting in a decrease in polishing effect.

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