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Thermal expansion coefficient analyses of electroless nickel with varying phosphorous concentrations

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ABSTRACT

Electroless nickel-phosphorus (NiP) layers with different phosphorous concentrations were deposited using in-situ techniques for measurement and control of the plating process. To achieve a constant Ni-concentration and pH, we utilized a control system including photometric-, pH-sensors and a batch feeder. A decreasing pH value leads to increasing phosphorous concentrations. Furthermore, we devised a complexometric titration technique to analyze the chemical composition of electroless NiP and confirmed its accuracy by comparison to well-established gravimetric analysis. The coefficient of thermal expansion (CTE) at temperatures ranging from 86 K to 373 K of electroless NiP layers containing different phosphorous concentrations was analyzed using a push-rod dilatometer. Finally, we demonstrate that the CTE of electroless NiP is precisely adjustable via the deposition parameters of the electrolyte.

1. Introduction

High precision metal mirrors with shape deviations <150 nm (peak-to-valley) at a clear aperture of 100 × 100 mm^2 are key components of sophisticated scientific instruments in astronomy and space applications. Especially for the use at cryogenic temperatures, detailed knowledge and control of thermal expansion of the applied materials is crucial. Al6061 is a widely used substrate material for metal optics [1]. This alloy can be coated with electroless nickel-phosphorus (NiP), enabling lower roughness values of metal optics. The bimetallic bending caused by the different coefficients of thermal expansion (CTE) of Al6061 and the polishable layer electroless NiP leads to a disadvantageous increasing shape deviation of metal optics at cryogenic usage [2]. An approach for reducing the bimetallic bending is the manufacturing of metal mirrors made of CTE matched aluminum alloys and electroless NiP [3]. After the deposition of electroless NiP, the optical surface is processed by ultra-precise diamond turning. Furthermore, X-ray amorphous NiP provides the opportunity for local shape corrections (e.g. magnetorheological finishing) and polishing techniques [4] to achieve the specified shape deviations.

Previously, different values of the phosphorous concentration dependent thermal expansion coefficient at 273 K were published [5–8]. However, a detailed understanding regarding the influence of phosphorous concentration on the CTE at ranging temperatures (86 K to 373 K) is necessary. The objectives of this paper are three-fold: (i) development of a plating equipment, which enables the adjustment of defined Ni-concentration and pH with low standard deviations during the complete plating process; (ii) investigation of a wet chemical technique to analyze the chemical composition of NiP alloys; and (iii) evaluation of the influence of the phosphorous concentration on the thermal expansion coefficient at temperatures ranging from 86 K to 373 K.

2. Materials and Methods

2.1. Materials

Electroless nickel is a supersaturated alloy containing nickel and phosphorus, deposited by chemical reactions from an electrolyte on metal substrates [9]. The pH value of the electrolyte influences the phosphorous concentration of the resulting NiP layer [9–12]. The phosphorous concentration influences many properties, e.g. hardness [13], crystallinity [9,11–15], and CTE [5–7].

During our experiments the Ni-concentration, pH value, and temperature of the electrolyte were kept constant during the complete deposition aiming at electroless nickel layers with different phosphorous concentrations and a thickness of >100 μm. To ensure no temperature fluctuation greater than ±0.5 K, a heating element and a temperature control system were used. An automatic batch feeder, including a photometric sensor analyzing the Ni-concentration and a pH-sensor analyzing the pH value of the electrolyte, was used to keep all parameters constant. If the nickel content dropped below the set point by 0.01 g/l, the batch feeder dispensed dissolved nickel salt and

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Table 1
Summary of parameters for electroless nickel depositions.

Layer	Nickel content [g/l]	Reductant content [g/l]	pH value	Temperature [K]	Deposition time [h]
NiP-1	6.00	40	4.80	359	19
NiP-2	6.00	40	4.50	359	24
NiP-3	6.00	40	4.35	359	18

reductant in a defined ratio of 2:1, automatically. In the case of pH fluctuations, dissolved ammonia was dispensed in the same manner. Therefore, the technique enables electroless depositions of NiP with various phosphorous concentrations using different set points for the pH value at the deposition process. In preparing electroless NiP layers with a specified thickness, aluminum sheets were plated up to 24 h, using plating equipment with 24 l. Hereby, a conventional electroless nickel bath based on sodium hypophosphite as reductant was used for NiP sample preparation. For the aim of different phosphorous concentrations of electroless NiP layers, the layers were deposited at different pH values, keeping the content of nickel and reductant as well as temperature of the electrolyte constant, cf. Table 1.

After deposition, the layers were mechanically separated from the aluminum substrate. Thereafter, electroless nickel is available as bulk material without any debris of the substrate material.

2.2. Gravimetric analysis

Gravimetric analysis is a well-established wet chemical method for analyzing the chemical composition of electroless NiP [16,17]. The mass of precipitated ammonium phosphomolybdate ($(NH_4)_3PO_4 \cdot 12MoO_3$) is used to analyze the phosphorous concentration. In contrast to surface measurement techniques like energy-dispersive X-ray spectroscopy (EDS) or X-ray photoelectron spectroscopy (XPS), the entire layer of material is analyzed by the gravimetric method. For gravimetry, 200.0 ± 0.5 mg electroless nickel (m_{NiP}) was dissolved in 65% nitric acid. By dripping potassium permanganate in the solution, all phosphorus compounds occupy the oxidation state V; which is necessary for a complete reaction of phosphorus to phosphate. While heating the solution, the manganese oxide precipitates, which was then dissolved in 25% hydrochloric acid. This solution was added with water, nitric acid, and dissolved ammonium nitrate. Afterwards, ammonium molybdate was added to the solution. The precipitated ammonium phosphomolybdate was dried and weighed. Using stoichiometry, the phosphorous concentration was calculated:

$$\mathrm{conc_P[wt.\%]} = \frac{m_{(NH_4)_3PO_4\cdot 12MoO_3} \cdot M_P \cdot 100}{m_{NiP} \cdot M_{(NH_4)_3PO_4\cdot 12MoO_3}} \quad (1)$$

where m is the mass and M is the molar mass of the substances.

2.3. Complexometric titration

The here-described wet chemical method is a novel approach to analyze the chemical composition of electroless nickel. Complexometric titration was performed on samples with a weight of 25 mg, which were dissolved in 65% nitric acid. The solution was diluted with water, ammonia buffer solution and murexide. Afterwards, the solution gets titrated with 0.01 g/mol ethylenediaminetetraacetic acid (EDTA). At the equivalence point, the yellow solution turned violet. The phosphorous concentration of pure nickel-phosphorus-alloys was calculated using the following equation:

$$\mathrm{conc_P[wt.\%]} = 100 - \frac{V_{EDTA} \cdot c_{EDTA} \cdot M_{Ni} \cdot 100}{m_{NiP}} \quad (2)$$

where V_{EDTA} is the used volume of EDTA at the equivalence point, c is the concentration, m is the mass, and M is the molar mass of the substances.

2.4. Dilatometry

Published CTE analyses of electroless nickel were performed at different temperature ranges using a dilatometer [5–7]. In this study the CTE measurements were accomplished with a Low-Temperature Dilatometer (DIL 402 C, NETZSCH, Selb, Germany) enabling CTE measurements at cryogenic temperatures. Before analyzing electroless nickel samples, the push-rod dilatometer was calibrated with a Fused Silica standard depending on the sample's length and samples were subjected to a heating cycle at 393 K (1 h) to evaporate penetrated moisture. In order to avoid any bending of the samples caused by the load of the push-rod of the dilatometer, NiP plates with a thickness of >100 μm are prepared. NiP samples were cut by a picosecond-laser to a width and length of 6 × 12 mm^2, respectively. Both front faces of the samples were polished until they were plane parallel and smooth. The lengths of the samples were analyzed at room temperature with a micrometer caliper. Afterwards, each sample was placed on a Fused Silica table. The push-rod and temperature sensor of the dilatometer were aligned as shown in Fig. 1.

Thus, the aligned push-rod moved without additional moments with a constant load of 30 cN. The samples were analyzed at temperatures ranging from 86 K to 373 K. The detailed temperature regime is shown in Table 2.

During each measurement, the test chamber was purged with 45 ml/min helium. Therefore, the heat of the sample was transferred to the liquid nitrogen cooled furnace. For calculation of the CTE, the heating segments ranging from 86 K to 373 K were used with NETZSCH Proteus® software. Using Eq. (3) the CTE is calculated as a

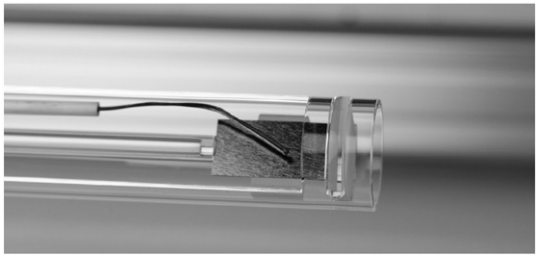

Fig. 1. NiP sample in a push-rod dilatometer DIL 402 C by NETZSCH.

Table 2
Temperature regime for performed CTE measurements.

Temperature [K]	Rate [K/min]	Holding time [min]
273	–	1
86	1	–
86	–	30
373	1	–