Research Article

Electroless Ni-P Coatings: Preparation and Evaluation of Fracture Toughness and Scratch Hardness

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Ni-P chemical coatings have been used to prevent wear, corrosion and as an alternative for hard chromium, since the latter's deposition processing is very harmful to the human health and the environment. In the present paper, Ni-P coatings with 8 and 10% P were deposited in steel AISI 1020 and thermally treated. Ni-1wt%P coatings with incorporation of hard particles of Al_2O_3 were also investigated. The microstructure and phase relationships were analyzed and correlated with the fracture toughness and scratch hardness of the coatings. The results show that the fracture toughness of the coating was smaller when thermally treated at 400°C for 1 hour and the scratch hardness reached a peak in this temperature. The relation of chemical composition and microstructure with mechanical properties of Ni-P coatings is presented. The phosphorus contents, the crystallization, and the incorporation of hard particles in the coatings change the values of toughness fracture and scratch hardness.

1. Introduction

The use of coatings in surface engineering continues to increase in recent decades. Ni-P coatings, commercially available, combine high wear resistance and adhesion to the substrate. These kinds of coatings present a uniform thickness and can be used instead of hard chromium, decreasing health and environment problems. The wide use of these coatings stems from new prospects for improving the tribological properties of the coatings by thermal treatment and by the incorporation of hard particles such as alumina [1]. The process consists of electroless chemical reduction of Ni^{+2} to Ni^0 and P^{+1} to P^0 and simultaneous deposition on desired substrates. In the present study the effects of thermal treatment and the alumina hard particles incorporation were evaluated and related to fracture toughness and scratch hardness of Ni-P coatings.

2. Methodology

The coatings were deposited on steel AISI 1020. Before the coatings, the substrate was polished in SiC of 100 and

180 mesh. The substrates were cleaned through the use of absolute alcohol and etching with HCl, 30 wt%, before the coatings to be applied [2]. The process was performed in a nickel sulphate and sodium hypophosphite solution at 90°C and the hydrogen ions concentration at the solution (pH) was monitored according to the phosphorus content in the coatings. Figure 1 shows the influence of pH on the percentage of phosphorus in the coatings [3].

Branco et al. in 2006 [4] noted that for a pH = 4 the coatings present 10 wt%P content, for a pH = 5 the phosphorus content is 8 wt%, and for a pH = 8 the phosphorus content is 1 wt%P. As the pH of the bath has a tendency to lower to it becomes necessary drip an alkaline solution with ammonium hydroxide to 50% by volume. The higher the deposition time is, the increased the thickness of the coating. The Ni-8 wt%P, Ni-10 wt%P, and Ni-1wt%P/ Al_2O_3 coatings were prepared in three chemical baths as shown in Table 1.

After the coatings the samples of Ni-P were thermally treated in furnace at 300°C, 400°C, and 600°C for 1 hour and cooled in the air.

The Ni-P/ Al_2O_3 coatings were performed by incorporation of alumina with 3 μm size particles. The use of calgon

TABLE 1: The chemical baths used in Ni-8%P, Ni-10%P, and Ni-1%P/Al₂O₃ coating source [5].

Constituents	Bath I (Ni-8%P)	Bath II (Ni-10%P)	Bath III (Ni-1%P/Al ₂ O ₃)	Role
Nickel sulphate	34 g/l	21 g/l	15 g/l	Nickel source
Sodium hypophosphite	35 g/l	24 g/l	30 g/l	Phosphorus source
Malic acid	35 g/l	—	—	Accelerator
Succinic acid	12 g/l	5 g/l	10 g/l	Accelerator
Lactic acid	—	28 g/l	50 g/l	Complexing agent
Thiourea	1 ppm	2 ppm	3 ppm	Stabilizer
Ammonium hydroxide	15 ml	15 ml	10 ml	pH controller
Alumina	—	—	5 g/l	Source
Calgon	—	—	5 g/l	Surfactant
pH	5	4	8	—
Temperature	90°C	90°C	90°C	—
Deposition rate	15 µm/h	15 µm/h	10 µm/h	—

FIGURE 1: Variation curve of the phosphate content with the pH of the solution.

FIGURE 2: The schematic representative of crack by Vickers indentation.

surfactant is necessary in the chemical baths to stabilize the dispersion and improve the deposition of Ni-P/Al₂O₃ coatings.

The chemical composition of the coatings was analyzed by inductively coupled plasma optical emission spectroscopy

(ICP-OES). The thickness of the coating was determined by an optical microscope coupled with a graduated scale. The identification and the evaluation of the present phases in the coat were performed by X-ray diffraction (XRD). The microstructure of the sample and the present precipitates was examined by a scanning electron microscope (SEM). The coated samples were polished in SiC at 240, 400, 600, 800, and 1500 mesh, and the last step was 1 µm diamond. The chemical etching was carried out by 20 seconds in aqueous solution with 50% nitric acid and 30% acetic acid [6].

The fracture toughness (K_{IC}) for the Ni-P coated samples was measured by indentation test. A load “P” of 100 N with a Vickers indenter was applied for 20 seconds in order to cause cracks in the samples. The value of semi-diagonals of impression (“a”) and the length of cracks (“2c”), Figure 2, was measured by optical microscope.

The fracture toughness of coating, in MPa.m^{1/2}, was determined by Equation (1), proposed by [7].

$$K_{IC} = 0,0319 \times \frac{P}{a\sqrt{c}}, \quad (1)$$

where

K_{IC} is the value of fracture toughness (MPa.m^{1/2});

P is the value of applied load indentation (N);

a is the semidiagonals of indentation (m);

2c is the length of cracks in the direction of diagonal (m).

The scratch test was used to evaluate the hardness of the coatings. The tests were performed with a Rockwell C indenter, with a diamond cone and opening angle of 120° at rate of 100 N/min and speed of 10 mm/min. The scratches measured roughly 7 mm and were analyzed by optical microscope.

The scratch hardness of coatings was determined using (2) [8]:

$$H_s = 8 \frac{F_N}{\pi b^2}, \quad (2)$$

where

FIGURE 3: XRD patterns of Ni-8%P coatings as deposited, thermally treated, and with alumina.

H_s is the scratch hardness of the material (MPa);

F_N is the normal force in scratch test (N);

b is the width of scratch (mm) relative to this normal force.

3. Results and Discussion

3.1. The Thickness and Chemical Composition of Ni-P and Ni-P/ Al_2O_3 Coatings. The thickness of the coating measured roughly $10\text{ }\mu\text{m}$. Table 2 shows the chemical analyses of Ni-P and Ni-P/ Al_2O_3 coatings. The phosphorus content in Ni-8% P and Ni-10% P coatings is the same, as estimated by the chemical baths with their $\text{pH} = 5$ and $\text{pH} = 4$, respectively. Note that Al_2O_3 content in the coatings is roughly 31%.

TABLE 2: Nickel, phosphorus and Al_2O_3 contents in coatings by weight.

Coatings	Ni (%)	P (%)	Al_2O_3 (%)
Ni-8%P	92.3 ± 0.5	7.7 ± 0.5	—
Ni-10%P	89.7 ± 0.2	10.3 ± 0.2	—
Ni-1%P/ Al_2O_3	62.0 ± 0.4	7.3 ± 0.4	30.7 ± 0.4

3.2. Analyses of X-Ray Diffraction. The diffractograms of Ni-8%P coatings, thermally treated, and Ni-1%P/ Al_2O_3 are shown in Figure 3. The profile of Ni-8%P coatings, as deposited, is characteristic of amorphous materials. There is a peak at $2\theta = 44.5^\circ$ for Ni- β phase, which has a face-centered cubic (FCC) structure. The α -alumina phase, present in Ni-1%P/ Al_2O_3 coatings, has a rhombohedral structure at 2θ

FIGURE 4: Samples of Ni-10%P coatings as deposited (a) and with incorporation of Al_2O_3 hard particles (b). Images by SEM.

FIGURE 5: The crack Palmqvist in Ni-1%P/ Al_2O_3 .

FIGURE 6: Values of fracture toughness of Ni-P coatings thermally treated for 1 hour.

= 35.1°, 37.1°, and 45.3°. Li et al. in 2004 [9] also found similar results in their studies. The phase that corresponds to the nickel phosphides appears when the coatings of Ni-P are treated at 300°C for 1 hour. At this temperature, the amorphous Ni crystallizes to FCC. The structure of the nickel phosphide is tetragonal [10]. The intensity of the peaks of

Ni-P coatings increases with annealing temperature because of the crystallization of phosphides. At high temperatures, 400°C and 600°C the peaks of Ni, Ni_3P and Al_2O_3 have high intensity. Gao et al. in 2005 [11] also found similar results in their works.

3.3. Microstructure. The microstructures of the coatings are shown in Figure 3. The β phase consists of a solid solution of nickel and phosphorus that can hold up to 4.5%, by weight, of phosphorus. The γ phase is metastable where the phosphides precipitates appear between 11 and 15%P [2]. The nickel phosphides are a hard phase. Figure 4(a) shows a sample of Ni-10% P coating as, deposited and Figure 4(b) shows the Ni-P coatings with incorporation of Al_2O_3 . This phase is harder than the nickel phosphides [12].

When the phosphorus content increases, from 8 to 10%, this increases the nickel phosphides content and the propagation of Palmqvist type cracks (Figure 5). The increase of phosphides precipitates embedded in nickel matrix decreases the fracture toughness of the coatings. The propagation of cracks has a higher probability of finding a hard phase of nickel phosphides. The toughness fracture of coatings with 8%P is greater than coatings with 10%P in same conditions. For the coatings with alumina hard particles, such as the case of Ni-1%P/ Al_2O_3 coatings, this probability increases.

3.4. Toughness Fracture of Coatings. The fracture occurs when the hard phase is subjected to stress fields [13]. The influence of temperature on the fracture toughness of the Ni-P coatings can be evaluated in the graphs shown in Figure 6. There were no cracks in Ni-P and Ni-P/ Al_2O_3 coatings as deposited.

Note that there is a decrease in fracture toughness when the coatings were treated until 400°C for 1 hour. The fracture toughness of Ni-P coatings has a lower value, 1.4 $\text{MPa}\cdot\text{m}^{1/2}$ (Ni-10%P), at 400°C. The highest toughness values occur at 600°C, about 2.3 $\text{MPa}\cdot\text{m}^{1/2}$ (Ni-8%P) and 1.9 $\text{MPa}\cdot\text{m}^{1/2}$ (Ni-10%P). The values of fracture toughness are high for these amorphous coatings, that is, as deposited. Bozzini et al.

FIGURE 7: Values of scratch hardness for the coatings evaluated.

FIGURE 8: Image of the scratch in the Ni-8%P coating thermally treated at 600°C.

2001 [14] obtained a value of $7.5 \text{ MPa} \cdot \text{m}^{1/2}$ for the fracture toughness in Ni-9% P coatings. Increasing the fracture toughness is related to the coalescing of particles Ni_3P , where the ductile matrix Ni isolates the hard particles of Ni_3P , preventing the spread of breakage particle to particle.

3.5. Results of Scratch Hardness. The scratch hardness was determined by (2) where b is the width of the scratch. The values are shown in the graph in Figure 7. On the Mohs scale, used by mineralogists, diamonds have a hardness of 10 which corresponds to 61 GPa [8]. The scratch hardness of Ni-P/ Al_2O_3 coatings as deposited, 18 GPa, is greater than the hardness of Ni-8%P and Ni-10%P in same conditions, 15 GPa and 17 GPa, respectively.

At temperatures below 400°C, the hardness increases due to phase transformation of amorphous Ni-P to cermets Ni_3P embedded in matrix of crystalline Ni [15]. For the temperature at 400°C, the scratch hardness of coatings reaches greater values. The larger value is roughly 21 GPa for Ni-10%P coating. At temperatures above 400°C, the size of the particles of phosphides grows and reduces the hardness.

Figure 8 presents an image of the scratch after delaminating of the substrate, obtained in the scratch test for Ni-8%P coatings treated at 600°C for 1 hour.

4. Conclusions

The evolution phase of coatings thermally treated was observed from the results of X-ray diffraction that show the presence of Ni- β phase and nickel phosphides that crystallize from the amorphous phase. These peaks of crystallization increase with annealing temperature.

Ni-1%P/ Al_2O_3 composite coatings plated from stable dispersions in EN baths exhibit excellent particle distribution even at particle incorporation levels approaching 30% by weight. A large increase in particle concentration in the growing layer during plating was observed for surfactants systems plated from baths with particle concentration of 5 g/L.

The fracture toughness and scratch hardness vary depending upon the annealing treatment. This fact is due mainly to the crystallization and precipitation of the phases present and the coalescing of phosphides. The values of fracture toughness decrease until the thermal treatment of 400°C and increase after this temperature. The values of fracture toughness by Vickers indentation of Ni-P and Ni-1%P/ Al_2O_3 coatings, as deposited, were not found. These values are very large because there was no crack by indentation. The value of scratch hardness of Ni-P coatings increases until the thermal treatment temperature of 400°C and decreases after this temperature. The incorporation of Al_2O_3 particles on the Ni-P coatings, as deposited, increases the scratch hardness of these coatings. This process is the hardening by incorporation of hard particles. The Ni-P/ Al_2O_3 coatings, as deposited, are harder than the Ni-8%P and Ni-10%P coatings.

The results of the present study reveal a relation of chemical composition, microstructure with mechanical properties of Ni-P coatings. Thus, the phosphorus contents, the crystallization, and the incorporation of hard particles in the coatings change the values of toughness fracture and scratch hardness.

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