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ALUMINA INFLUENCE ON THE CORROSION RESISTANCE OF Ni-P-Al_2O_3COMPOSITE LAYERS

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ABSTRACT

This paper aims to analyze the corrosion resistance of composite layers based on Ni-P matrix and disperse phase alumina of 10 µm size, present in amounts of 5, 10 and 20 g / L in the nickel plating bath. The influence of alumina on the corrosion resistance of Ni-P-Al_2O_3 composite layers was tested in 0.1N hydrochloric acid solution compared to Ni-P layers with different phosphorus contents. The samples immersed in the corrosive environment were weighed every 7 days for 4 weeks. The corrosion rate was appreciated considering the loss of mass per area in time. Mass loss was calculated considering the total time of corrosion and the mass lost each week for determining the kinetics of the process. The variation curves of the corrosion rate are presented, depending on the chemical composition of the analyzed layers and the corrosion time.

KEYWORDS: Ni-P-Al_2O_3, composite coatings, corrosion rate, HCl 0.1N

1. Introduction

Ni-P-Al_2O_3 composite layers are an improved version of Ni-P coatings. Ni-P layers are obtained by electroless method, a method based on an autocatalytic reducing process.

Phosphorus is supplied by the reductant used, respectively sodium hypophosphite, and the content in the layer depends on the pH of the nickel bath. When the pH of the nickel plating bath is low (4-5%P), the phosphorus content is higher in the coating layer [1-3].

Ni-P layers have a different corrosion behavior depending on the content of phosphorus.

Thus coatings with high phosphorus content (9-12%) have best corrosion resistance, in diverse environments [4, 5]. Coatings with low-phosphorus content have good corrosion resistance in basic environments [1].

Ni-P layers were developed especially for high hardness and wear resistance, practically comparable to hard chrome layers. This characteristic was improved by achieving composite structures with disperse phases: SiC, WC, Al_2O_3 etc. [6 7]. The influence of these particles on corrosion resistance was also investigated as well as the influence of other particles such as TiO_2, Zr O_2, SiO_2 etc. [8, 9].

The influence of alumina on the corrosion resistance of Ni-P-Al_2O_3 composite layers is the subject of many research studies in the field, presenting different opinions and results [4, 10-14]. Some authors reported an increase of the corrosion resistance in the presence of alumina and another insignificant or even negative influence. These different results are given by the particles size and the amount of alumina introduced into the electroless nickel bath.

This paper aims to analyze the corrosion resistance of Ni-P matrix composite layers and disperse 10 µm size phase alumina, present in amounts of 5, 10 and 20 g/L in the nickel plating bath.

2. Experimental research

The experimental research studies aimed to obtain Ni-P coatings with different phosphorus content and composite layers by including in the Ni-P matrix alumina particles of 10 µm size for different quantities of alumina from the nickel-plating bath, respectively 5 g/L; 10 g/L and 20 g/L. This study also aimed to verify some controversial or insufficiently explained aspects, presented in literature, regarding Al_2O_3 influence on corrosion resistance. The composite and Ni-P layers were performed on samples with sizes of 30x60 mm, made of 0.4 mm thick steel sheet, with low carbon content. The strip surface was prepared by:

- chemical degreasing, at 80-90 ^{o}C, followed by washing in warm (80-90 ^{o}C) and cold water;
- hydrochloric acid 20%, pickling and washing in warm water (85-90 ^{o}C).

The Ni-P coating was obtained in a solution of 25% nickel sulfate and 23% sodium hypophosphite. The sodium acetate was used as the complexion agent and the lead acetate was used for bath stabilizing. Working temperature was 85 °C. To vary the phosphorus content in the coating layer, the pH of the solution was varied, respectively, pH=3.64, for a high phosphorus content (9-10% P), pH=4.87 for the medium phosphorus content (7-8% P), and pH=6.60 for the low-phosphorus (5-6% P) content.

To obtain layers with similar thicknesses, the influence of pH on this parameter was taken into consideration (at the increase of the pH, the layer thicknesses increases) and the immersion duration was varied. The plated samples at pH=3.64 were kept in the solution for 15 minutes. The plated samples at pH = 4.87 were kept in the solution for 20 minutes and the plated samples at pH = 3.64 were kept in the solution for 25 minutes.

To remove the hydrogen a stirring at 200 rot./min. was imposed. To obtain composite layers in Ni-P matrix and alumina as disperse phase, the same solution was used in which was introduced alumina powder of 10 μm size in amounts of 5 g/L, 10 g/L and 20 g/L. The applied working parameters were: bath temperature - 85 °C, duration - 20 min, and pH = 4.83 and magnetic stirring 500 rot./min. to maintain the alumina in suspension. The samples were analyzed considering surface quality and were selected for corrosion process.

The corrosion resistance was made according to standard G31/2004. The test was conducted for a period of four weeks and the samples were weighed at every seven days.

The corrosion rate was calculated in g/m^2h depending on the total time of corrosion and each week to determine the kinetics of the process [15].

3. Results and discussion

The alumina influence on the corrosion resistance of the Ni-P-Al_2O_3 layers was examined in comparison with the Ni-P layers with different phosphorus contents. Figure 1 shows the corrosion rate of Ni-P layers. It was observed that after 168 h, 336 h and 504 h, the layers obtained at the lowest pH, which has the highest content of phosphorus, have had the best corrosion behavior. After 672 h, the corrosion rate of these layers is very similar to the corrosion of layers obtained at pH=4.87. The layers obtained at pH = 6.6 present the highest corrosion rate. These layers have the lowest content of phosphorus. The results confirm data from the literature.

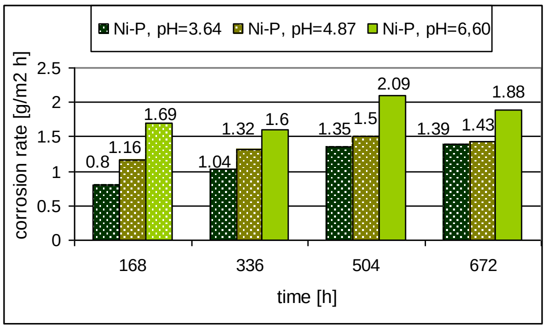

Fig. 1. *Corrosion rate of Ni- P layers in 0.1N HCl solution*

Figure 2 shows the kinetics of the corrosion process of the Ni-P layers every week. It was observed that layers with high phosphorus (pH=3.64) and medium (pH=4.87) content have similar behavior respectively the corrosion rate increases until week 3 and decreases in week 4 (due to the formation of the corrosion products on the surface). The layers with low phosphorus corroded more slowly in the 2nd week and very fast in week three, when corrosion products were formed that reduced the corrosion rate in week 4.

Figure 3 presents the results of the corrosion test for composite layers obtained in nickel plating bath with different content of alumina. The results show a very good corrosion behavior of the composite layers with Ni-P matrix and 10 μm size disperse phase alumina obtained in nickel bath with 20 g/L alumina.

The corrosion rate of these layers is almost twice lower than the other composite layers that behave comparably. This behavior is explained by the passivation of the surface by the alumina particles. Increasing the amount of particles, a larger area will be occupied by alumina which will ensure a higher resistance to corrosion.

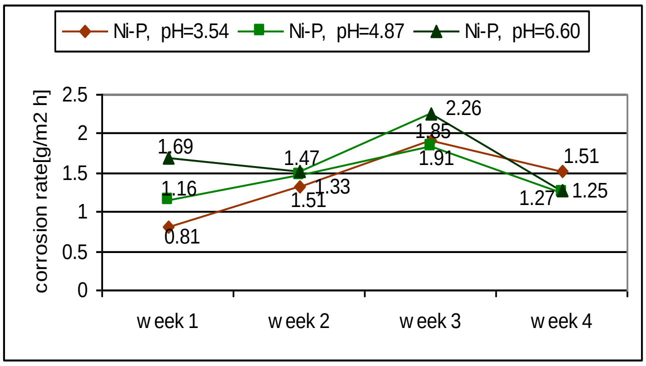

Fig. 2. Kinetics of the corrosion process of the Ni-P layers

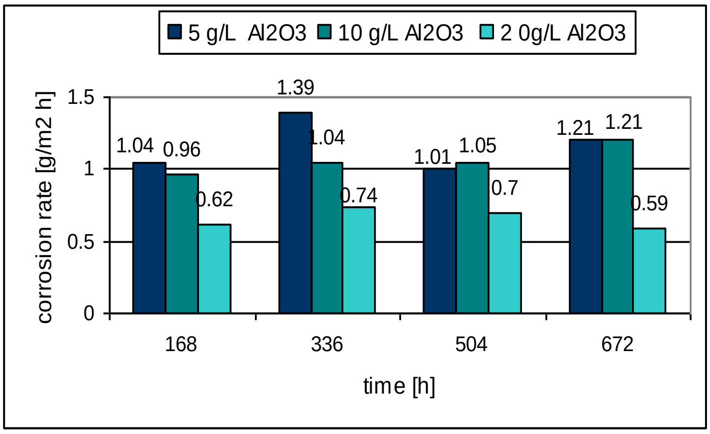

Fig. 3. Corrosion rate of Ni-P-Al_2O_3 layers in 0.1N HCl solution

The kinetics of the process presented in Figure 4 shows that in all weeks the layers obtained with 20 g/L alumina in the bath have the lowest rate of corrosion. Increasing the corrosion rate in week 2 is explained by the surface morphology of these layers. Because alumina is not a catalytic support for Ni, it causes the formation of dimples on the surface, resulting in a rough surface with nickel in relief and alumina in dimples (Figure 5). So the corrosion rate increases in week 2 through the preferential corrosion of nickel and in week 3 the surface is passive due to alumina and the corrosion rate decreases. In week 4 a higher quantity of alumina in the layers obtained in nickel bath with 20 g/L provides high resistance to corrosion compared to other layers that continue to corrode with higher rates.

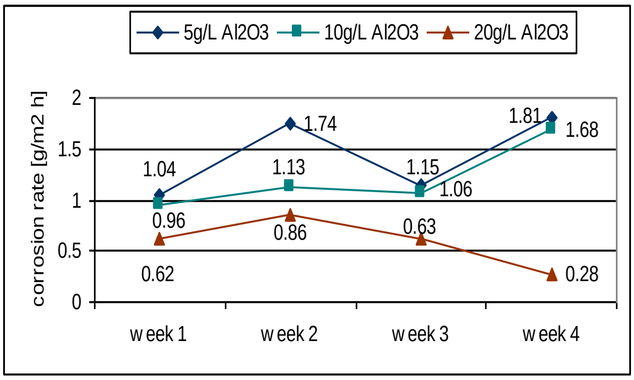

Fig. 4. Kinetics of the corrosion process for Ni-P-Al_2O_3 layers

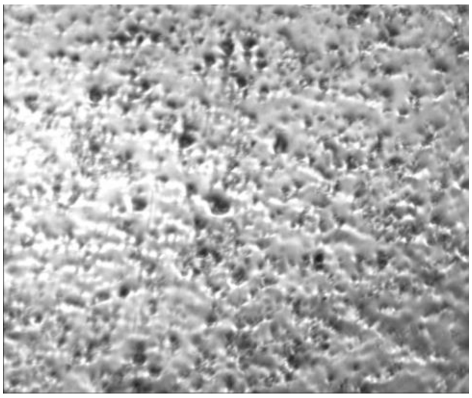

Fig. 5. Surface aspect of the Ni-P-Al_2O_3 composite layers

In Figure 6 is compared the corrosion behavior of Ni-P layers with high phosphorus content obtained at pH = 3.54 and of the composite layer of Ni-P-Al_2O_3 with different Al_2O_3 content depending on the amount of particles of alumina in the electrolyte. It can be noticed that all composite layers show a higher resistance to corrosion compared to Ni-P layers.

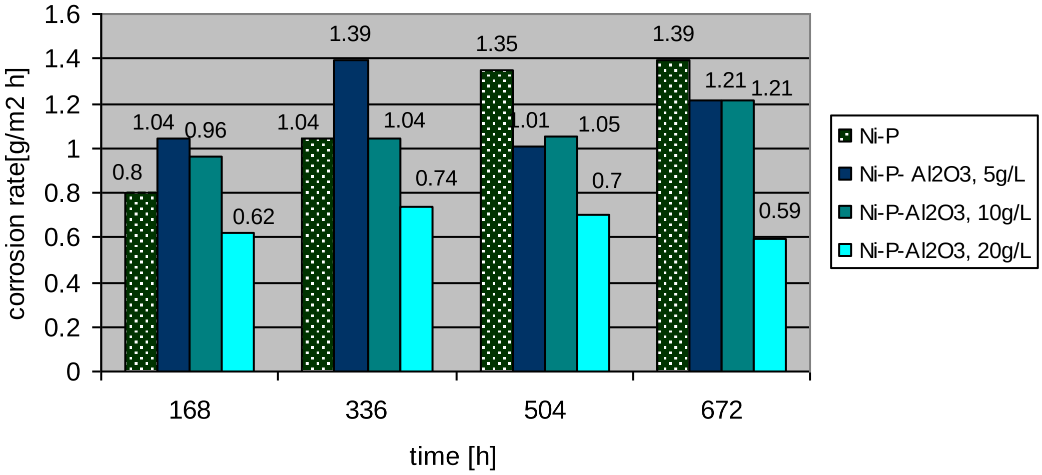

Fig. 6. *Comparative corrosion rate for the Ni-P layers and composite layers*

The different corrosion behavior of the layer is explained by the different kinetics of the corrosion process on the time intervals analyzed as shown in Figure 7. The Ni-P layers were subject to continuous corrosion until week 3 vs. the composite layers at which the process of corrosion slows in week 3.

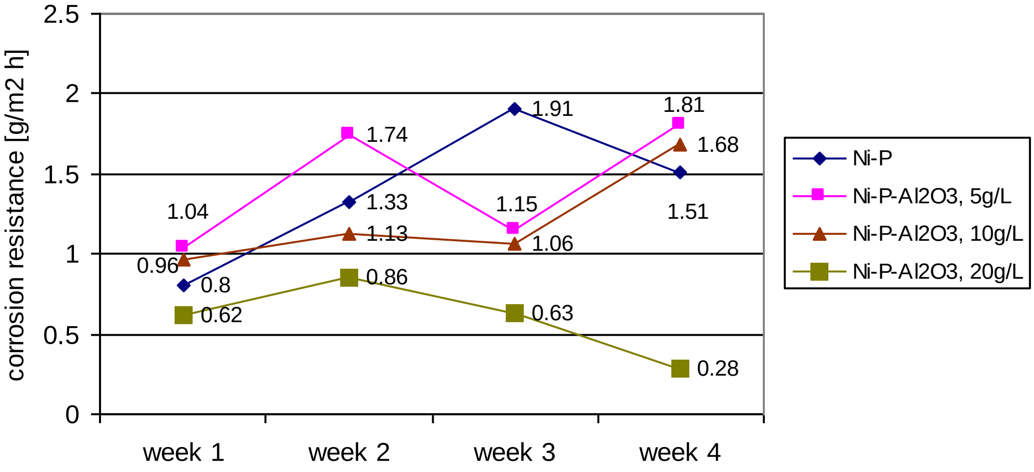

Fig. 7. *Comparative analysis of the kinetics of the corrosion process for the Ni-P and Ni- P-Al_2O_3 layers*

4. Conclusions

The research has shown better corrosion behavior in 0.1N HCl for composite Ni-P-Al_2O_3 layers compared to Ni-P layers.

The presence of alumina of 10 µm size as disperse phase in Ni-P matrix leads to increased corrosion resistance in 0.1N HCl.

The highest corrosion resistance was shown by the layers obtained in nickel bath with 20 g/L alumina, respectively 0.59 g/m^{2}h;

The different kinetics of the corrosion process for Ni-P layers and composite layers explains the different behavior of corrosion. Because alumina is not a catalytic support for Ni, it forms dimples on the surface resulting in rough surfaces with nickel in relief and alumina in dimples. This surface structure will lead initially to a higher corrosion rate of the composite layers. The surface leveling and passivation effect given by the alumina will ensure thereafter a lower corrosion rate of these layers.

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