Influence of working parameters on the composite electrodeposition

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Abstract. Composite materials are extensively studied, especially in recent years, which have a wide application in industry. Among these composite materials, in this paper we studied about electrolyte composites obtained. The matrix is made up of particles of Ni-P on which have been deposited Si-C hard particles. The amount of phosphorus incorporated into the layer increases with increasing the content of phosphorous acid in the electrolyte. The content of phosphorus incorporated into the coating composition evolves as both solid as well as particle-free solutions. When the content of phosphorous acid in the electrolyte is low and where alloys are micro crystallized, the presence of particulates changes a little the phosphorus content. At the increase of phosphorus content included in the coating is observed that the incorporation of phosphorus is higher for increasing the amount of silicon carbide particles. This matrix study was done according to the amount of phosphorus in the deposited layer. The co-deposited phosphorus modifies the crystallization mechanism so the super saturation nickel network by phosphorus allows the inhibition of the growth of nickel crystallites whose size decreases until the complete amorphization of the solid solution. The development of these deposits was aimed at determining the influence of the variation of phosphorous acid in the electrolyte, and therefore the change in the content of phosphorus included in the layer for the SiC particulate, on the one hand, and, on the other hand, it was intended the influence of heat treatment on the deposition hardness. After the measurements, it is noted that the layer thicknesses are higher for the deposition obtained from electrolyte with small containing of phosphorous acid. The structure of the Ni-P alloy and the composite material Ni-P / SiC, depends on the amount of phosphorus contained in the layer and varies from the crystalline state (the low content of phosphorus) to the amorphous state (the high content of phosphorus). Metallographic investigation and X-ray diffraction on the P20S40 sample structure reveals the existence of nano-crystalline state of the layer, and it is noted that the grains of Ni-P alloy is lower than that incorporated SiC particles that are more evident. Following heat treatment, it was found that the microcrystalline structure of the deposits, consisting of a solid nickel solution supersaturated in phosphorus, is maintained up to 463 K, and at higher temperatures it is producing the precipitation of the Ni_th_P compound into the nickel matrix.


1. Introduction

The composites of metal/ceramic having a metal matrix reinforced with ceramic particles dispersed in the form of fibers. Making composer electrodeposited metal/hard particles are the result of interactions of various particles/electrolyte, the electrolyte/cathode and particle/cathode. Lately, due to their outstanding properties, were made of composite materials that phosphorus nickel matrix and particles are incorporated in it are diverse (chromium carbide, boron carbide, etc.). Recently were started researches on the introduction of silicon carbide particles in the matrix of nickel-phosphorus [1,2]. Preparation of an electrochemical composite coating requires suspending the particles in an electrolyte. It is necessary above all to ensure the stability of the hard particles in a nickel-phosphorus acidic electrolyte. The incorporation of particulate matter is susceptible to change certain intrinsic characteristics of the deposit; it is first necessary to know the physicochemical characteristics and properties of the deposit when it was obtained from a particle-free electrolyte. Co-deposition yield of solid particles is related to the hydrophobic of the surface charge of the particles and not superficial. The incorporation of hydrophilic particles is more difficult than incorporating hydrophobic particles because it is difficult to remove water around the particles. In the case of silicon carbide, oxidation, leads to the formation of a silicon oxide layer on the surface, where the hydrophilic.

2. Experimental procedure

The development of the samples studied in this paper was made electrolytic, because they have advantageous characteristics. By the electrolytic deposition, made in an electrolytic cell, layers are obtained with a special appearance at the surface and at the same time ensures the atmospheric corrosion protection, to that produced by some chemical and mechanical damage due to friction, abrasion etc. Electrolyte development is a relatively simple process, and the layers thus obtained can be controlled in terms of composition, appearance and mechanical properties. It is a process that takes place at low temperature electrolysis cells have a relatively high life and low cost. Before carrying deposition was performed a media surface preparation. This was necessary because the adhesion between the support and the metal coating material, achieving uniform and homogeneous coating protective structure can be guaranteed only through adequate training support. Surface preparation support included the following:

a) chemically cleaned and degreased surface to be removed traces of fats or oils;
b) they started to surface polishing particles becoming finer to remove existing scratches on the surface;
c) has been supporting the polishing cloth.

Before being introduced into the electrolytic bath, the previously prepared substrate was degreased with acetone. After electro-deposition, the samples were placed in de-mineralized water and subjected to ultrasound for 3 minutes for removal of silicon carbide particles which have not adhered to the substrate. The samples were named PxSy, where X and Y represent the content in g/l of phosphorous acid, respectively content in g/l of particles of silicon carbide (SiC) in the electrolysis bath. Silicon carbide used for the preparation of composite layers had purity of 99.9%, and the particles have size of about 1 μm and the specific surface area of 10.4 m²/g. The main impurities in silicon carbide were: iron: 0.03%; Aluminum: 0.02%; Vanadium: 0.02%.

Figure 1 shows micrographs of silicon carbide particles and in figure 2 in the powder X-ray diffractogram of silicon carbide appear only characteristic peaks of silicon carbide.

The substrate on which the depositions were conducted is E24 steel with the following composition: C-0.17%; S-0.045%; Mn-1.4%; Mn; P-0.045%; N<0.007%; carbon steel (unalloyed); hardness indicated time: 235-255HB. The support of electrolytic copper from electrolysis cell was 99.9% purity, hardness 100 HV, and the thickness of the discs were made of composite layers was 3mm samples, for the samples where phosphorous acid content remained constant and varied the content of silicon carbide particles. These samples were applied a thermal treatment at 463 K. Samples were named as follows: P20S40 TT-463 K. The development of these deposits was aimed at determining the influence of the variation of phosphorous acid in the electrolyte and therefore the
change in the content of phosphorus included in the layer for 40 g/l SiC, on the one hand, and, on the other hand, it was intended to influence of heat treatment on hardness deposits. The heat treatment by diffusion phases which it operates, determining structural changes and the increase of adhesion of the coating layer to the sub-layer. Studies in the literature show that the electro-deposition of Ni-P for hard metal heat treatments has a significant influence on the structure and adhesion by removing hydrogen [3,4]. Ni-P alloys are thermodynamically unstable and changes that occur during the thermal stresses are dependent on the phosphorus content. At a temperature of 463 K meets an optimal peak hydrogen evolution, whatever the type of submission. Temperature is falling to exothermic phenomena for that occurring structural change. Because this temperature affects the Ni-P alloy structure and composition of Ni-P / SiC, they will influence the mechanical properties and tribological properties of these materials. The structure of the Ni-P alloy and the composite material thus Ni-P / SiC, depends on the amount of phosphorus contained in the layer varies from the crystalline state (the low content of phosphorus) to the amorphous state (the high content of phosphorus) [5]. Metallographic investigation and X-ray diffraction on the sample structure reveals the existence P20S40 layer of nanocrystalline state (figure 3 and figure 4), and it is noted that the grains of Ni-P alloy is lower than that incorporated SiC particles become more apparent.

![Figure 1. Silicon carbide particle micrographs.](image1)

![Figure 2. X-ray diffract gram of the powder of silicon carbide.](image2)

Qualitative analysis results presented in figure 5 X-ray from below, reveals on the diffraction the presence of two phases, namely: SiC single-phase and majority phase manifested on the diffraction by highest pick. It is noted that this pick is much widened which indicates a very fine grain structure. The position of this maximum corresponds to the Ni structure or to a nickel-based solid solution, in fact a solid solution of Ni-P.
Figure 3. Optical micrograph P20S40 untreated deposit.

Figure 4. Optical micrograph P20S40 sample treated at 463 K (x150).

Figure 5. X-ray diffraction for P20S40 untreated thermal deposition (a); X-ray diffraction for P20S40 heat-treated at 463 K (b).

The same can be seen in the diffraction figure above for sample P20S40 - heat-treated at 463 K. We meet the same compounds as raw deposit P20S40. As noted before, phosphorous acid and thus phosphorus plays an important role in obtaining the composite material Ni-P / SiC [6]. Variation of phosphorous acid in the electrolyte causes changes in physicochemical and structural layers deposited. Therefore for these samples was measured Vickers micro-hardness by applying loads 15g, 25g, 50g, 100g, 200g, 300g, 500g perpendicular to the surface layer. In the scientific literature specifies that the application of a temperature of 463 K appears strong hydrogen de-sorption, which causes changes in the properties of deposited layers. For this reason the hardness of the deposits was determined annealed at this temperature toughness has been obtained perpendicular to the surface of the film, as well as heat-treated deposits. In Table 1 are presented the results obtained when measuring the hardness and thickness of the coating layers according to the load applied perpendicular to the surface of the film.

Influence of phosphoric acid and the load applied to the layer hardness is shown in the graph of figure number 6.
For this series of samples it shows that the micro-hardness measured changes according phosphoric acid composition in three areas: for low content of phosphorous acid in the electrolyte ([H₃PO₃] <5 g/l, the composition domain I), the hardness of the deposits increases with the increase in the content of phosphorous acid; the content of H₃PO₃ between 5-10g/l (the composition domain II), the hardness decreases, then, from [H₃PO₃]=10g/l (the composition domain III) present in higher hardness. It also notes that, as the load applied is bigger the hardness decreases. For loads up to 200g hardness varies not very high (especially in the domain I and II). The load applied 300g hardness begins to decrease and the hardness decreases 500g load increased. Since the variation of the content of H₃PO₃ influence the amount of phosphorus incorporated into the layer, the curves were plotted and give change in hardness depending on the content of phosphorus incorporated in the layer as shown in figure number 7 from below:

When we studied the graph in the figure 7 from above we can see that it has the same allure as the graph of figure 6 given by the hardness variation depending on phosphorous acid in the electrolyte and vary also by the three domains. In the first domain, where the percentage of phosphorus is up to 8.4 at.%, the hardness shows a significant increase; in the second domain (percentage of phosphorus is situated around 16 at.%) we can see a small decrease in hardness which is not greatly influenced by the variation of phosphorus, and over 16% at. the hardness presents a slight increase (domain III). This variation in hardness can be attributed to structural changes arising from the variation of phosphorus content in the layer [7, 8]. When the phosphorus content increases the micro structural changes occur this manifests itself by a gradually structural change of the layer from the amorphous state to the crystallized state. In the area I, the increase in hardness due to the reduction of the crystallite size, and
the coating has a crystal structure. In the area where the micro hardness decreases (domain II) where there is a structural disorder coexist micro crystallized phase and nano-crystalline phase.

3. Conclusions
In this paper were studied the conditions of development of deposits by electro-deposition of composite electrolytes containing variable phosphorous acid and constant content of silicon carbide. It was found that by increasing the content of phosphorous acid in the electrolyte between 5% and 20%, we obtained an increase in the amount of phosphorus incorporated into the layer as it evolves as both the solid composition and particle-free solutions. Thermal treatments were carried out at 463 K for phosphor deposits with different content and it was found that the deposition of microcrystalline structure, consisting of a solid solution supersaturated nickel phosphorus, is maintained up to 463 K, and at higher temperatures is produced Ni₃P compound precipitation of nickel matrix. All layers deposited and presented in this paper are characterized by uniform thickness and very good quality of the interface. Metal matrix ensures adherence to the substrate and electrochemical corrosion resistance, anti-friction material is soft phase and hard phases take the mechanical friction, which is a new research direction in the future.

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