EVALUATION OF THE CORROSION RESISTANCE OF NI-P/SIC COMPOSITE FILMS OBTAINED BY ELECTRODEPOSITION

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ABSTRACT: Composite materials have superior properties due to the controlled combination of the metallic matrix with reinforcing particles. Ni-P/SiC composite coatings obtained electrolytically are distinguished by a high mechanical and anti-corrosion resistance. The paper analyzes the influence of the composition of the electrolysis bath and the heat treatment on the electrochemical behavior of these deposits. Cyclic voltammetry tests performed in saline environment demonstrated the stability of the passive film and the variations between samples. The P10S40 sample subjected to treatment at 420°C had the best corrosion resistance. The results highlight the major importance of optimizing the process conditions in obtaining high-performance composite layers.

KEY WORDS: composite material, properties, corrosion, electrodeposition, layers

1. INTRODUCTION

Composite materials are obtained by combining two or more materials that have different properties, so that by uniting them a new material results, which has superior characteristics compared to each constituent taken separately.

Composite materials have been artificially created to increasingly substitute classic materials, ferrous or non-ferrous because they have various limitations related to the method of obtaining, the method of processing, weight, dimensions, geometry, costs, fields of application.

Composite materials have anisotropic properties and are made up of several elements, whose arrangement and obtaining technique allow the best characteristics of each element to be exploited.

The major, essential advantage of composites lies in the possibility of modulating properties and thus obtaining a very varied range of materials, whose use can be extended to almost all fields of technical activity [1-4]. Practically, composite materials are made up of a matrix (plastic, ceramic or metal) and reinforcing elements (reinforcers), which are arranged in the matrix in different proportions and orientations. The reinforcement gives the composite material high resistance and represents the main load-bearing element, and the matrix has the role of connecting material between the reinforcing elements and the external load transfer medium to them.

By combining the materials that make up the composite, the new material is obtained that has superior properties from a mechanical, physical, chemical, tribological, functional point of view.

From a mechanical point of view, composite materials have good fatigue resistance, a high specific strength, have high toughness, and increased rigidity [5,6].

Among the physical properties of composite materials are the low density (they are light), the special behavior they have at various temperatures, depending on the type of matrix and high dimensional stability. As for chemical properties, composite materials have excellent resistance to corrosion, to saline environments and to other aggressive chemicals. From a technological point of view, composites can be easily integrated into various materials, their characteristics can be modified by varying certain parameters, etc.

Functionally, composites have a low thermal conductivity, being good insulators, are resistant to ultraviolet rays, and retain their properties at very high temperatures, etc.

Composite materials have the ability to modulate their properties, which contributes to obtaining a wide variety of composites used in vast applications in engineering and technology.

Composite materials have various benefits such as high shock resistance; the destruction of a fiber does not cause the entire composite to break, good durability; reliable vibration damping; operational safety, high tensile strength, low expansion coefficient compared to metals.

There are several methods for depositing thin layers on various metal surfaces. This results in coatings that have good adhesion to the layer and exhibit superior properties [7].

2. TECHNICAL REQUIREMENTS

2.1. Electrodeposited composite layers

Electrodeposited composite layers are metallic deposits of Ni, Cu, Zn, Co, Cr, etc. in whose matrix are integrated uniformly dispersed non-metallic phases, most often in the form of solid particles. This fact shows that the deposited film possesses superior functional properties such as high wear resistance, superior corrosion protection and controlled conductivity and special mechanical properties, including superior hardness, high resistance to local stresses and good dimensional stability.

These coatings are manufactured by electrodeposition using both aqueous and non-aqueous solutions.

2.2. Corrosion resistance of composite materials

Corrosion of layers exposed to an aggressive working environment is a major problem, influencing both the lifetime of the layer and the evolution of its main properties over time. Regardless of the purpose for which any protective layer was designed, it is essential to consider the possible interactions between the layer material and the working environment, thus ensuring its performance and durability over time [8].

Layers intended for anti-corrosion protection partially meet the specific requirements over the estimated service life and operating conditions.

2.3. Localized corrosion

Localized corrosion is a form of electrochemical degradation that manifests itself only in limited areas of the surface of a metallic material, even if the rest of the material may appear intact.

It is dangerous because it can evolve rapidly in depth, without showing obvious traces on the outside, which can cause deep cracks.

Localized corrosion occurs in several forms: pitting corrosion (small and deep cavities, difficult to observe with the naked eye, which appear in a working environment with chlorides); intergranular corrosion (occurs at the grain boundary, in places where inhomogeneities or segregations develop); filiform corrosion (appears in the form of threads under protective layers that have not adhered uniformly); crevice corrosion (appears due to the simultaneous action of mechanical stresses and the corrosive environment) [8,9].

The factors that lead to localized corrosion are: material inhomogeneities (impurities, non-metallic inclusions, segregations); environmental inhomogeneities (local pH variations, areas with accumulations of aggressive ions); mechanical aggressions (friction, abrasion, cavitation).

Pitting corrosion is a form of localized corrosion through which small deep cavities (of the millimeters order) are formed on the metal surface, called pitting.

Pitting is triggered when the material potential exceeds a critical value called the critical pitting potential. The formed pitting develops in a wider potential range whose maximum value is given by the repassivation potential.

The critical pitting potential is the potential value at which localized pitting corrosion begins on the surface of a metallic material or a protective layer. Below this potential, the passive layer (protective film) remains stable and protects the metal; above this potential, the passive film is locally destroyed and pitting corrosion begins to develop rapidly.

The critical pitting potential is the potential at which the equilibrium between the active and passive states is established or the minimum electrode value required for the aggressive anion to cause the reversible displacement of oxygen and water from the metal surface. Therefore, the critical pitting potential is the lowest potential value at which pitting initiation occurs [10].

The pitting phenomenon is triggered when, in the absence of polarization, the critical pitting potential exceeds the stationary potential of the metal in the corrosive environment in terms of activity.

The pitting characteristic reflects a higher affinity of the metal towards passivating anions compared to aggressive ones, such as halogen ions.

The appearance of the critical pitting potential highlights that the environment has a sufficient oxidizing character to trigger pitting. The higher the value of the pitting potential, the more oxidizing the corrosive environment is.

The resistance of the material to localized pitting corrosion decreases as the temperature of the environment and the concentration of chlorides increase.

The composition of the material, the presence of inclusions, the surface geometry and the physicochemical properties of the layer influence the resistance to pitting corrosion, by modifying the stability of the passive layer and the points of initiation of pitting.

The resistance of the layer to pitting corrosion is given by several factors (material composition, inclusions, surface shape, physicochemical properties) that affect the stability of the passive layer and the points where pitting is initiated.

The speed of expansion of the pits is conditioned by their density: the more there are, the slower the growth of each one will be, because the available cathodic current is distributed between them.

Heterogeneities play an important role in localized corrosion. The material presents heterogeneities in the form of inclusions and precipitates at the grain boundaries, to which are added surface heterogeneities resulting from processing (pollution, foreign particles, scratches, etc.).

The presence of heterogeneities can produce both a diminished local passivity and active areas, both determining an increase in the local corrosion rate.

Inclusions represent preferential points of the passive film where localized pitting corrosion starts more easily.

2.4. Determination of corrosion by cyclic voltammetry

The dependence between current and potential is represented by a graph called a cyclic voltammogram (figure 1).

The cyclic voltammogram represents the electric current measured at an electrode as a function of the applied potential, when the potential is varied cyclically (i.e. back and forth) within a specified interval.

The technique allows the investigation of oxidation and reduction processes that occur at the surface of materials [9].

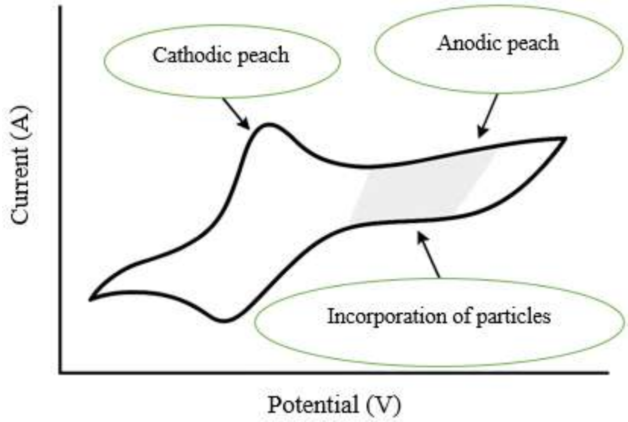

Figure 1. Cyclic voltammetrye for composites layer

Potentiodynamic curve results from measuring the electric current as a function of the potential applied to a material in a corrosive environment, with the potential varying linearly over time. It is often used to measure the corrosion resistance and electrochemical behavior of materials.

A potentiodynamic curve presents different zones: The Active region, where the corrosion current increases rapidly with increasing potential, and the metal is in an active state, the passive film is non-existent. In this zone, the corrosion current (I_corr) and the corrosion potential (Ecorr) are found. The Passivation region, where a passive film is formed that protects the metal surface, and the current stabilizes or decreases to low values. The passivation current and the passivation potential meet here. The pitting zone, also called the passivation breakthrough zone (Breakdown region), is characterized by the degradation of the passive film and the appearance of localized corrosion (pitting), and the current increases suddenly again. In this area the critical pitting potential (Epit) is encountered. The return curve (Reverse scan, in the case of cyclic scanning) where repassivation or persistence of defects can be highlighted, if the scan is done backwards, it can show repassivation or persistence of defects. Cyclic voltammetry has a number of advantages, being a fast method, providing clear and in-depth information about corrosion processes; it is important in fundamental research of the behavior of the metal surface.

3. EXPERIMENTAL RESULTS

Corrosion tests were performed in a saline solution with 30g Na Cl /l by cyclic voltammetry in a specific facility [10], on samples of Ni-P/SiC composite material, which were obtained from an electrolyte with a variable content of H_3PO_3 and 40g/l hard silicon carbide particles and which were subjected to a heat treatment of 420^0C. The samples are named taking into account the H_3PO_3 concentration, and the heat treatment of 420^0C is represented by the number 4.

Evaluation of the corrosion resistance of electrodeposited NiP-SiC composite layers involves taking into account hydrogen absorption and their structural heterogeneity.

The presence of hydrogen modulates the electrochemical properties of the material, favoring the occurrence of localized corrosion (pitting). It is essential to consider the differences in behavior in the localized corrosion phenomenon between the hydrogenated and the reference material. The anticorrosive character of the composite electrodeposition depends on the composition,

morphology and structural heterogeneity. Corrosion tests have highlighted the influence of the phosphorus concentration in the Ni-P alloy matrix and the applied thermal treatments (dehydrogenation and precipitation of phosphides) on the corrosion resistance of layers with the same SiC concentration. The cyclic voltammetry diagrams for these composite deposits are presented in figure 2.

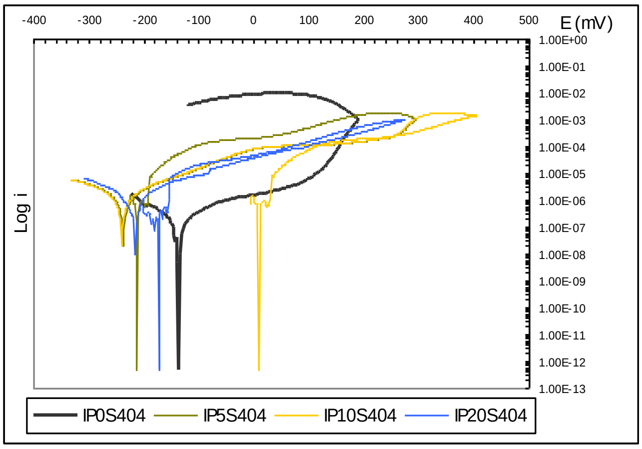

Figure 2 Cyclic voltammetry diagrams for composite deposits with different phosphorus concentrations finished at 420°C

For the samples with different phosphorus concentrations, thermally treated at 420°C, the presence of passive layers is always noted. Comparing all the samples treated at 420°C, the best corrosion behavior is that of the P10S40 sample, which presents the largest passive layer and a small area of the voltammetric curve.

3. CONCLUSION

Composite materials are innovative solutions created by combining two or more materials that possess different properties, obtaining structures that exceed the performance of each component material separately.

Composite materials are superior to classic materials, as they have the ability to modulate their characteristics by varying the components and the obtaining technique.

Due to their versatile properties, they allow the deposition of thin layers on metal surfaces, which adhere well and have improved performance, thus expanding the fields of application in engineering, protection and materials technologies.

Localized corrosion is a dangerous form of electrochemical degradation, which affects only certain points of the metal surface and can cause deep cracks without being visible from the outside.

This form of corrosion occurs in different forms such as pitting, intergranular, filiform or through cracking, each of which is determined by the structure of the material and the conditions of the aggressive environment.

Resistance to localized corrosion is determined by the material composition, the presence of inclusions, the surface geometry, the physicochemical properties of the layer, as well as the temperature and concentration of chlorides.

Electrodeposited layers of Ni-P/SiC composite material have remarkable mechanical and anti-corrosion properties due to the uniform dispersion of hard silicon carbide particles in the Ni-P matrix.

Cyclic voltammetry is a fast and efficient method, providing detailed information about the corrosion mechanisms and being essential in fundamental research on the electrochemical behavior of metal surfaces.

Cyclic voltammetry curves in saline environment revealed the presence of stable passive zones for all analyzed samples, which confirms the formation of effective protective films.

The P10S40 sample heat-treated at 420°C presents the best electrochemical stability, evidenced by the expansion of the passive layer and the reduction of the voltammogram area. These results highlight the essential influence of electrolyte composition and heat treatment in optimizing the anti-corrosion performance of Ni-P/SiC composite deposits.

The P10S40 composite sample heat-treated at 420°C records the best electrochemical stability, evidenced by the extension of the passive layer and the reduction of the voltammogram area. These results highlight the major influence of electrolyte composition and heat treatment applied in optimizing the anti-corrosion properties of electrodeposited Ni-P/SiC composite layers.

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