NANOSTRUCTURED MATERIALS DEVELOPMENT WITH APPLICATIONS TO THE PETROLEUM INDUSTRY

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ABSTRACT
The purpose of this work is a threefold; a) to produce both nanostructured Ni-Mo alloys and SiC nanoparticles, and b) to study the corrosion protective properties of the later when used as reinforcing nanoparticles in a water-based polymeric paint. After mixing the as-milled powders with paint, it was applied to steel sheets and then exposed to an electrochemical treatment. It was observed that, in the case of silicon carbides, when the carbide content concentration was 4%, the corrosion process in all substrata was directly related to carbon content. On the other hand, carbides contents of 0.5, 1.0 and 2.0% provide a good corrosion protection when used in polymeric paints. Also, Ni-Mo alloys had a satisfactory performance as corrosion inhibitors in all cases. The samples were studied by both scanning electron microscopy (SEM) and high resolution transmission microscopy (HRTEM), and analyzed by energy dispersive spectroscopy (EDX). X-Ray dispersion patterns of the as-milled powders were also analyzed.

Keywords: Water based paints, composite, nanoparticles, mechanical alloying

DESARROLLO DE MATERIALES NANOESTRUCTURADOS PARA APLICACIONES EN LA INDUSTRIA DEL PETRÓLEO

RESUMEN
Los objetivos del presente trabajo fueron; a) la producción de aleaciones nanoestructuradas de niquel molibdeno (Ni-Mo) y carburo de silicio (SiC), además b) estudiar las propiedades de estas nanoestructuras como inhibidoras de corrosión, cuando son usadas para reforzar pinturas poliméricas base agua. Las nanoestructuras fueron obtenidas por aleado mecánico y tratadas térmicamente para posteriormente ser mezcladas en distintas concentraciones con las pinturas, que fueron aplicadas sobre láminas de acero y después sometidas a un tratamiento electroquímico para evaluar la corrosión en las láminas. Se observó en particular, que en las muestras que contenían SiC, cuando la concentración de carburo era de 4%, el proceso de corrosión era fácilmente observable a simple vista; sin embargo, al disminuir el contenido de carburo a porcentajes del 0.5, 1 y 2% se observó que el carburo proveía una buena protección contra la corrosión. En el caso de las aleaciones Ni-Mo, para cualquier concentración se observó que existía siempre protección satisfactoria contra corrosión. Las muestras fueron estudiadas por microscopia electrónica de barrido (SEM-FIB), de transmisión de alta resolución (HRTEM) y se realizaron análisis químicos en el SEM-FIB por espectroscopía de energía dispersiva.

Palabras clave: Pinturas base agua, compósito, nanopartículas, aleado mecánico.

INTRODUCTION

Corrosion problems are so important that industrialized countries spend about 5% of their PIB in corrosion protection [1]. Adding alloying elements to metals often promotes corrosion resistance properties in materials. Other important treatments for corrosion protection involve the use of inhibitors or environment-inert coatings, which are resistant to chemical deterioration. Materials used for this purpose are metals, ceramics, polymers or mixtures of them, also known as composites [2]. Composites usually consist of a base material, reinforced with particles or fibers from another material. Sometimes corrosion protection coatings consist of alloyed particles reinforcing a polymer. Some alloys act as either mechanical reinforcements or catalysts; they inhibit or promote chemical reactions such as corrosion-isolating oxide film formation. Some of the well known materials used as reinforcement in corrosion protection systems are based on ceramics and glass, among them metallic carbides [3]. Metallic alloys and oxides, and metallic oxicarbides help to solidify the coating, providing hardness and improved optical properties. Spheroid and fiber shaped plastics and polymers help to increase the hardness, even when they can not withstand polimetil-metacrylate based corrosive acids. New polymeric materials and hybrid composites have profoundly impacted many human fields of activity, among them the oil industry, with the development of a wealth of applications for oil and gas piping and storage facilities protection [4,5]. Nanostructured polymeric particles allow for the development of inexpensive, environmentally friendly and efficient coatings. Similarly, polymeric coatings (either water or solvent based) can be reinforced with nanoparticles or nanostructured materials to obtain hybrid composites. Obviously the application properties of these hybrid materials will strongly depend upon the polymeric-matrix to nanoparticles interface interaction. Nanoparticles encapsulated by polymeric materials contribute to enhance interfacial adhesion and increases the coating workability.

Coatings regularly used to protect metals in the different oil and gas industry areas, as well as metallic coatings, are usually applied to metal surfaces at high temperatures, where the protective layers provide isolation (by simple barrier effect) or inhibition (when the metal absorbs a chemical component through the painting, obstructing corrosion). Often, used paintings are nitrocelulosic, synthetic, alquidic, phenolic, acrylic and epoxic), oil-based, polymeric (solvent-based), etcetera. Still the most used paintings are the acrylic epoxic and the solvent-based polymeric. However, and because of their high resistance to environmental corrosion, their chemical formulation is harmful to the environment, since they release certain substances. Thus, some environmental protection protocols such as Kioto´s, recommend using water-based paintings, which release the least substances. Nevertheless it is required to improve these paintings´ strength to corrosion, temperature and environment. Nowadays new ecologic paints reinforced with polymeric particles are being developed. But although they improve the corrosion-strength of the protective layer, these formulations can not withstand high temperatures as metallic or carbide reinforced paints do. Thus we consider relevant to develop a hybrid formulation consisting of a water-based painting, reinforced with polymeric nanoparticles plus nanostructured metals and carbides, and then to determine whether their overall performance, including corrosion strength, is improved.

For this work, we selected Silicon carbide (SiC) covalent ceramic nanoparticles as reinforcement material because of their inert behavior in corrosive environments with heat-exchange environments, where they have been often used. SiC nanoparticles will have a strong protective effect that it is important to analyze when they are used as reinforcement in polymeric composites. Ni-Mo alloys are widely used for corrosion protection in acidic and marine environments, systems were chemical processes are present and other devices, to control pollution [6].

EXPERIMENTAL PROCEDURE

Two powders mixtures, silicon-carbon (C-X% at Si with X= 50 and 75) and Nickel-Molibdenum (Ni-10%at Mo) were milled under an inert atmosphere. This was done in a Fritsch Pulverissette Analyssette Laborette mill (Type D.6102 No.1861) at 700 rpm, with powders to balls weight ratio 1:10, for five, ten and fifteen hours. The 15h resultant powders were heat-treated at 800°C for 15 minutes, after that they were mixed with anti-corrosive paint at room temperature and applied to steel sheets. The paint was elaborated by polymerization in emulsion using a semi-continuous reactor, and consisted of acrylic styrene particles with diameter sizes around 400nm.

The particles were functionalized with acrylic acid (AA), to obtain a protective effect against corrosion, with the following functionalization degrees: 0, 1, 2, 4, 6 y 10 % (AA). Permeability percentage, water adsorption and superficial adhesion were measured according to the ASTM-E-96 standard. Finally Powder samples were characterized by X-Ray Diffraction in a Siemens D-500 difractometer using Cu Kα (λ=1.54 Å). Table 1 presents a summary of the results. The samples were studied with two instruments, a Scanning Electron Microscope (SEM) SEM /FIB NOVA 200 with point resolution (PR) of 1.7 Å and a High Resolution Transmission Electron Microscope (FEI Tecnai 20) with PR of 1.8 Å.

RESULTS AND DISCUSSION

Characterization of powder samples by X-Ray diffraction are reported in table 1. As shown in Table 1, it could not be obtained a silicon-carbide single phase in the C-50%at Si compound after 15 hours milling at 700 rpm, nonetheless in the as-obtained remaining samples it was possible to obtain a one-phase homogeneous material. However we decided to use all the paintings samples to be developed, to determine the impact of both homogeneous and inhomogeneous reinforcements on the paint properties. In the nickel-based alloy case, it was possible to obtain one single phase after 15 hours milling. Table 1 presents lattice parameters and the existing phases.

Table 1 XRD results for 15 h mechanically alloyed samples.

Sample	**Phases Observed in samples**	**Lattice Parameters**
C-50% at. Si	Cubic Si,	a_{Si} = 5.42 Å
	Hexagonal Graphite	$a_{graphite}$ = 2.465 Å , $c_{graphite}$ =6.721 Å
	Hexagonal Moissanite-6H CSi	a = 3.073 Å c =15.08
C-25% at Si	Hexagonal Moissanite-6H CSi	a = 3.073 Å c =15.08 Å
Ni-10%At Mo	Cubic FCC	a = 3.558 Å

Fig. 1 presents a SEM micrograph of a water-based paint sample reinforced with polymer spheres of about 200nm in diameter. Polymer reinforcement nanospheres have homogeneous sizes and apparently are hollow. Fig. 2 presents the SEM micrographs of a) C-50%At Si, b) C-25%atSi and c) Ni-10%at Mo milled powders. In the case of carbides (Figs. 2a, 2b), the as-milled powders had a flake like shape with smooth surfaces. This sample presents a lamellar structure. Average flake diameter size for sample C-50% at. Si, is 12 μm; and for sample C-25% at. Si is 750 nm. Fig. 2c) Ni-10%atMo shows that the observed powder shape is different from that of the carbides; here, particles are semi-rounded some having one flat face and rounded borders, the lamellar structure is absent in the image.

Samples C-50% at Si and C-25%at Si were observed after heat treatment of milled powders by electron transmission microscopy. In sample C-50%At Si particles with diameter sizes of 1μm and several crystalline phases are observed.

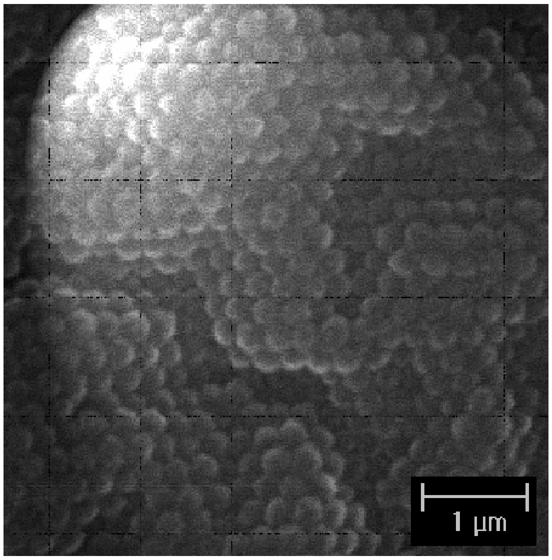

Fig. 1 SEM micrograph of a Water-based paint sample

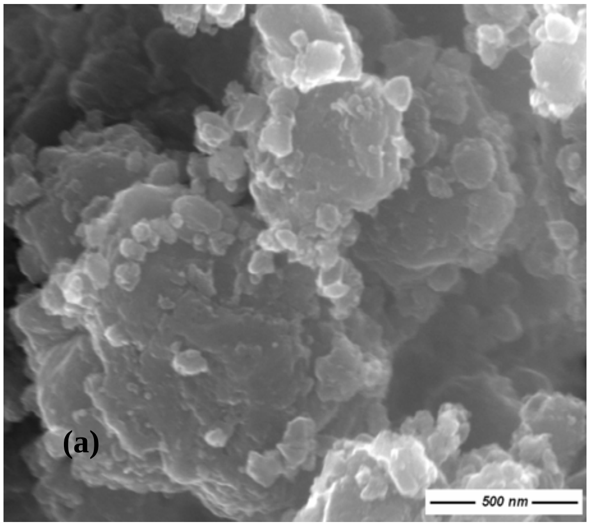

Fig. 2 a) C-50% at Si SEM micrograph

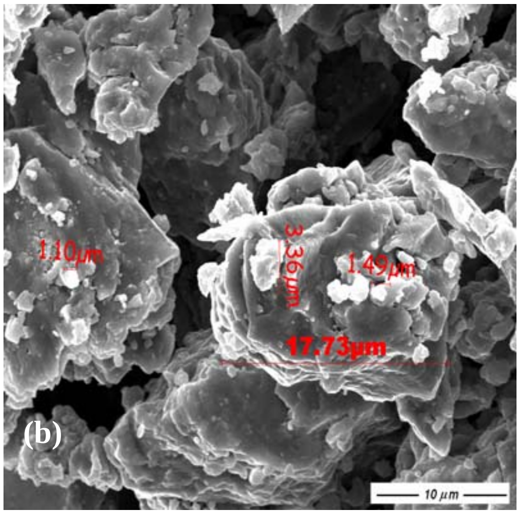

Fig. 2 b). C-25%at Si after 15 h milling micrograph.

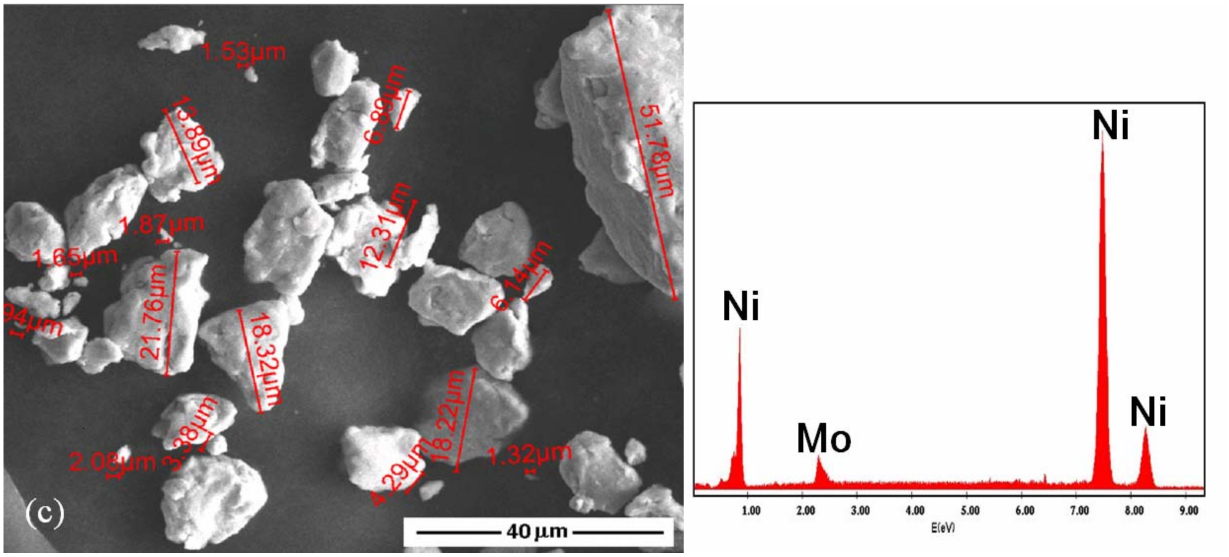

Fig. 2c) Ni-10%at Mo and its chemical analysis by EDS (d)

Figs. 3a) and 3b) show electron micrographs corresponding to the sample C-25%at Si. Fig. 2b) shows both, a 5nm SiC particles and its fast Fourier Transform where an hexagonal point array is observed. Fig. 3 shows C-50%At Si (sample 1) and C-25%at Si particles (sample 2) after heat treatment of milled powders. The first sample (Fig. 3a) depicts particles smaller than 1 µm in diameter. The second sample (Fig. 3b) shows particles of around 5 nm. The lattice parameters calculated for SiC, using interplanar measurements obtained by fast Fourier Transform FFT from Digital Micrograph Program, were a = 3.067 Ǻ, c =15.10Ǻ. Fig. 3c) shows a Ni-10%At Mo alloy micrograph. Here policrystallinity is apparent. After measurement of interplanar distances on several areas of the sample it was determined that the average net parameter by this technique is a = 3.61 Ǻ, which is 2% off.

Fig. 4 presents Permeability %, water adsorption and superficial adhesion plots results. The best adhesion and adhesion to surface occur in samples with small amounts of SiC nanoparticles. Fig. 3c shows a Ni-10%at Mo alloy sample where a plane (111) is observed. The alloy

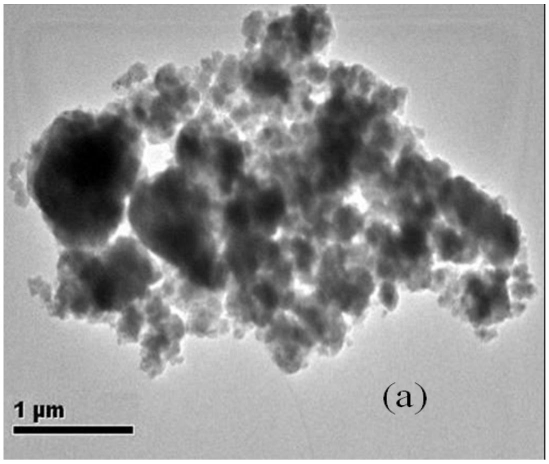

Fig. 3. a) C-25%at Si particles.

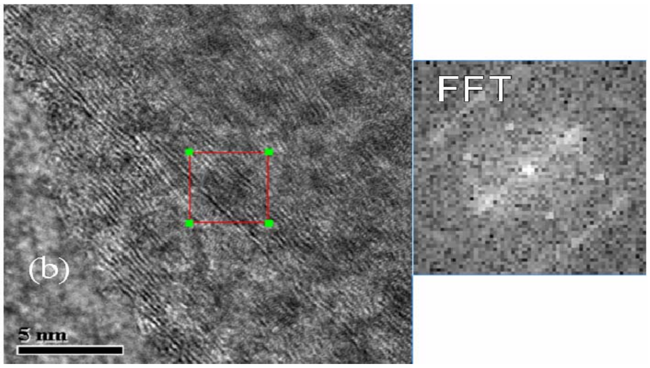

Fig. 3. b) SiC nanoparticles and its fast Fourier Transform

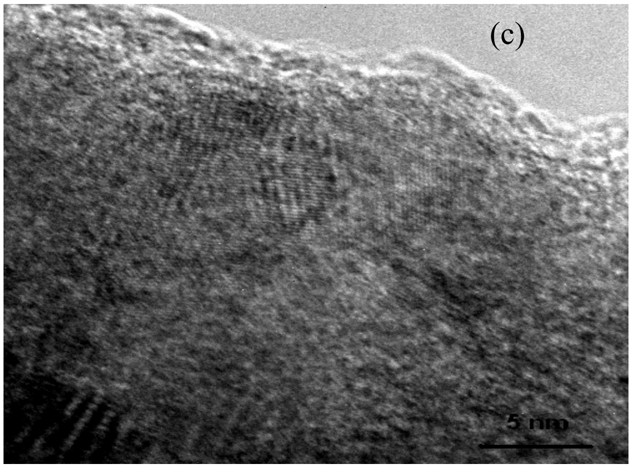

Fig. 3 c) Nanostructured Ni- Mo alloy

structure is FCC and its lattice parameter measured from the micrograph was a = 3.56 Å, which is in good agreement with that of XRD.

Micrographs in Fig. 5 correspond to a) steel sheets painted with both, carbides and b) alloy particles reinforced paints. It was observed a homogeneous powder dispersion and instantaneous corrosion inhibition at low percentages (0.5, 1.0, and 2.0%) of powders in the paint.

For the Silicon carbide, it was apparent a superficial protective layer, the thickness of which is related to the carbon concentration in the carbide. It was observed both, an apparent instantaneous corrosion inhibitive effect and good carbides dispersion inside the polymeric film at 0.5, 1.0 and 2.0% carbide dispersions in the polymeric colloid. After the paint application on carbon steel, it was appreciated an accelerated instantaneous corrosion phenomenon at all strata, directly related to the carbon concentration, particularly beyond the material's 5% wt.

The reason for the occurrence of these phenomena is observed in Fig. 5, where carbide particles are located out of painted region.

As it can be seen, they avoided the polymer and reside at the boundary between the metallic sheet and the polymer, forming a carbide cover film which, in low concentrations, protects the material. A thin ceramic layer could stop the corrosion development. If the percentage in weight is greater than 5%, then it promotes corrosion. Ni-10%atMo alloy behavior in the paint was completely different, regardless the amount of Ni-Mo powders in the paint, the particles remain inside it, promoting corrosion protection.

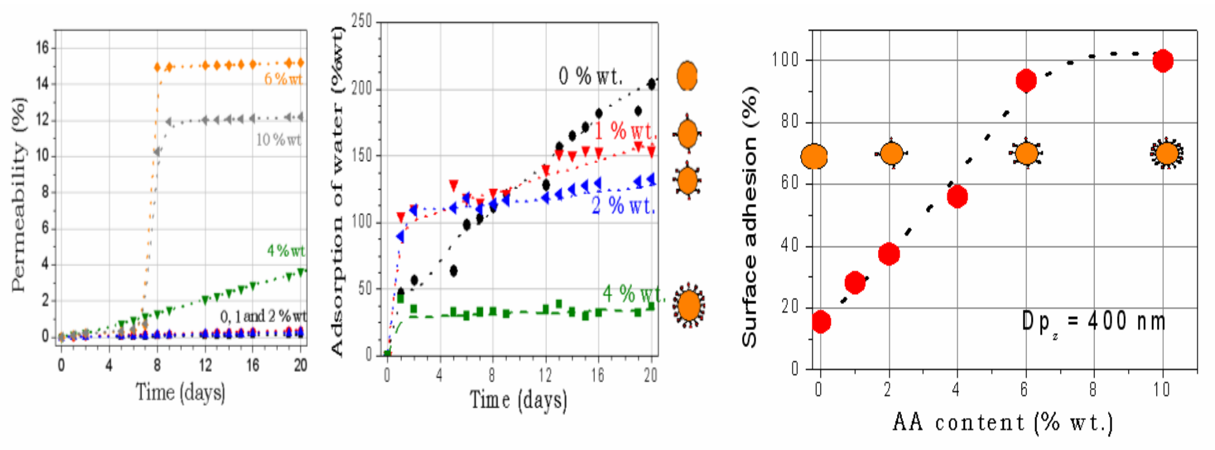

Fig. 3 a) Permeability %, b) water adsorption and c) superficial adhesion

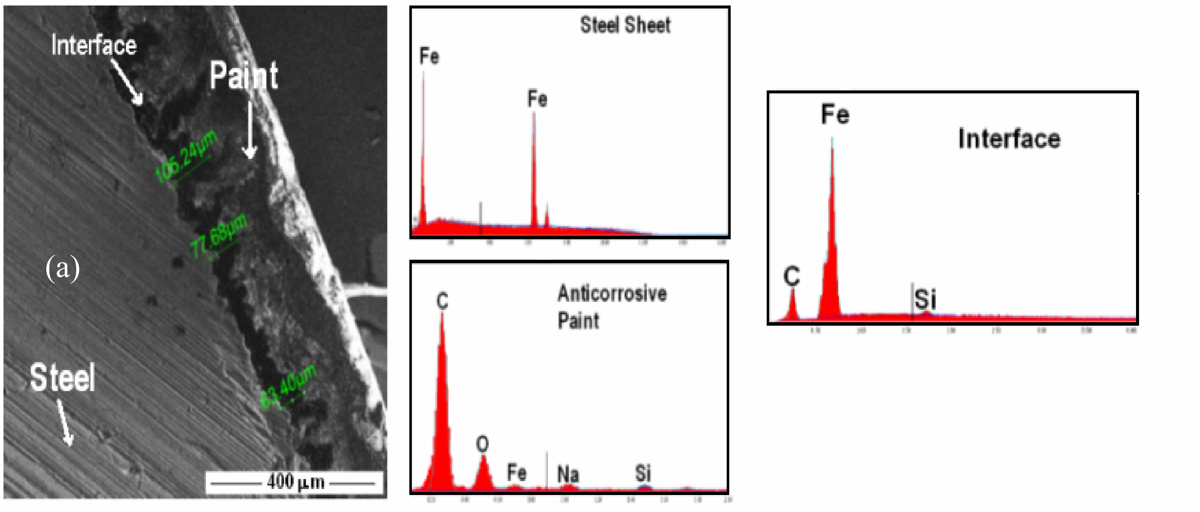

Fig. 4 a) nanoparticles behavior (distribution) and EDS at different regions on a painted steel sheet

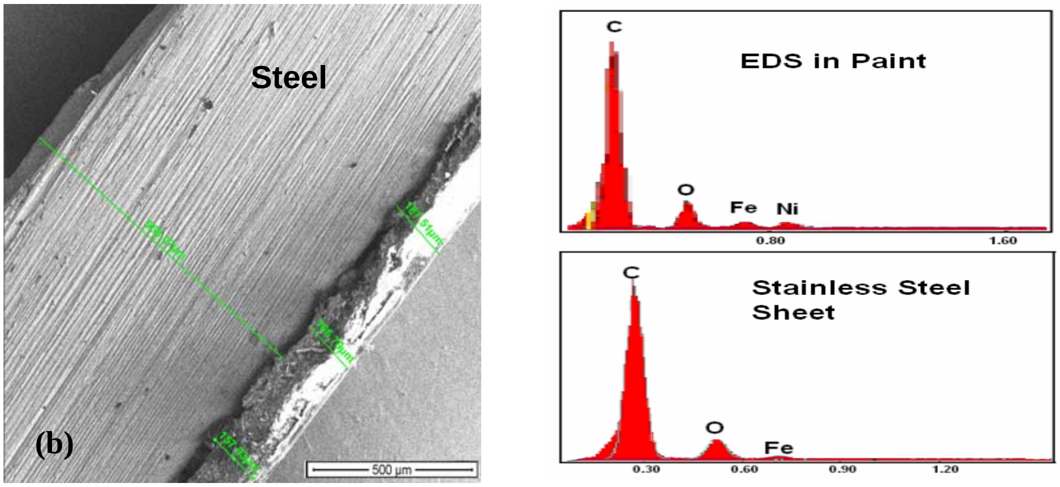

Fig. 5 b) Ni-10%atMo alloy behavior an local EDS in two regions

CONCLUSIONS

Corrosion phenomenon, in the reported experiment, is function of the carbon content for carbide reinforced water base paints. Silicon-carbide nanoparticles are hydrophobic and tend to form a layer at the metal-paint interface. It is intriguing how the carbide particles mobility is towards the metal-polymer interface and not towards the paint layer surface, as it happens in the painting production process; probably due to change in electric properties in the solidified panting layer, as opposed to the liquid one. The study of this phenomenon could lead to the development of nanostructures thin layers on metallic surfaces without the need of high temperatures, particularly in the carbide coating field.

Nickel-molybdenum particles were kept inside the paint and promoted corrosion protection, regardless the concentration used. Here it is interesting to observe that the painting polarity do not repel bimetallic particles. This happens precisely because of its high electric conductivity, which promotes good nanostructures retention in the polymer, so that if it is required to produce a low cost and corrosion protective water-based polymer, the most appropriate nanostructure is that having the highest electric conductivity, particularly bimetallic systems which are corrosion inhibitors by themselves.

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