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# **The Use of Electrochemical Noise in the Study of Nanometric Coatings**

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Additional information is available at the end of the chapter

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## **1. Introduction**

Nanostructured materials are a new class of materials that are distinguished from conventional polycrystalline materials by their extremely fine crystallite size from 100 nm down to several nm. Interest to nanostructured materials has been growing rapidly due to reports showing that they possess remarkable mechanical, magnetic and optical properties.

R. Smalley, R. Curl and H. Kroto discovered a new form of carbon (carbon-60). Thereafter, in 1993, came the discovery of “carbon nanotubes”, by S. Iijima and D. Bethune. Today nanotubes have been joined by nanocrystals, nanowires, nanoroads and other nanoforms.

Highly sophisticated surface related properties, such as optical, magnetic, electronic, catalytic, mechanical, tribological, chemical as well as magnetic, electronic and optical can be obtained by advanced nanostructured coatings, making them attractive for many modern industrial applications. There are many types of design models for nanostructured coatings, such as nano-composite coatings, nano-modulated multilayer coating, nano-graded coatings. Design of nanostructured coatings needs consideration of many factors, e.g. the interface volume, crystallite size, single layer thickness, surface and interfacial energy, texture, epitaxial stress and strain, etc., all of which depend significantly on materials selection, deposition methods, processing parameters and what is specially important service condition of coated parts [1].

Reduction in the weight of engines is a key factor in improving the fuel efficiency. The use of lightweight materials has become more prevalent as car manufacturers strive to reduce vehicle weight to improve performance, lower fuel and oil consumption, and to reduce emissions [2]. Employment of nanotechnology in current and future automotive, aero and other engines will

go long way in solving energy crisis [3]. Most manufacturers have replaced cast iron engine blocks with lightweight and low-cost aluminum-silicon crankcases. Several Al based alloys and metal-matrix composites are in use.

The function of a protective coating is to prevent industrial vapors, liquids, solids or gases from coming into contact with metallic structures. Paints have been used which offer only a physical barrier. Engine components are subjected to severe environmental stimuli for corrosion. The higher temperature, fuel and combustion products mixed with oxidizing atmosphere and thermal shock add to the corrosive media. Diesel engine and internal combustion (IC) engine even produces sulfuric and formic acid as a product of combustion under certain conditions such as cold weather [4].

Energy producing fossil steam turbine and boiler components operate in a severe environment at elevated temperatures. To protect these components from degradation by the operating environment, MCr (M: Fe, Ni or Co) coatings are used in the industry [5]. In particular Fe-Cr or Ni-Cr are predominantly used. These coatings provide corrosion / oxidation protection by formation of a stable and slowly growing protective oxide scale such as  $\text{Cr}_2\text{O}_3$  on the external surface, which separates the component substrate in contact with the corrosive environment.

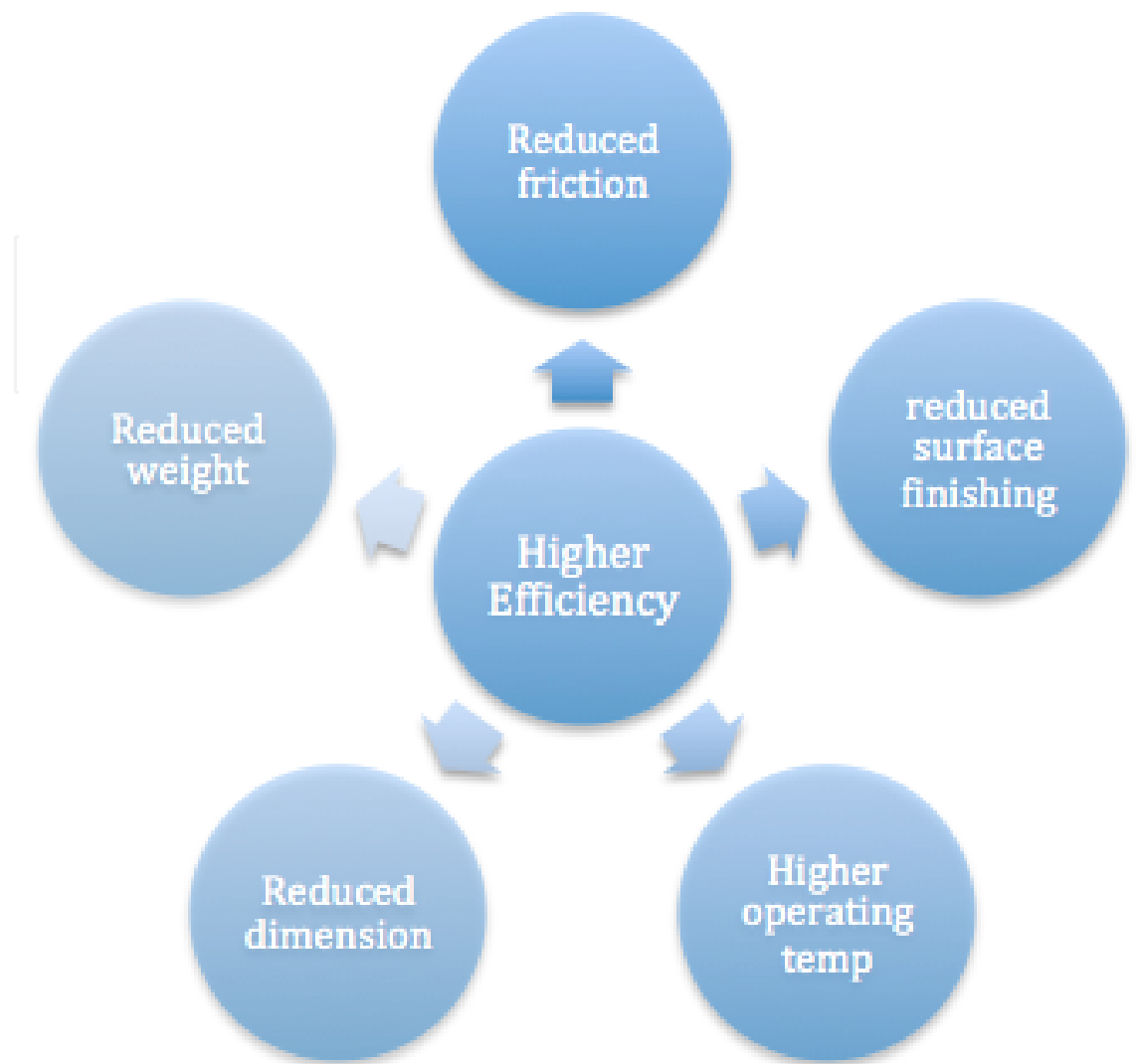
Coatings, particularly nanocoatings can help to improve performance and life of engines. Higher efficiency is obtained from various aspects of coatings, like reduced: dimension, weight, surface finishing, friction, etc., as presented in figure 1.

Thin films are fabricated by the deposition of individual atoms on a substrate. A thin film is defined as a low dimensional material created by condensing atomic – molecular – ionic species of matter. Thin films have been used for more than a half-century in making many devices and coatings, however, thin film technology is still being developed on a daily basis since it is a key in the development of new materials such as nanometer materials [6]. Thin film processing also saves on energy consumption in production and is considered an environmentally being material technology for the next century.

Thin films are deposited on a substrate by thermal evaporation, chemical decomposition or the evaporation of source materials by the irradiation of energetic species. The thin films origin starts with a random nucleation process followed by nucleation and growth stages. Nucleation and growth are dependent upon various deposition conditions, such as growth temperature, rate and substrate chemistry. Film microstructure, defects and film stress depend on the deposition conditions at the nucleation stage.

The deposition process using the irradiation of energetic species is known as sputtering, that was first observed by Bunsen and Grove 150 years ago. However, this process has a low level efficiency and an optimum sputtering design is necessary for each material.

The sputtered structure modifies the material properties, they may show features that are different from the bulk materials in terms of mechanical strength, carrier transportation, superconductivity, ferroelectricity, magnetic and optical properties. These films may be characterized by a strong internal stress and a number of lattice defects. The defect density [4] in nanoscale materials is very high, but not high enough as in amorphous. As depicted in fig.



**Figure 1.** Aspects that provides higher efficiency to coatings.

(1-j), hardness as a function of grain size, Hall-Petch relation (hardness for a polycrystal with average grain diameter  $d$ ,  $H_d$ =hardness of single crystal,  $H_0+kd^{-1/2}$ ) predicts increase of hardness and flow stress as the grain size decreases. However, as the grain size is very small (in the range of 100 nm), the deformation mechanism changes from dislocation controlled slip to grain boundary sliding increasing plasticity at the same time. When the grain size further reduces almost to become amorphous, the material behaves in visco-elastic manner. This provides a global maximum in properties such as hardness, flow stress, toughness, ductility and thermal insulation (because the conductivity of nanoscale material is much less in certain metallic system such as aluminum due to phonon scattering by high defect density) when the grain size is in nanoscale.

Thin film process is also essential for making nanometer materials. Nanomaterials are defined as materials thereof in other materials, having one or more dimensions of nanometer size ( $1\text{nm} = 10^{-7}\text{ cm} = 10\text{ \AA}$ ). Nanomaterials are classified in three types: Zero-dimensional (three dimen-



sions of nanometer size), One-dimensional (two dimensions of nanometer size) and two-dimensional (one dimension of nanometer size). Nanostructured thin film and coatings possess properties different to homogenous materials due to the deliberate engineering of nanoscale features into the structure [7, 8].

Much of research activity is focused on the synthesis and processing of nanostructured bulk materials [9, 10, 11]. In spite of growing interest and research activities to the nano-structured multifunctional coatings in the last years there is still a lack in understanding the effect of processing methods and processing parameters on microstructure and properties of nanostructured coatings including those that are used or are intended for use in wear and oxidation/corrosion service conditions. Attack of the corrosive medium on the substrate is severe due to the defects within the coating (such as micro-cracks, pores, pinholes, grain boundaries, etc.) [12, 13, 14].

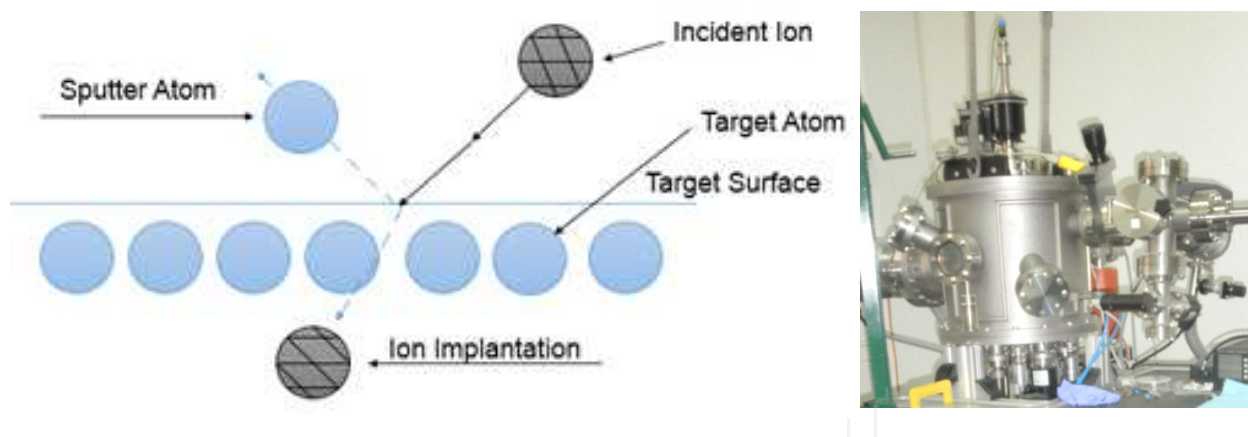
The potential market for coatings and coated objects is very wide range from large scale Steel, Ni and Ti alloys sheet products to cutting and processing tools; wear resistant parts for automotive, aircraft / space and chemical industries; biocompatible and wear resistant surgical implants down to miniature parts for electronics and microelectronics. Another alternative is the use of multilayer metallic coatings, but very few studies are reported [15,16, 17, 18, 19, 20].

## 2. Deposition process

The physical process is composed of the physical vapor deposition (PVD) and the chemical processes are composed of the chemical vapor deposition (CVD) and the chemical solvent deposition. The PVD process is divided in two categories: thermal evaporation and sputtering. The thermal evaporation comprises evaporating source materials in a vacuum chamber below  $1 \times 10^{-6}$  torr ( $1.3 \times 10^{-4}$  Pa) and condensing the evaporated particles on a substrate. The thermal evaporation is conventionally called vacuum deposition [7, 21, 22, 23].

In the sputtering when a solid surface is bombarded with energetic particles such as accelerated ions, surface atoms of the solid are scattered backward due to collisions between the surface atoms and the energetic particles (figure 2). This phenomenon is called sputtering. When a thin foil is bombarded with energetic particles, some of the scattered atoms transmit through the foil. Cathode sputtering is a cathode disintegration and the can say impact evaporation. Several sputtering systems exists: diode, magnetron and ion-beam (McClanahan and Laegreid, historical review of sputtering deposition) [24].

In magnetron sputtering, a magnetic field is superposed on the cathode and glow discharge, which is parallel to the cathode surface [25, 26, 27]. The electrons in the glow discharge show cycloidal motion, and the center of the orbit drifts in the direction of  $E \times B$  with the drift velocity of  $E/B$ , where  $E$  and  $B$  denote the electric field in the discharge and the superposed transverse magnetic field, respectively. The magnetic field is oriented such that these drift paths for electrons form a closed loop. This electron-trapping effect increases the collision rate between the electrons and the sputtering gas molecules. This enables one to lower the sputtering gas



**Figure 2.** Sputtering process and sputtering chamber.

pressure as low as  $10^{-5}$  torr. In the magnetron system, the magnetic field increases the plasma density, which leads to increases in the current density at the cathode target, effectively increasing the sputtering rate at the target. Due to the gas's low working pressure, the sputtered particles traverse the discharge space without collisions, which results in a high deposition rate.

Sputtering is accomplished by an energetic particle bombarding a target surface with sufficient energy (50 eV – 1000 eV) to result in the ejection of one or more atoms from the target. Typically, the target, which is called the cathode and is the material to be deposited, is connected to a negative voltage supply [28]. The anode is the substrate. In the sputtering process, the positive ions from ionizing gas strike the target surface and remove neutral target. The neutral atoms leave the target, condense on the substrate surface and form into thin films. In magnetron sputtering a magnetic field confines the plasma around the surface of the target.

Gheriani R. [29] analyzed the effect of substrate surface ion bombardment etching on reaction between chromium thin films (magnetron sputtering deposited) and Steel substrates (1 wt.% C). The study was carried out by X-ray diffraction, Auger electron spectroscopy, SEM (scanning electron microscopy) and Vickers micro-hardness measurements. They found that the reaction between carbon and chromium atoms leads to the formation and growth of  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_6$  carbides in the considered temperature range. A significant increase in micro-hardness and adhesion of the coating films is associated with ion pre-cleaning and with increasing annealing temperature.

The recent evolution of coating technology allows deposition of multilayer coatings, with enhanced mechanical and corrosion behaviors. In 2010, Cekada M., et.al. [30], did an analysis of the diffusion processes in Al/Cr, Al/Fe and Cr/Fe bimetallic multilayers. They deposited 6 layers by sputtering deposited, and applied different annealings 240 – 650 °C, for measure depth distributions of elements in the films. Auger depth profiling was conducted, and finds that in Al/Fe and Cr/Fe systems the dominant contribution to the depth was roughness. The activation energies are rather low, which can be attributed to the porous microstructure of films.

Grips W. [31] studied the electrochemical behavior of single layer CrN, TiN, TiAlN coatings and TiAlN/CrN multilayer coatings prepared by magnetron sputtering. They analyzed the corrosion behavior in 3.5% NaCl solution by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The potentiodynamic polarization measurements showed that for all the coatings the corrosion potential shifted to higher values as compared to the uncoated substrate. Similarly, the corrosion current density decreased for coated samples, indicating better corrosion resistance of the coated samples. The multilayer coatings exhibited superior corrosion behavior as compared to the single layer coatings. The values of the charge transfer resistance and the pore resistance showed gradual increase from TiN – CrN – TiAlN/CrN multilayers. For all the coated samples, the coating capacitance and the double layer capacitance did not show significant variations, indicating that the surface of the coated substrate was less affected.

The thermal spraying process has commonly been accepted as the most effective and economic method for the fabrication process of the nanostructured coatings, and thus has contributed in a wide variety of high performance applications requiring improved wear, erosion, corrosion, and thermal insulation resistance [32, 33, 34]. In thermal spraying, feedstock materials in the form of powder or wire are fed into a heat source of spray equipment, where they are fully or partially melted and accelerated in a gas stream toward a substrate to be coated. The high-temperature exposure and the following rapid quenching, which intrinsically involved thermal spraying, can either improve or deteriorate the nano-scale microstructures of the coatings. Therefore, several challenges still remain in terms of feedstock preparation and processing itself, and an intense research. [35] Studied the properties of nanostructured thermal spray coatings WC-Co. They present Cr<sub>2</sub>O<sub>3</sub> based solid-lubricant coating as one of new applications of the nanostructured coatings and its mechanical properties are compared to those of conventional counterpart. With the results, they finds that the advanced nanostructured WC-Co feedstock powders having desirable morphology was successfully fabricated and the resultant coatings showed significant improvement of wear-resistance in comparison with the conventionals. Also concludes that fine mixture of multi-components inside each powder particle of the nanostructured feedstock results In not only homogenous microstructure but also high performance of the coatings.

Electroplating is the application of a metal coating to a metallic or other conducting surface by an electrochemical process [36, 37, 38]. The article to be plated is made the cathode of an electrolysis cell through which a direct electric current is passed. The article is immersed in an aqueous solution containing the required metal in an oxidized form, either as an aquated cation or as a complex ion. The anode is usually a bar of the metal being plated. During electrolysis metal is deposited on to the work and metal from the bar dissolves.

Cr electroplating is regularly employed to coat the piston rings in engine. Different types of ferrous-based powders, containing C, Si, Sn, Ni, Cr, Mo, Cu, Ti, V and B, etc., are also employed to coat Al alloys for diesel engine applications [4]. Atmospheric plasma spray “APS” and Laser Surface Engineering “LSE” are extensively used for thermal barrier coating of nickel based super alloys component of aero and gas turbine engine components [39,40].

### 3. Corrosion

The high corrosion resistance of hard coatings used for decorative and / or wear protection applications is well known. However, when deposited on less noble materials like Steel, brass, Al or Mg alloys, the coated parts suffer from severe corrosive attack due to inherent coating defects or in homogeneities (cracks, pores, transient grain boundaries) [41, 42]. They opens possible paths for the corrosive media to reach the substrate. In the case of a less noble substrate material galvanic corrosion at the substrate will occur. This kind of corrosion is localized to the defect area and is characterized by the anodic dissolution of the substrate material with a high anodic current density at the defect site. It is also called galvanic corrosion and in the case of pores and pinholes as defects it is called pitting corrosion. The intensity of the corrosive attack depends strongly on the potential difference of the coating and the substrate material in the respective electrolyte. If this potential difference is large enough, galvanic corrosion will occur. A lot of research has been undertaken to get rid of this problem. There are several ways to improve the corrosion resistance of coated parts: thicker coatings [43], dense coatings (fine grained or amorphous), elimination of droplets (by modification of the deposition process: pulsed magnetron sputtering, filtered cathodic arc, etc), multilayers [44], duplex coatings [45], intermediate etching [46], alloying of the hard coating with less noble elements [47].

Fenker M. [48], studied the corrosion behavior of Ti and Cr multilayer coatings in sodium chloride media by circuit potential measurements, potentiodynamic corrosion tests and salt spray tests. The CrN, Nb<sub>2</sub>N, Nb-C:H, TiN, TiMgN multilayer depositions were carried out. The substrate material was high speed steel. The corrosion behavior was electrochemically studied using open-circuit-potential measurements and potentiodynamic corrosion (polarization) tests. In their results they show that all measures lead to an improvement of the corrosion behavior in potentiodynamic polarization test in NaCl environment. Only one measure was able to avoid red rust sites after 24 h of salt spray testing. This was the alloying of TiN with magnesium with Mg contents up 17 at.%. The electrochemical effect of this alloying is a reduction of the electrochemical potential with increasing Mg content in a NaCl solution. As a consequence, the potential difference between the coating and the steel substrate is reduced and, therefore, the driving force for galvanic corrosion can be diminished.

Al coatings are candidates for the cathodic protection of construction steel due to their good corrosion resistance in aggressive media. However the mechanical properties and pitting corrosion sensitivity of some Al in chloride media have limited its application. Different alternatives have been investigated to improve mechanical resistance and sacrificial behavior of Al based coatings on steels. The addition of transition metals like Cr or Ti have been studied, and the best result there are been obtained for Al-Cr alloys deposited by magnetron sputtering, and is has been reported that the addition of Mo or Mg could limit the sensitivity to pitting [49]. Creus, et.al. [50] developed a study to improve the mechanical properties of Al based coatings, conserving a sacrificial protection characteristics. Al/Cr multilayer architectures, deposited by dc magnetron sputtering, were tested. Three architectures composed of a bilayer, a multilayer and a nanolayer were compared. The mechanical properties and corrosion resistance in saline solution were discussed and compared to single Al and Cr coatings. The open circuit potential



and polarization resistance ( $R_p$ ) of the coated substrate versus time were recorded during long immersion tests. A cyclic polarization technique was used to estimate the pitting resistance. They show that configuration parameters like composition of the layers and the thickness influence the mechanical and corrosion properties. The Al/Cr bilayer coating does not lead to significant improvement of mechanical and corrosion properties compared to single Al coating. The mechanical properties are increased for the multilayer configurations leading to the best behavior for the nanolayer coating, and multilayer architectures seem to be a way to improve the mechanical properties of Al based coating.

The long term oxidation behavior of nanocrystalline 304 SS and 304-4Al coatings has been investigated by Cheruvu and Wei [51]. The coatings were deposited on 304 SS samples using a plasma enhanced magnetron sputtering process. Cyclic oxidation tests were conducted on the coated and uncoated samples at a peak temperature of 750°C for up to 1000 one-hour thermal cycles between the peak and room temperature. The addition of 4% Al stabilized the  $\alpha$ Fe structure and prevented the formation of the  $\sigma$  phase. The external oxide scale on the coated samples exhibited good spallation resistance compared to the scale on the uncoated samples. The ultrafine grain structure of 304SS coating had promoted selective oxidation of Cr and the addition of Al to the 304SS coating promoted selective oxidation Al over Cr.

Liu, et. al. [52] have investigated the effect of grain size on the protective external oxide scale formation on Ni-20Cr-3Al nanocrystalline coatings. Their results showed that the external oxide formed on the fine grained coatings varied from  $\text{Cr}_2\text{O}_3$  to  $\text{Al}_2\text{O}_3$  as the grain size decreased from 500 to 50 nm. The ultra fine grain structure promotes grain boundary diffusion, which facilitates selective oxidation of Al over Cr. The critical Al or Cr required for the formation of a continuous  $\text{Al}_2\text{O}_3$  or  $\text{Cr}_2\text{O}_3$  is significantly lower for the ultra-fine grains coatings than that for conventional materials.

Corrosion generally refers to the electrochemical attack process that takes place on most of metals. Metals are susceptible to suffer this attack because they have free electrons and are capable of establishing electrochemical cells in their structures. But the thermodynamic energy or chemical energy stored in them, varies from one metal to other. The energy is higher for numerous metals (Mg, Fe, and Al), and relatively low for other metals like Ag, Au, Cu, etc. Many metals experiments corrosion when in contact of an electrolyte and any contaminant like Cl. From an engineering point of view, corrosion is a progressive and destructive process that compromises structural integrity and represents an enormous economic loss [53].

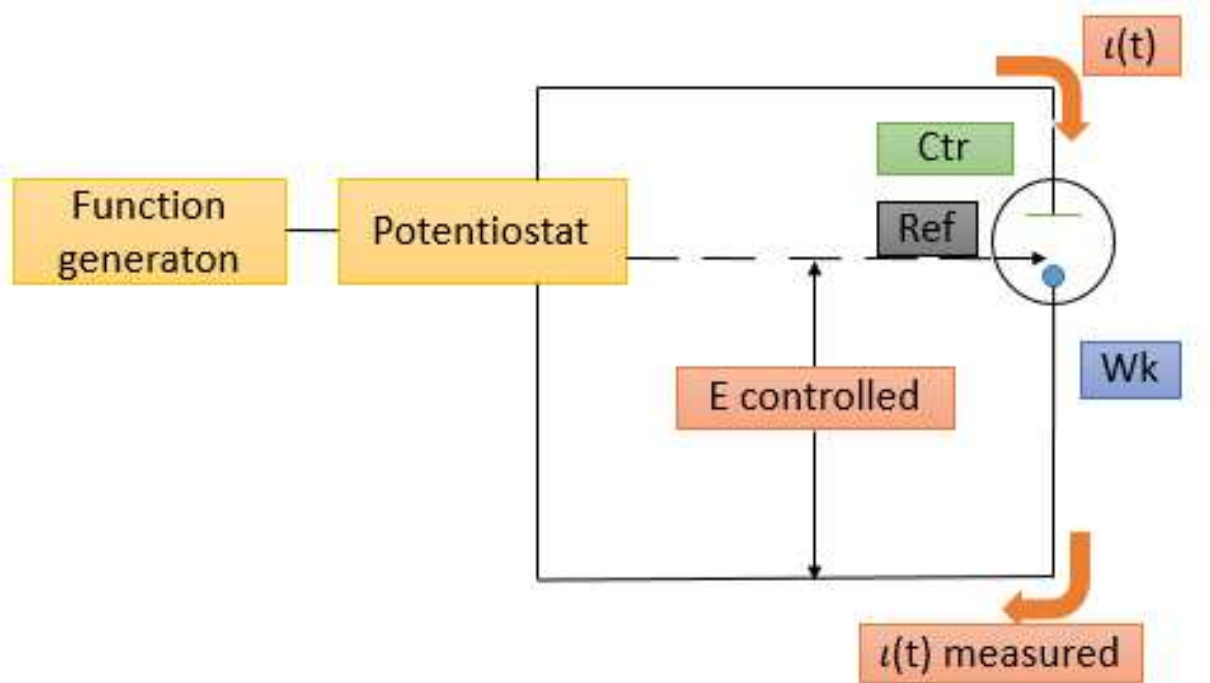
During corrosion, at least two electrochemical reactions, an oxidation and a reduction reaction, occur at a metal-electrolyte interface. Because corrosion is due to an electrochemical mechanism, it is clear that electrochemical techniques can be used to study corrosion reactions and mechanisms. Then many techniques have been used to monitor the rate of corrosion and to study both, the corrosion and its inhibition mechanisms.

### 3.1. Electrochemical Noise (EN)

In a typical experimental system, an instrument known as a potentiostat has control of the voltage across the working electrode – counter electrode pair, and it adjusts this voltage to

maintain the potential difference between the working and reference electrodes (which it senses through a high-impedance feedback loop) in accord with the program defined by a function generator, see figure 3.

The potential and the current can be measured, stored, and analyzed with this method. The evaluation of spontaneous fluctuations of the current and potential of corroding electrodes, which is commonly referred to as electrochemical noise “EN” analysis, has been studied extensively [54, 55, 56]. EN is a generic term for low-level random fluctuations, usually less than 1 millivolt and nano to micro amps, in a corroding material.



**Figure 3.** Experimental arrangement for controlled potential experiments.

Eden in 1986 [57], introduced a new parameter that depends on voltage and current standard deviations, correlate the EN resistance ( $R_n$ ) with polarization resistance ( $R_p$ ):

$$R_n = \frac{(\beta_a)(\beta_c)}{2.3(i_{corr})(\beta_a + \beta_c)} \quad (1)$$

where:

$R_p$  = polarization resistance

$\beta_a$  = anodic Tafel constant

$\beta_c$  = cathodic Tafel constant

$i_{corr}$  = corrosion current ( $A\ cm^{-2}$ )

The corrosion rate is related to the polarization resistance by Stern-Geary:

$$i_{corr} = \frac{B}{R_p} \quad (2)$$

where B is the Stern-Geary coefficient polarization resistance is the slope of the steady-state potential current curve at the corrosion potential. In 1993, Mansfeld and Xiao [58] have reported some data and correlations between  $R_p$  and  $R_n$ .

To measure be use three identical electrodes placed in an electrochemical cell. One electrode is connected like working electrode WE, another like reference RE, and the remaining like ground, GE. Then the potential noise is recorded with the RE and current is recorded with the WE. The GE enables the passing of the current. The current and potential transients are recorded simultaneously. However, EN requires monitoring of very small signal fluctuation, which may be susceptible to outsider sources of noise if improperly used.

The EN technique has some advantages related other corrosion monitoring techniques (e.g. linear polarization resistance or potentiodynamic curves), mainly the absence of an applied voltage or current perturbation, and that the measurements can be taken at very short intervals. The difficulty in the interpretation of time series, graphs and data is the major disadvantage.

This analysis technique is so versatile that it can be applied to various materials, applications and processes. Recently Estupiñan L., et.al [59], performed a statistical analysis of electrochemical noise transients to correlate with the morphologies observed by SEM in different steels, in order to identify the type of corrosion developed; and Almeraya C., used EN to study Ni-Mo alloys fabricated by mechanical alloying and densified by spark plasma sintering [60]. García H., et.al [53] performed in 2009 a comparative study on carbon steel, of three corrosion resistant hybrid coatings, by using a loop reactor to measure the corrosion by means of the EN technique. They obtain the time series responses of current and potential, and by means of these signals, the EN resistance ( $R_n$ ) was calculated according to  $R_n$  equation. Find that the hybrid-bi-component coating produced the highest resistance and consequently exhibited the lowest corrosion rate.

### 3.1.1. Study of nanometric coatings

In this chapter we present the results of a study in order to know the characteristics and corrosion resistance of nanostructured bilayer coatings. As discussed before, Al alloys are candidates in aerospace industry due to their corrosion resistance. However, their pitting corrosion sensitivity limits its application in many marine environments. Have been investigated that addition of Cr improve the mechanical resistance and sacrificial behavior. In this work, electrochemical noise has been carried out to investigate the corrosion behavior of Al and Cr coatings on Aluminum alloys AA6061-T6 and AA2024-T3, with different architecture organization (Al/Cr y Cr/Al).



### 3.1.2. Experimental methodology

Coatings consisted of Al and Cr deposited by magnetron sputtering on aluminum alloys AA6061-T6 and AA2024-T3 (2 cm x 2.5 cm). On each substrate was deposited an array of bilayers in a different order (1 micron thick), one with an initial layer of Al and an outer layer of Cr (Al / Cr), and another with an initial layer of Cr and a coating over it of Al (Cr / Al). We also used non-coated substrates (blank). The nomenclature used was: substrate / inner layer / outer layer.

### 3.1.3. Microscopy analysis (MEB)

Can be seen in figure 4 the micrographs of the systems on the substrate Al2024. In 2024AlCr few pits can be observed on the substrate, center-starry shaped, as is common in this material. Not corroded area presents a surface with large grains and dripped aspect. According to the mappings, appear Cr and oxygen, which can be an oxide, it is a common topography in coatings with outer layer of transition metal. In contrast to the previous system, in 2024CrAl pits are not observed. In this case the topography is more "smooth" because the nodules are larger, but fewer, as reported for outer layer coatings of Al. Regarding to Al corrosion products, appear to have been dissolved, since there is nothing on the surface.

Can be seen in figure 5 the micrographs of 6061AlCr and 6061CrAl. Observed in the first few and very small pits. The coating appears to have poor adhesion, associated to the Al substrate or even the stresses produced by the corrosion products of Al, leading to partial delamination of the coating.

In the 6061CrAl the surface is smooth and there aren't visible pits, but gives an appearance that the coating becomes brittle, since this coating is susceptible to internal stresses that exceed the cohesive forces of the aluminum substrate. In the case of both coatings don't observe corrosion product layer, so it could have been dissolved

### 3.1.4. Electrochemical tests

Was used a conventional pitting cell, as shown in figure 6. Electrochemical tests were conducted by electrochemical noise, according to equation 3 and ASTM G-199-09 standard [61], with a data acquisition rate of one data per second (1024 points). The results were analyzed from time series and statistical parameters.

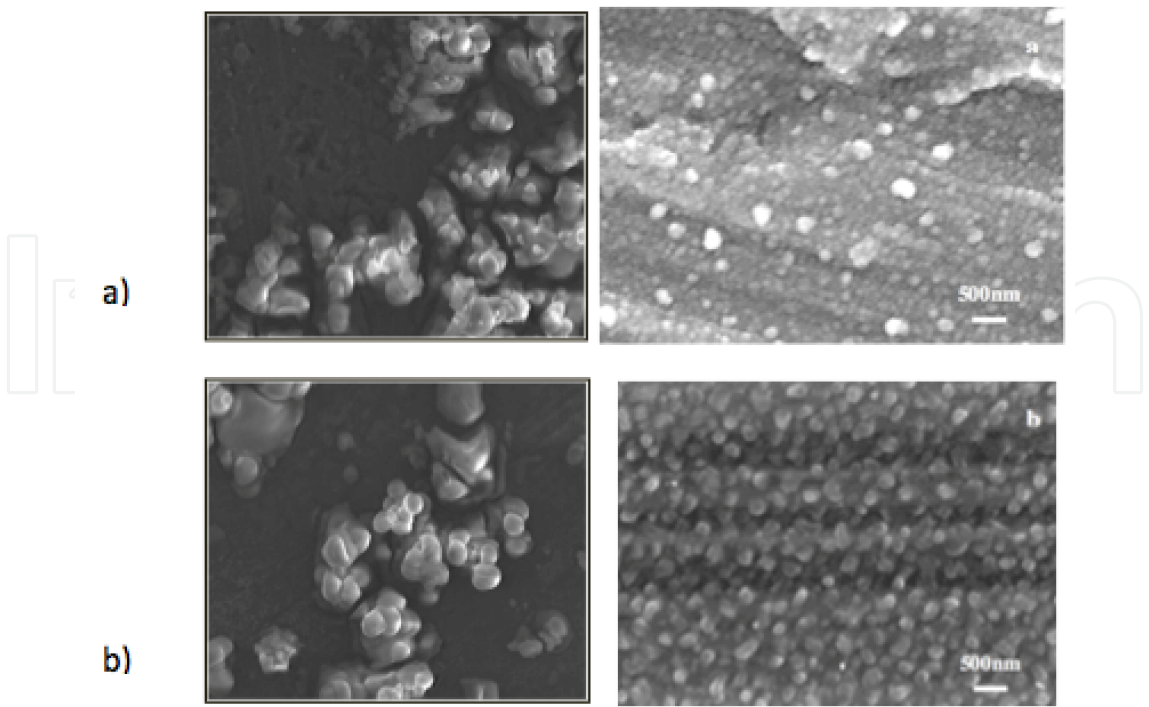
$$R_n = \frac{\sigma E}{\sigma I} \quad (3)$$

where:

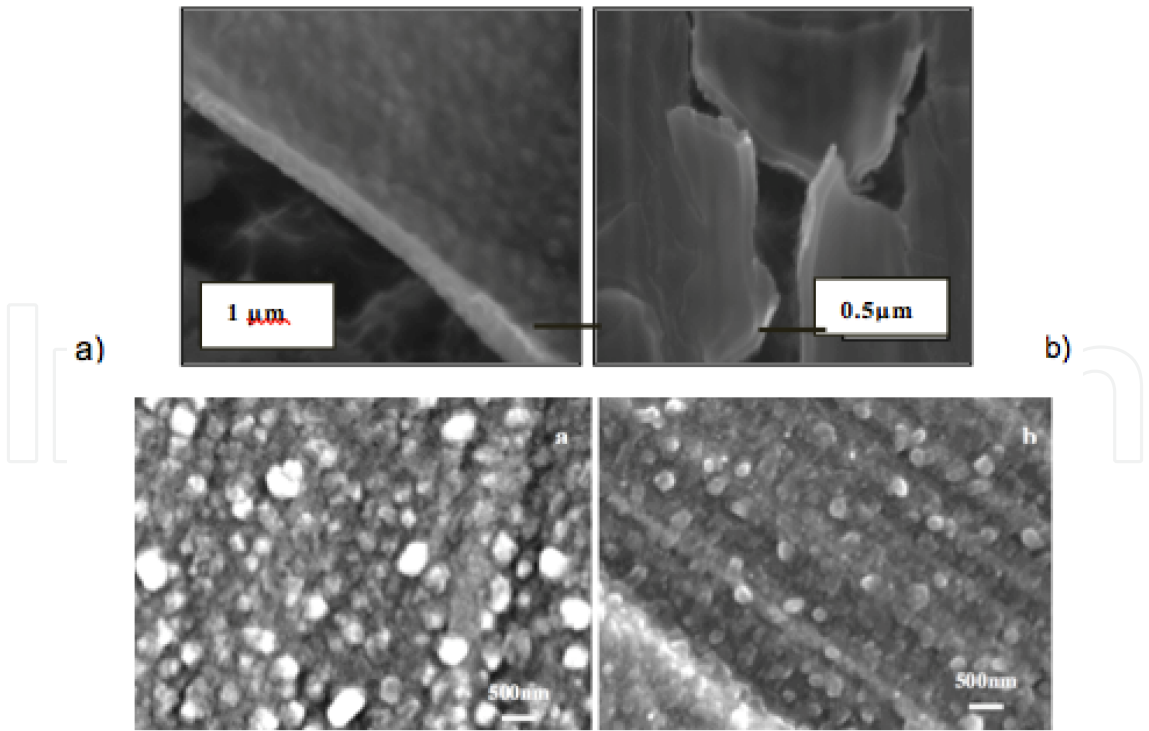
$R_n$  = noise resistance

$\sigma E$  = standard deviation of potential

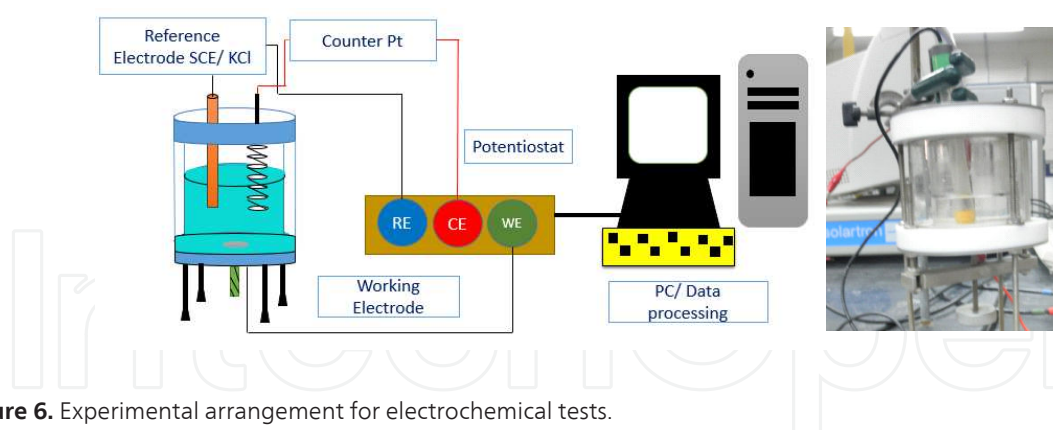
$\sigma i$  = standard deviation of current



**Figure 4.** Micrographs of 2024AlCr a) y 2024CrAl b).



**Figure 5.** Micrographs of 6061AlCr a) y 6061CrAl b).



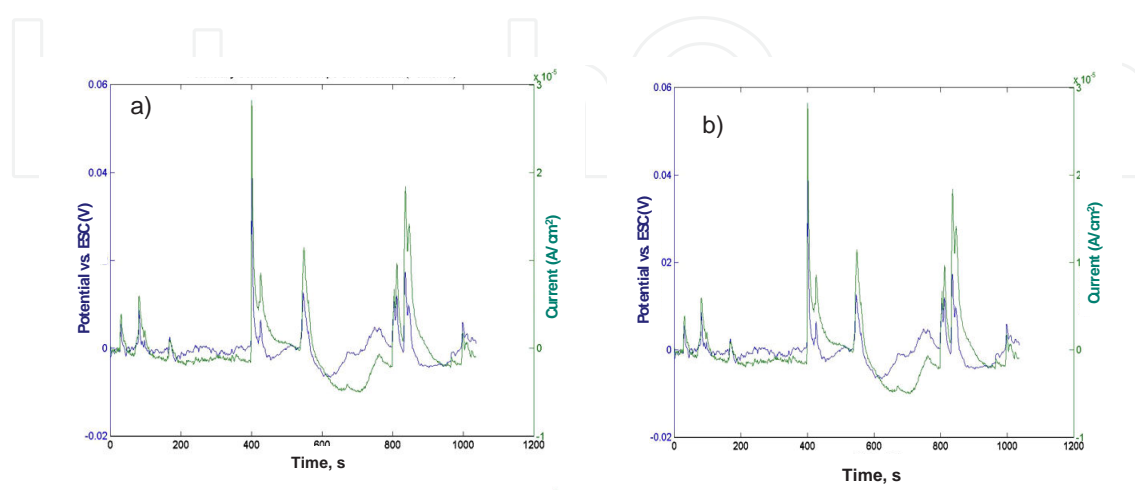
**Figure 6.** Experimental arrangement for electrochemical tests.

### 3.1.5. Analysis of non coated substrates

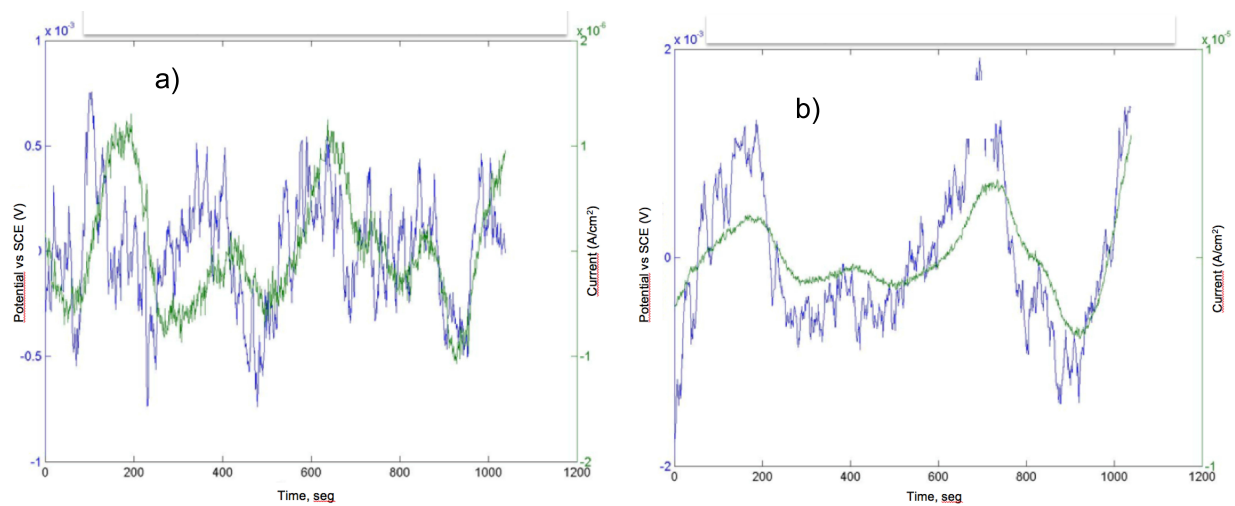
In the time series, figure 7, the transients have great amplitude and long term, with a fast rise and exponential fall, characteristic of metastable pits. In statistical analysis resulted an  $R_n$  of  $1.07 \times 10^3 \text{ Ohm/cm}^2$  and  $1.054 \times 10^3 \text{ Ohm/cm}^2$ , to blanks 2024 and 6061 respectively, due to blocking of pits by corrosion products of the substrate, corresponding to that reported by other researchers in previous works [62,63].

### 3.1.6. Analysis of coated substrates

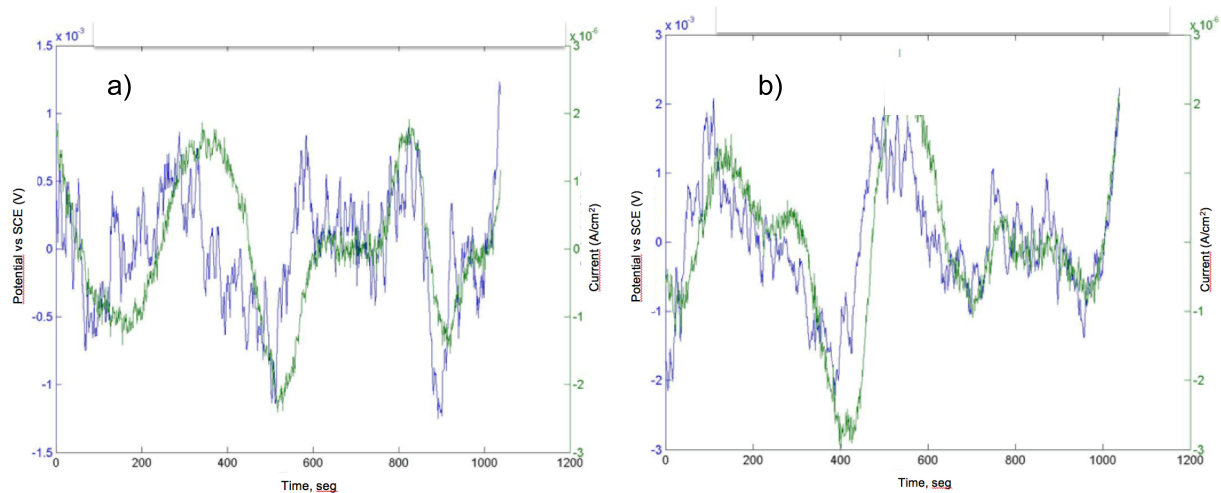
There were few events, all of low amplitude and high frequency (Figures 8 and 9), characteristic of a uniform corrosion process [64]. Potential noise is very stable in both, while in the current noise there are very fast fluctuations.



**Figure 7.** Potential and current time series, for uncoated substrates: a) blank 2024) blank 6061.



**Figure 8.** Potential and current time series for systems: a) 2024Al/Cr and b) 2024Cr/Al.



**Figure 9.** Potential and current time series for systems: a) 6061Al/Cr and b) 6061Cr/Al.

The statistical parameters (Tables 1 and 2). In the analysis, the SDC is higher in systems 6061AlCr and 2024AlCr than in 2024CrAl and 6061CrAl, because corrosion processes occur more rapidly in systems AlCr. SDV is higher in 6061AlCr than in 6061CrAl and 2024CrAl. In the first case due to corrosion is even more localized and passive processes are lower. In the second case is because the  $R_n$  in interface is greater. Regarding SDAV, for all systems is approximately 10.5 V / SCE indicating uniform corrosion process, except for 6061CrAl, which has a value of 4.10 V / SCE, which is characteristic of a slight corrosion or passivation. This interpretation agrees with that made by direct inspection of the time series. Regarding the LI (equation 4), indicates that the corrosion type for the system AlCr is mixed in both substrates, and is uniform for CrAl system. Which means that you may see some localized pitting, and uniform corrosion as the dominant form. Again, this parameter leads to the same information

obtained by direct analysis of SDAV.  $I_{corr}$  is higher in the arrangement AlCr for both substrates, as a result of charge transfer processes, facilitated to the system with the Cr surface layer. Resume, the statistical analysis indicated that corrosion processes occur faster in arrangements Al / Cr, consistent with other studies reporting [65,66, 67], and the dominant mechanisms were uniform corrosion and light passivation, similar to that found by Hladky [68] y Castillo [69].

$$LI = \frac{\sigma I}{I_{rms}} \quad (4)$$

where,  $I_{smr}$  = root mean square.

$R_n$  is the noise resistance ( $\text{ohm}/\text{cm}^2$ ),  $I_{corr}$  is the corrosion current ( $\text{A}/\text{cm}^2$ ), SDV is the standard deviation of the potential (V), SDC is the standard deviation of current (A), SDAV is the standard deviation of the average potential (V) and LI is the location index.

system	$R_n$	$I_{corr}$	SDV	SDC	SDAV	LI
2024Al/Cr	424.52	$6.12 \text{ E}^{-5}$	$1.43\text{E}^{-4}$	$8\text{E}^{-7}$	$5.11\text{E}^{-5}$	0.0141
2024Cr/Al	768.04	$3.4\text{E}^{-5}$	$4.2\text{E}^{-4}$	$5.44\text{E}^{-7}$	$8.75\text{E}^{-5}$	0.0086

**Table 1.** Statistical parameters obtained for systems 2024 Al/Cr and 2024Cr/Al.

system	$R_n$	$I_{corr}$	SDV	SDC	SDAV	LI
6061Al/Cr	353.7	$7.34 \text{ E}^{-5}$	$5.33\text{E}^{-4}$	$1.5\text{E}^{-7}$	$8.2\text{E}^{-5}$	0.0229
6061Cr/Al	684.8	$3.8\text{E}^{-5}$	$4.2\text{E}^{-4}$	$6.2^{-7}$	$1.43\text{E}^{-5}$	0.0085

**Table 2.** Statistical parameters obtained for systems 6061 Al/Cr and 6061cr/Al.

According to the results, it is possible to establish a mechanism for both systems Al / Cr, Cr / Al, regardless of the substrate.

In systems Al / Cr, once breaking the passive film of Cr,  $\text{Cl}^-$  ions can enter through these defects to reach the interface with the Al, such that due to the area ratio, the Al area smaller behaves as an anode and forms a galvanic couple, causing it to begin to dissolve the Al, and the corrosion products cause internal stresses at the interface, causing a delamination of the coating. Thus also showed higher  $I_{corr}$  values and mixed type corrosion.

In coatings Cr / Al, once breaking the oxide film of Al, the  $\text{Cl}^-$  can penetrate, with the difference that here the ratio of areas is different. Al acts as the anode and has a much larger area, then dissolves and corrosion products blocking Cr defects of the inner layer, so that increase the  $R_n$  and decrease the  $I_{corr}$ . Both systems however decreased density of pits, compared with those presented in the uncoated substrates. The types of corrosion that occurred in the systems were mixed, uniform and also a slight passivation.

4. Conclusions

In study of ECN for nanocoatings, all systems are considered cathodic, because they were dependent on the defects present in the coating. CrAl systems are the most stable, regardless of the substrate, due to the outer layer of Al which provides cathodic protection, and a second barrier constituted by the corrosion products. AlCr systems are less resistant to corrosion due to the corrosion product layer formed in the interface, which causes internal stresses leading to coating delamination. All studied systems decreased propagation of pitting, leading to a state of passivation or uniform corrosion, each by different mechanisms. Coatings possess superior corrosion resistance over the individually substrate.

5. Summary of previous works

Year	Ref	Author	Work
1991	44	J. Munemasa	Research the effect of the surface roughness of substrates on the corrosion properties of films coated by physical vapour deposition. Ti and TiN were deposited on substrates by magnetron sputtering method.
1995	45	A. Matthews	The characteristics of Vacuum plasma based coating and treatment methods are discussed, especially with regard to their beneficial influence on wear or corrosion.
1998	52	Liu	Have investigated the effect of grain size on the protective external oxide scale formation on Ni-20Cr-3Al nanocrystalline coatings.
2000	46	H.S. Park	A thick CrN film was deposited by magnetron sputtering on high-speed steel substrates, but the coating process was interrupted several times. The corrosion resistance was characterized by electrochemical potentiodynamic and potentiostatic measurements.
2004	29	R. Gheriani	Analyzed the effect of substrate surface ion bombardment etching on reaction between chromium thin films (magnetron sputtering deposited) and Steel substrates. The study was carried out by X-ray diffraction, Auger electron spectroscopy, SEM and Vickers micro-hardness measurements.
	49	Griguceviciene	The addition of transition metals like Cr or Ti have been studied, and the best result there are been obtained for Al-Cr alloys deposited by magnetron sputtering.
2006	31	Grips	Studied the electrochemical behavior of single layer CrN, TiN, TiAlN coatings and TiAlN/CrN multilayer coatings prepared by magnetron sputtering. They analyzed the corrosion behavior by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).
	48	Fenker	Studied the corrosion behavior of Ti and Cr multilayer coatings in NaCl media by circuit potential measurements, potentiodynamic corrosion and salt spray tests. The CrN, Nb <sub>2</sub> N, Nb-C:H, TiN, TiMgN multilayer depositions were carried out.
2008	50	Creus	Al/Cr multilayer architectures, deposited by dc magnetron sputtering, were tested. The open circuit potential and polarization resistance of the



Year	Ref	Author	Work
			coated substrate were recorded during long immersion tests. A cyclic polarization technique was used to estimate the pitting resistance.
	51	Cheruvu	The long-term oxidation behavior of nanocrystalline 304 SS and 304-4Al coatings has been investigated. The coatings were deposited on 304 SS samples using a plasma enhanced magnetron sputtering process. Cyclic oxidation tests were conducted on the coated and uncoated samples.
2009	53	García H.	Comparative study on carbon steel, of three corrosion resistant hybrid coatings, by using a loop reactor to measure the corrosion by means of the EN technique.
2010	30	Cekada M.	Analysis of the diffusion processes in Al/Cr, Al/Fe and Cr/Fe bimetallic multilayers.
2011	59	Estupiñan L.	Performed a statistical analysis of electrochemical noise transients to correlate with the morphologies observed by SEM in different steels, in order to identify the type of corrosion developed.
2012	60	Almeraya C.	Used electrochemical noise to study Ni-Mo alloys fabricated by mechanical alloying and densified by spark plasma sintering.
	69	Castillo M.	Electrochemical Impedance Spectroscopy Behavior of Nanometric Al-Cr and Cr-Al Coatings by Magnetron Sputtering. Find that bilayers had good homogeneity and adherence with substrates. The Cr/Al coatings were more stables.

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