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A New Approach — In-Situ Codeposition of Composite Coatings

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Abstract

Present chapter is organised to give general information about electrolytic coating and electro codeposition, factors affect the coating structure and the main layers'-property relation in details. This relation is expressed by a simple schematic and electrolytic codeposition parameters affect the process such as pH, zeta potential, agitation and etc. are explained. Additionally, in-situ codeposition, the new approach is given with examples, and some experimental results belonging to our research group and with comparison to approaches belonging to some others.

Main aim of this chapter mentioned is to define electro codeposition technique and to introduce the relatively new technique, in-situ codeposition method. According to the specific research example on this process, fabrication of composite coatings by electro codeposition system and obtaining metal-ceramic composite structures with additional heat-treatments are discussed. The obtained results showed that the composite coatings can be fabricated successfully by in-situ codeposition technique with an additional heat-treatment. The effect of heat-treatment conditions on the in-situ phase formation and their corrosion and mechanical behaviors are given. The results mentioned, both corrosion and mechanical, implies that the metal matrix-carbide and/or nitride reinforced composite coatings have potential application to industrial fields in many respects.

Keywords: Coatings, Electro codeposition, In-situ method, Heat-treatment, Oxidation, Phase transformation, Structure

1. Introduction

In most cases, materials have a limited lifetime, which strongly depends on the actions of external factors and the operating environment. Occasionally, chemical or electrochemical

reactions with the environment take place, which will sooner or later damage functionality by attacking the surface. Because of the atomic structure, the surface of a material or a component is the most vulnerable site for various forms of attacks and, therefore; it might be deemed. These attacks could be present individually or in combination of mechanical, chemical, electrochemical or thermal in nature [1]. The coating processes which maximize the lifetime of the materials can be classified as evaporation, hot metal processes, painting, thermal spraying, and **metallising**. Metallising appears to have particular importance in these main coating processes compared to others. Metallising is divided in two sub-groups, such as **electroless metal coating**, and **electrolytic metal coating**.

Among the processes concerning the production of nanostructured composites, the electro-deposition technique has further demonstrated the following benefits: a smoother surface, a better bonding between particles and a metal, an easier control of the thickness of the coating, appropriacy to automation, availability for obtaining metallic alloys and composite coatings, and, finally, a possibility to achieve higher microhardness [2].

It is known that combining the best properties of different materials to obtain one material with excellent properties is the main idea of fabricating composites. **Electrolytic co-deposition technique** seems to be feasible based on the idea determined.

In the present chapter, entitled **A New Approach: In-situ Codeposition of Composite Coatings**, general information about electrolytic coating and electrolytic codeposition is given and the factors affecting the coating structure, the main layer-property relations are explained in details. The electrolytic codeposition section explains the parameters, such as pH, zeta potential, agitation and etc., affecting this process. Under the section 3, property-performance relations of these coatings are examined. Finally, **in-situ codeposition** is detailed with examples and the experimental findings of our and other research groups are presented.

2. Electrolytic coating

In this method, a metallic protective layer is applied to a surface as a coating for the component typically carried out in aqueous solution. This process is supported by using an external voltage source generally called rectifier. On the other hand, for electroless deposition, a reduction medium is present in the electrolyte. The latter process is widely used for non-conducting materials' coating such as ceramics and plastics. The electrochemical method (electrocoating, electroplating) is used for deposition onto electrically conducting substrates.

Electrochemical deposition onto an object is achieved by putting a negative charge on it to be deposited and immersing into a solution which contains a salt of the metal. The metallic ions of the salt carry a positive charge are thus attracted to the object providing electrons to reduce the positively charged ions to metallic form when they reach the negatively charged object [1].

2.1. Factors affecting the coating structure

In this complex phenomenon, there are many factors that affect the process, consequently the properties and the performance of the material. These factors can be classified in four groups basically.

- Substrate: material of the substrate and the preparation before plating.
- Electrolyte: composition, pH value, temperature, filtration and agitation.
- Coating metal: main coating metal or alloy.
- System parameters: current type and density.

The factors are described in Section 3.1 in details for both electrodeposition and electro co-deposition techniques.

2.2. Layers and the Properties Related to

In a coating system four different zones are described by Holleck [3] when protecting materials with coatings. These are:

- Substrate;
- Substrate-coating interface;
- Coating and;
- Coating-environment interface (see Figure 1).

The first layer is substrate where potential hydrogen embrittlement effects are of concern. Commonly, metals are preferable for this layer, steel for engineering application in particular. The second zone is the basis metal interface. In this region adhesion of the coating and diffusion between the coating and substrate takes place. The coating itself is described as the third zone where composition and microstructure determine the properties and factors. The interactions between environment and the coating has to be taken into account in terms of corrosion and/or wear in the final zone environmental interface.

Obviously, numerous layers are influenced in more than one zone. This phenomenon could be illustrated by the following examples. Firstly, porosity and/or stress in the substrate, rather than just in the coating, can noticeably change coating properties. Secondly, porosity can affect corrosion resistance and mechanical behaviour, such as tensile properties. Another one is hydrogen embrittlement as a factor not only for the substrates (concentrates heavily on steels) but also for some coatings. This is a generic term used to describe a wide variety of fracture phenomena having a common relationship to the presence of hydrogen as a solute element in the alloy or as a gas in the atmosphere [4]. Nickel, aluminium, titanium [5] and even electroless copper coatings [6] exhibit the phenomenon. It explains that any material can weaken by this effect [7].

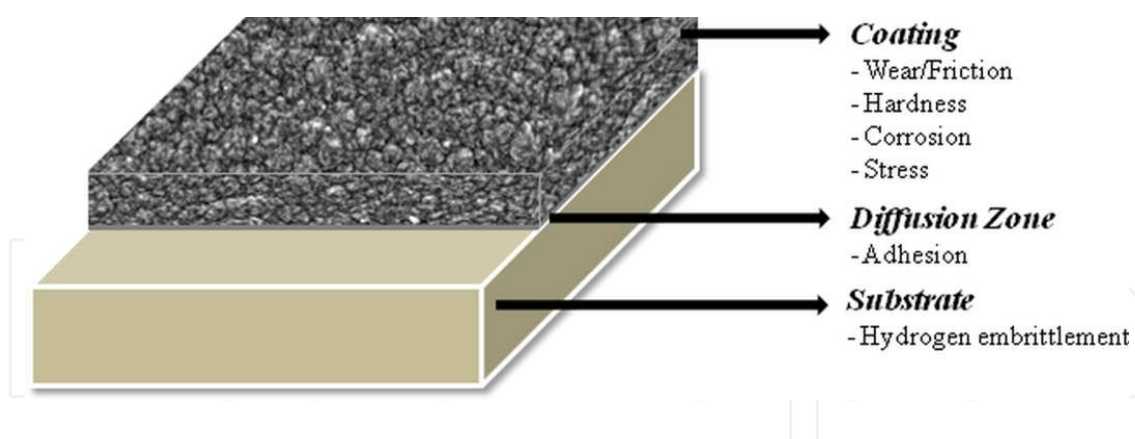


Figure 1. Zones in a coated material

The rest of the zones and the properties affected are clarified in Section 3.2 because these zones are related to the coating itself and the interfaces between coating.

3. Electrolytic codepositon

Codeposition of metals with ceramic particles is a new technique for obtaining hard, wear resistant coatings; therefore, its application to our daily life has not been studied in the engineering field enough. The deposition of two or more materials on a substrate simultaneously is defined as “electrolytic codeposition” or “electrolytic composite coating”. In this process, both materials (the matrix and the reinforcement) are subjected to the surface and the desired properties can be obtained in one step process easily. When considering the codeposition of Cr and SiC, the metal matrix (Cr) increases the hardness and the wear resistance of the material. Additionally, the reinforcement (SiC) improves corrosion behaviour and boosts both, the hardness and the wear resistance of the structure.

First examples of electro codeposited composite coatings are known to have been used for antislip stairs of marines which are Ni matrix sand (SiO_2) particles. Fink and Prince investigated the self lubricant properties of Cu-Graphite electrolytic composites for car engine applications in 1928. At the beginning of the sixties, the interest in this specific topic was increased and researchers were focussed on the engineering applications of these specific coatings. Especially, the interest in the application of Ni-SiC and Ni-PTFE in the automobile industry has grown significantly in the last decades.

From this perspective, codeposited composite coatings have excellent wear resistance and permit emergency dry-running of machinery. The following examples of practical utilisation illustrate the benefits of the mentioned coatings: Ni matrix coatings with 8-10% vol. of SiC are used to increase the life of internal combustion engine cylinder bores; composite coatings based on Cr_xC_y (chromium carbide) in a Co matrix are used as wear resistant coatings in gas turbines. Cr deposits with Al_2O_3 inclusions are used in piston rings for diesel engines. Diamond embedded into a Ni matrix form the cutting edge in tools such as chainsaws, grinding discs or dental drills [1].

A number of scientists have investigated the mechanism of the electrodeposition of composites. The mechanisms proposed by most of them include these steps [1]:

- Electrophoretic movement of positively charged particles to the cathode;
- Adsorption of the particles on the cathode surface by Van der Waals forces;
- Embedding of the particles into the layer.

There are a variety of models with a quantitative approach to the incorporation rate of the particles into the matrix; however the current and most widely-known one has been suggested by Roos et al. in 1990 [8].

Similarly, Wan-chang Sun et al. [9] described codeposition process for Ni- Al_2O_3 system in three steps. This is illustrated in Figure 2.

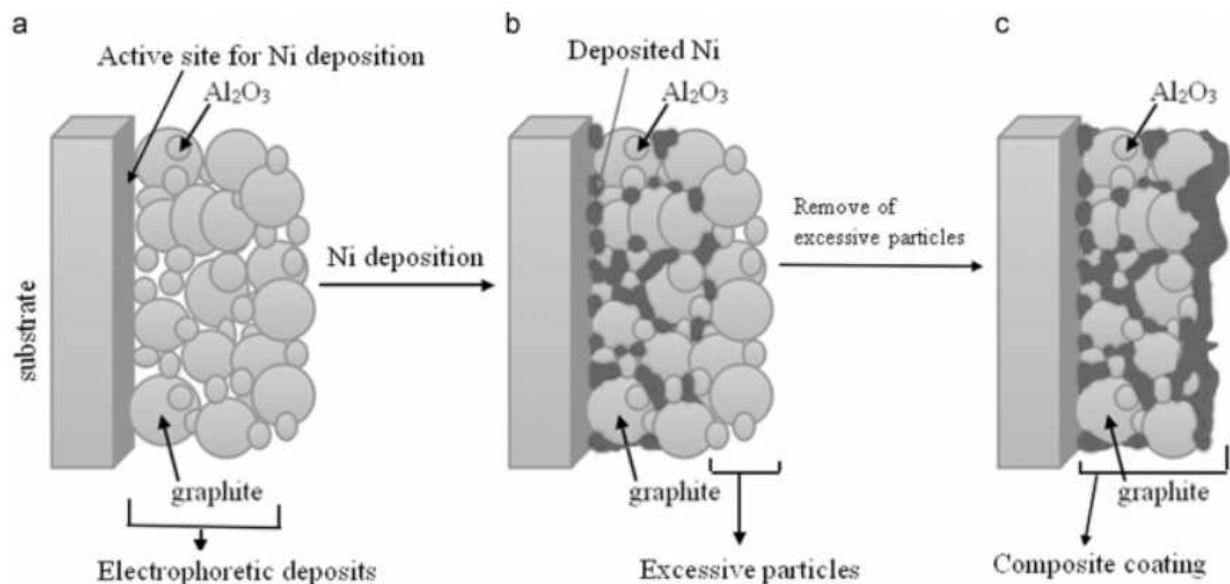


Figure 2. Schematic description of the three-step method of composite coating

These steps can be summarized for Ni- Al_2O_3 /graphite system as follows:

- nickel pre-plating and electrophoretic deposits of Al_2O_3 and graphite particles,
- composite after nickel deposition in the three step, and
- composite after removing the excess particles loosely adsorbed to the surface [9].

3.1. Effective parameters

The factors affecting the coating structure, subsequently, the properties and the performance of the material were given in previous sections (see Section 2.1 and 2.2). This section focuses on the specification of these factors; besides, the additional ones, which belong to the codeposition process, are described, namely zeta potential, particle size, circulation of the suspension (particle additional electrolyte) which belong to the codeposition process.

3.1.1. Substrate and substrate preparation

The main idea of coating processes is to protect the main material, to be specific, substrate, from environmental conditions, and to improve its mechanical properties. Undoubtedly, the perfect choice for such engineering applications is steel due to its unique properties. Even though this material group has a lot of advantages, the surface of the steel substrate has to be protected by several coating techniques. Electrical conductivity of steel substrates allows them to be coated by electrolytic deposition techniques, including electro codeposition. The quality of the substrate should be chosen according to the application and is the important detail; it should be coherent with the coating material properties-side (such as hardness and modulus of elasticity).

The preparation of the substrate before plating is another point to be taken into consideration. The coatings with perfect properties have no meaning without a good adhesion. Adhesion between the coating and the substrate identifies the coating quality and determines the life time of this structure. The preparation generally includes chemical and/or mechanical cleaning steps to remove contaminants from its surface [8].

3.1.2. pH

Electrolytes are prepared either acidic (nickel, copper, zinc and tin coating baths) or basic (zinc, cadmium, brass, gold and silver baths). It is important to know the pH in order to control and maintain the electrolyte composition stable for long term use. The electrolytes above or below specified pH values which show the acidic-basic characteristics affect and, generally decrease the coating quality [10].

In their research, Jia Man et al. [11] studied the zeta potential to describe the surface electrical behavior of nano-particles. Changes in the pH value of electrolyte can influence zeta potential. That means, zeta potential and pH are closely related to each other to determine the dispersive condition of particles in electrolytes.

3.1.3. Temperature

Temperature has two opposite effects on this process. On the one hand it increases the diffusion, and on the other hand, it also increases the crystal growth rate. It allows the grain size reduction, but decreases the cathode polarisation and because of hydrogen release this effect transforms the coating morphology into the spongy structure. Due to this reason, temperature should be adjusted and kept stable throughout the process [10].

3.1.4. Zeta potential

Zeta potential (ζ) of the particles is an essential parameter for the codeposition of composite coatings and provides details about the dispersion mechanisms of the particles. Simply, zeta potential can be defined as the value of attractive and repulsive forces between the particles. The behaviour of the particles in aqueous media is not determined by the surface charge but by zeta potential [10].

Zeta potential is directly related to pH due to the fact that in many aqueous systems, H^+ ions are the main ion content which determine potential. The value of zeta potential is measured

by zetameter in millivolts, which is important for the explanation of the colloidal suspension stability. The higher the zeta potential, the better the stability of colloidal suspensions [10]. This prevents the suspended particles from being agglomerated. Stability can be achieved mainly by two ways. These are:

- providing the particles electrically charged; and
- coating the suspended particles by a protective chemical (surfactant) [12].

J. Man et al. revealed pH and zeta potential effect on the α - Al_2O_3 particle codeposition. Results showed that H^+ absorption of particles at low pH can prevent the agglomeration of metallic ions, lower the size of grains and directly affect the particle content in the matrix [11]. Zeta potential and particle content versus pH value are given in Figure 3. It is obvious that zeta potential decreases with the increase of pH.

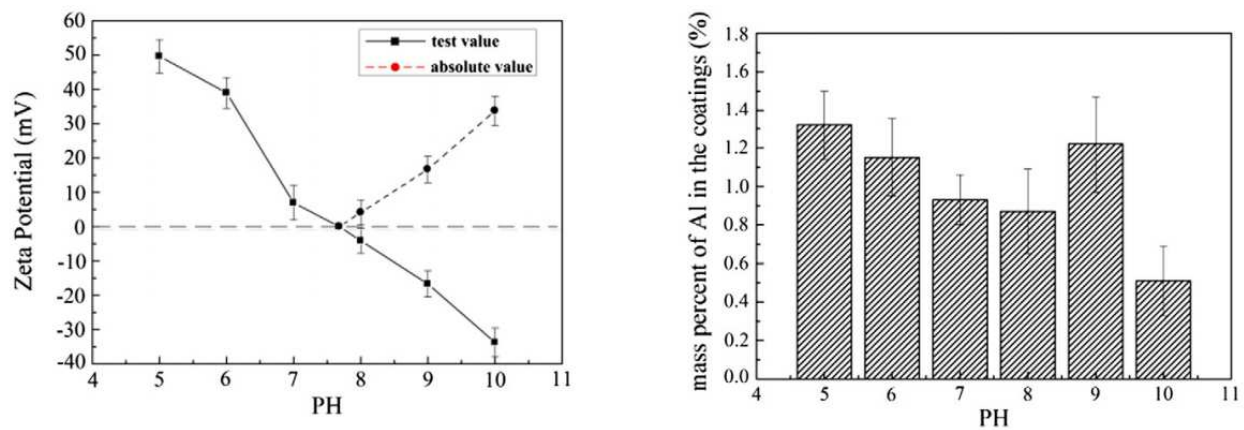


Figure 3. Zeta potential (left) and particle content (right) versus pH value [11]

In the case of ultrafine particles, a suitable surfactant, which, after ionising in solution, adsorbs on the surface of the particles allowing them to orient themselves according to their electric charge, is frequently added. Hence, the repulsive electrostatic forces minimise coagulation of the particles.

Meguno et al. accepted zeta potential as an effective quantitative parameter. According to their research, zeta potential values of both α -SiC and γ -SiC are negative but as a function of decreasing pH, the potential increases and reaches positive values for lower pH. In another study Lee and Wan mentioned that increasing the copper sulphate bath concentration and decreasing pH, zeta potential of α - Al_2O_3 approaches positive values. On the other hand, it is the opposite for γ - Al_2O_3 under the same conditions. This situation explains why α - Al_2O_3 particles are codeposited much more than γ - Al_2O_3 particles [13].

3.1.5. Agitation and filtration

A further factor affecting the coating structure is defined as the electrolyte composition. In other words structure and the stability of electrolyte affect crystal formation rate directly. With

the higher crystal formation rate, fine grained and better coatings coherent to the substrate can be obtained. In order to counteract the local ion concentration decrease near cathode surface, a motion can be given to the substrate. This is supported by the cathode motion generally but in some coating processes it is satisfied by the circulation of the electrolyte by several methods. In this case, there is a possibility of sticking the precipitated contaminants on the cathode surface. It is better filtering the electrolytes periodically to prevent the coatings from unwanted contaminations [10].

The coating baths are usually agitated by several methods.

These are:

- Cathode motion (vertical, horizontal or rotating) [8];
- Low pressure gas blowing into the electrolyte or unbalanced air circulation [13];
- Magnetic or mechanical stirring [13];
- Circulating by pumps [14];
- Sound or ultrasound vibrations [15-16].

Agitation in an electrolyte which can sometimes be in various combinations. To give an example, Tudela et al. used both the mechanical stirrer and ultrasonic agitation simultaneously. Figure 4 shows the sketch of the setup belong to their experimental set-up [16].

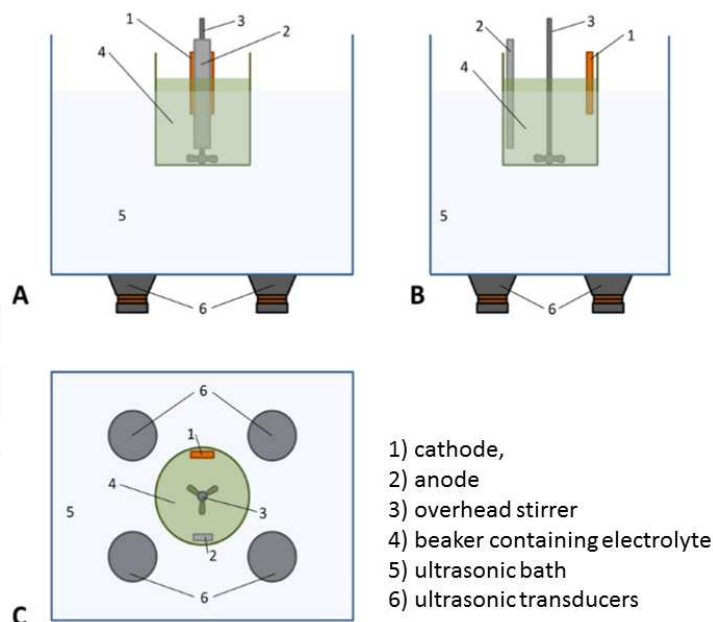


Figure 4. Schematic showing (a) front, (b) lateral, and (c) top views of the set-up [16]

Three main objectives for the agitation use are maintaining the temperature homogenous in the coating bath and carrying both the metal ions and the suspended particles to the cathode surface.

3.1.6. Particle size

The properties of composite coatings also depend on the particle size and distribution of the second phase. The second phase particles have to be suspended in the electrolyte uniformly. For this purpose, the tendency to settle under gravity must be constantly overturned using stirring, pumping electrolyte flow, ultrasonic agitation or air injection where it is desired to achieve a uniform distribution of the second phase through the matrix.

While the fine particles are suspended in the electrolyte easily, the coarser ones tend to agglomerate and/or settle by the gravitational force. Consequently, because of the aggressive circulation of the electrolyte effect the codeposition conversely, stabilizing the suspension has much more importance in this specific process. In this situation there are two alternatives. One of them is using submicron or nano particles in the electrolyte and the other one is adding surface active chemicals (surfactant) into the electrolyte to solve the stabilization problem totally or partially. This phenomenon is explained in Section 3.1.4.

The properties of electrodeposited metals or alloys can be substantially modified by arranging the codeposition of fine particles with the metal or alloy. Such particles may be inorganic (oxides, carbides, diamond), metallic (chromium) or organic (PTFE). The amount of second-phase incorporated particles will be a function of the deposition which has to be taken into account [11-12].

3.1.7. Current type and density

Until quite recently electrodeposition was carried out using direct current (DC) [1]. DC electrolysis can be represented with the connection of two electrodes immersed in solution to the output of a DC power supply (rectifier). The cathode may itself be a metal or might be a semiconductor or a non-metallic conductor such as graphite. The primary purpose of this is to complete the electrical circuit.

Another type of current used in electrodeposition is pulse current (PC, pulse plating or pulse electrodeposition). In pulse electrodeposition the potential or current is alternated swiftly between two different values. It is possible to control the film properties in an atomic order by regulating the pulse width and amplitude [8].

Huang et al. compared DC and PC on chromium coatings and found that the coatings fabricated using PC are showing less surface cracks than that of the coatings fabricated using DC. Additionally, corrosion resistance of these coatings is higher than that of the coatings obtained under DC conditions [8].

Another research group studied three different electrodeposition methods (direct, pulse, and pulse reverse current). According to their results, nanocomposite coatings' microhardness values significantly improved. When compared to the methods, hardness values were shown higher in the PRC coated materials due to increased reinforcement content (see Figure 5a). Additionally, Ni-Co alloy matrix nanocomposites exhibited better wear resistance as compared to pure Ni-Co alloy coatings [17].

Similarly, Nemes et al. [18] focused on both current type and frequency which are effective parameters of codeposition process. For all the same conditions oxide (CeO_2) addition increase the overall hardness (see Figure 5b). These results are affected by not only the codeposited ceramic content but also by the decrease of the grain size and the increase of deposit compactness affect [18].

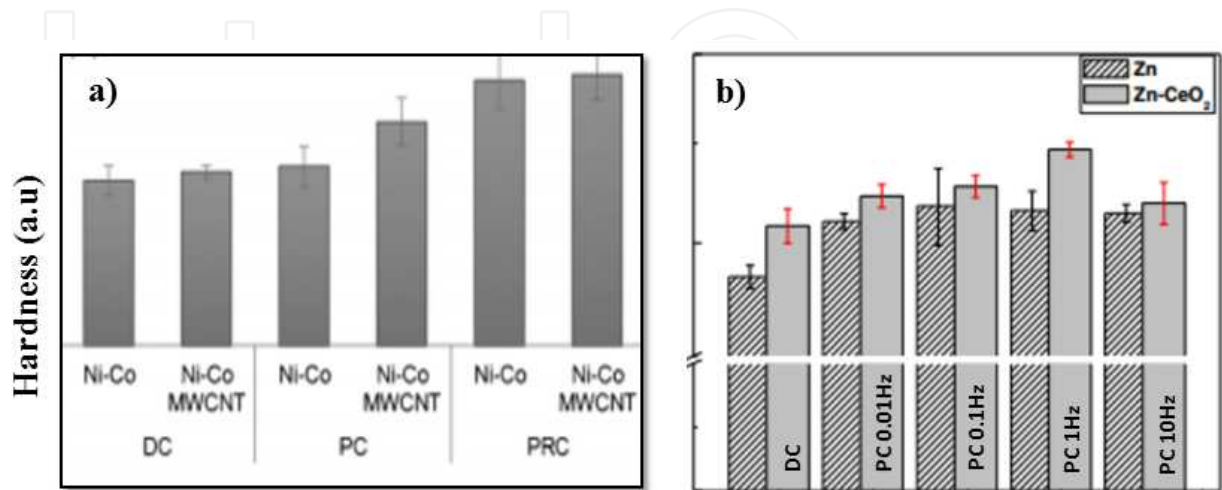


Figure 5. Hardness results of two different research due to process conditions

3.2. Property-performance relation

The properties of electrodeposits are important for several engineering applications. A fundamental concern of materials science is the connections between structure and properties, which is true for both bulk and coated materials. Properties of the electrodeposited composites are defined by the properties of the reinforcements used. Metal matrix is the phase for particles to be embedded. The particles used in applications such as diamond, SiC , and Al_2O_3 can be applied by vacuum coating techniques [1, 13-14] on metallic substrates. However, for the substrates that have girift geometry it is hard to obtain homogenous coatings with high adhesion. Metals and ceramics show different physical properties, such as thermal expansion coefficient; thus, multilayered structures could be necessary to acqiure better adhesion for codeposition process.

Electrochemically codeposited composite coating applications are divided into three groups. These are: dispersion hardening, wear, and electrochemical activity [13]. Dispersion hardening effect can be seen easily for oxide, nitride, carbide, and boride codeposited composite coatings when compared to pure metallic coatings. Dispersion hardening is defined as the increase against deformation. The main mechanism of deformation is motion of dislocations. The reinforcement in the composite coating structure blocks the dislocation motion and, as a result, strengthens the increase. Although there is no particular study of this phenomenon, grain size reduction can be seen in the matrix for codeposited composite coatings, which is thought to be the reason of increase in hardness. In scientific research, synergistic effect of grain size reduction and particles are given together [13]. Hardness is related to particle size, agglomer-

ation reduction and volume fraction of the particles in the metal matrix. Similarly, dislocation motion is defined with the distance of particles distributed in the coating layer. Increase in hardness is strongly affected by both the distance between particles and the volume fraction. However, it should be known that there is no limitless hardness increase in dispersion hardening, affected by reinforcement particles [13].

Composite coatings are commonly used in wear applications. Particle reinforcement to high and low frictional materials increases the wear resistance. Applications in equipments and contact surfaces of the motional parts of motors' can significantly extend their lifetime [13]. Composite coatings containing ceramic particles such as BN, diamond, SiC, WC, and Al_2O_3 show better abrasive wear resistance than the pure metallic coatings. Ramesh [19] found that Ni-TiC composite coatings with the volume ratio of 3% TiC showing four times less wear loss than the metallic Ni coatings.

In another research, open circuit potentials (the OCP curves) clarified that the values for in-situ co-deposited samples were shifted toward nobler potentials when compared. In addition, polarization curves of the coated samples were shifted toward the lower current densities. Upon the reversal of scanning, the increase in the zero-current potential also indicated the increased corrosion protection due to the in-situ phase transformations of electro codeposited composite coatings in inert atmospheres [15].

3.2.1. Porosity and grain structure

Porosity is the main sources of discontinuities in electrodeposits. It can noticeably affect corrosion behaviour, mechanical, and electrical properties, and also diffusion characteristics. It is influenced by the substrate, the plating solution and its operating conditions, and post-treatments [15]. An efficient method to minimize porosity is to use an under plate.

Moreover, the grain size of the coating metal affects several properties of the coating structure. The following properties change in size, hardness, surface roughness, brightness, resistance to deformation, stress, corrosion, and several mechanical properties. For a decorative coating, brightness is the major property, whereas the other properties are most important for industrial and engineering applications. If the grains consisting of the coating metal are coarser, coating will be both less hard and mat. On the contrary, metallic coating will be harder, smoother and brighter. Besides, coatings with finer grain size are expected to be less porous when compared to the coatings with coarser grains [10].

It is known that the reinforcement of ceramic particles dispersed in the metal matrix can increase the overall composite coating hardness by two possible hardening mechanisms. One of them is the dispersion of sub-micron sized hard particles in the matrix and another one is the grain size refinement of the metal matrix assisted by dispersed ceramic second phase particles. Therefore, according to the Hall-Petch effect, an increase in the hardness of matrix can be expected [20].

Bahkit & Akbari [21] revealed the synergistic effect of grain size reduction and particle reinforcement on the composite coatings fabricated by sediment codeposition technique

(SCD). In Figure 6, both metallic and composite coatings' hardness and grain size measurements are given, respectively.

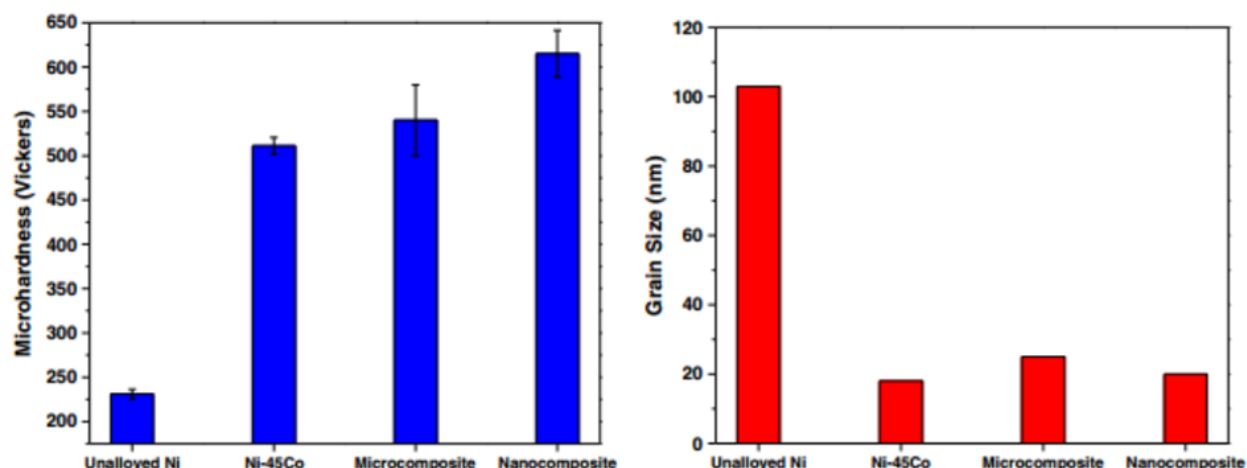


Figure 6. Hardness (left) and grain size (right) of unalloyed, Ni-45Co, microcomposite and nanocomposite coatings produced by SCD [21]

It is clearly seen that average particle size used in the process also affect the properties under same deposition conditions especially the grain size refinement of the metal matrix.

3.2.2. Size of the particles and second phase

The particles can create a dispersion-hardening effect so that they hinder the formation of dislocation in the grain, and act as pinning agents. Analogically, they can also hinder grain growth caused by annealing [8].

Reduction in the size of the particles in the composite coating increase the abrasion resistance. The reason for this case is less delimitation of the particles in the metal matrix. In a study on Cr-Al₂O₃ composite coatings, researchers indicated the reduction in the wear strength and brittleness when the amount of the particles was too big [10].

Another way to reduce the wear loss of surfaces moving relatively is to decrease the friction coefficient or lubrication. SiC particles create a lubricant film on the surface of Ni-SiC coatings. Because of the lubrication the wear resistance of the composite structure increases up to 2-3 times of a pure Ni coating. This has been proved by similar studies [10].

3.2.3. Particle distribution

The distribution of the particles and the second phase are important to obtain homogenous coatings. Otherwise, properties can change locally, regions to regions and can cause the decrease of coatings' lifetime. This would be because of local corrosion attacks and/or wear loss. However, it is hard to obtain a homogenous structure since it can be controlled by agitation of the electrolyte during the co-deposition process. For more details on several agitation types, revise Section 3.1.5.

3.2.4. Hardness/elastic module

The indentation hardness of materials can be measured in several ways by forcing an indenter having specific geometry [22]. The hardness and Young's modulus, two of the most commonly measured mechanical properties of materials, can be determined in an easy and reliable way due to the development of depth-sensing indentation equipment [23].

Furthermore, dynamic indentation method is more beneficial than the conventional Vickers microhardness testing in two aspects. Apart from microhardness the dynamic indentation method can also provide well-defined mechanical parameters such as elastic modulus of the material. Secondly, difficult and inaccurate optical observation and measurement of diagonal length of the indent/impression is no longer required because of the continuous monitoring of the load and depth of an indentation [24].

With the development of the nanoindentation technique, the mechanical properties within a sub-micron or nano scale have been widely discussed. The techniques are expected to be convenient for measurement of the mechanical properties of thin films [14].

The greater hardness values for composite coatings can be attributed to the greater hardness values of the reinforcements. The explanation of this phenomenon is based on the rule of mixture for composite materials. The rule states that the hardness of a composite can be formulated based on the volume fraction and the hardness of each individual component [20].

It is also known that the amount of wear volume (Q) during the wear tests is directly proportional to the compressive load (W), sliding distance (x) and inversely proportional to the hardness (H). It can be expressed by the Archard Equation (Eq.1) given below, where k_o is a non-dimensional wear coefficient that is specific to each material [20].

$$Q = k_o \frac{W \cdot x}{H} \quad (1)$$

On the contrary, H/E ratio of materials gives an extremely close agreement to their raking in terms of wear behaviour. This is detailed by a similar research [25].

Some of the experimental results are given in Section 4.3 in comparison for in-situ codeposition process. According to these results, one can easily understand the relation between hardness and elastic modulus and also how the second phase particles change these properties.

3.2.5. Adhesion and diffusion

Adhesion of the coatings can be identified both qualitatively and quantitatively by a specific testing method called scratch test. This test is applied according to the procedure of mechanical failure modes and adhesion strength of ceramic materials. It is appropriate for adhesion measurement and possible failure modes prediction of metallic and ceramic substrates coated by thin ceramic films. This method does not give a characteristic value of the material. Instead, it reveals a practical engineering approach for substrate-coating system because the results are

obtained depending on the several test parameters. Details of the test method can be reached from ASTM-C1624 standard [26].

3.2.6. Corrosion

Corrosion is known to be influenced by a variety of factors. It is not possible to separate corrosion from many of the other property issues related to coatings. For the proper selection of a coating, it is necessary to take its position, with respect to its substrate in the galvanic series for the intended application, into consideration [27]. Decorative nickel-chromium coatings developed for automotive industry applications are a suitable example of the application of materials science and electrochemistry for the corrosion protection of materials.

There are several examples of electro codeposited composite coatings for corrosion protection [28-30]. According to these results, it is supported that corrosion resistance of composite coatings increase significantly with respect to the pure metallic or alloy coatings [15, 21]. This phenomenon is suggested to be the effect of the inert properties of the reinforcements.

For the Ni-Co alloy matrix SiC reinforced composite coatings, Bahkit & Akbari [21] expressed the corrosion behaviour of these coatings through potentiodynamic polarization curves (Figure 7). Calculated corrosion current densities and measured corrosion potentials are summerized in Table 1.

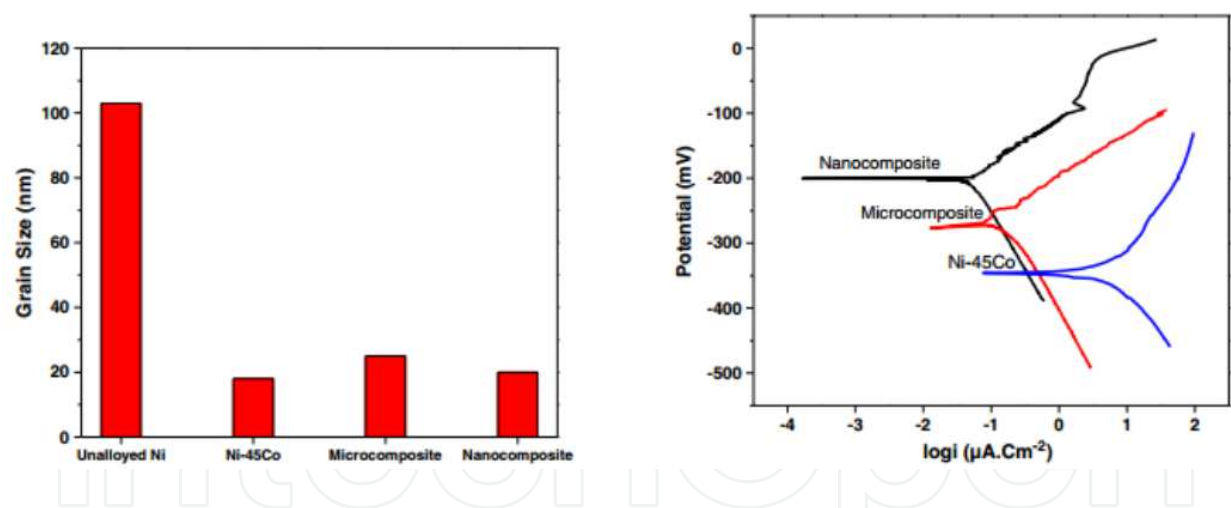


Figure 7. The potentiodynamic polarization curves of alloy coating and composite coatings

Coating	Eocp (mV)	βa (mV/dec)	βc (mV/dec)	Ecorr (mV)	icorr (μA.cm ⁻²)	Rp (kΩ.cm2)
Ni-Co	-346	177.26	120.9	-354	6.570	4.75
Microcomposite	-277	71.94	162.1	-257	0.137	158.48
Nanocomposite	-201	71.18	176.5	-199	0.050	439.46

Table 1. Calculated and measured corrosion data for alloy and composite coatings

Based on the data, Ni-Co/SiC nanocomposite coating has the highest corrosion potential whereas the pure alloy coating (Ni-Co) has the lowest. Additionally, the corrosion current density of nanocomposite coating is lower than the micro scale SiC reinforced composite coating and shows the higher corrosion resistance (R_p) [21].

Additional examples belong to the main topic of the present chapter, in-situ codeposition, and the relation between metal matrix and inert reinforcements are given in Section 4.3.

3.2.7. Wear/friction

To give some examples for the practical wear applications of coatings, one can count chromium, electroless nickel, precious metals, anodized aluminium and so on [31]. But for engineering applications pure metallic coatings, or the conventional coatings mentioned are not enough to satisfy. Based on this idea, researchers have been focussed on recent advancements include codeposition of dispersed particles with metals. There are two alternatives to improve the wear resistance of a composite coating. The first method is to use hard particles in the metal matrix so as to increase the strenght of the surface against to the other frictive part. The second way includes creating the composite structure by using self lubricant reinforcements such as graphite, MoS_2 , h-BN and WS_2 [16, 32-34].

Due to their specific study [9], as a function of graphite particle content in the electrolyte, reduction in the hardness is appeared but decrease in the wear loss (Figure 8a). It can be expressed by the self lubricant property of graphite. Furthermore, the phenomenon of composite friction/wear for Ni- Al_2O_3 /graphite composite structure are described in Figure 8b as shown.

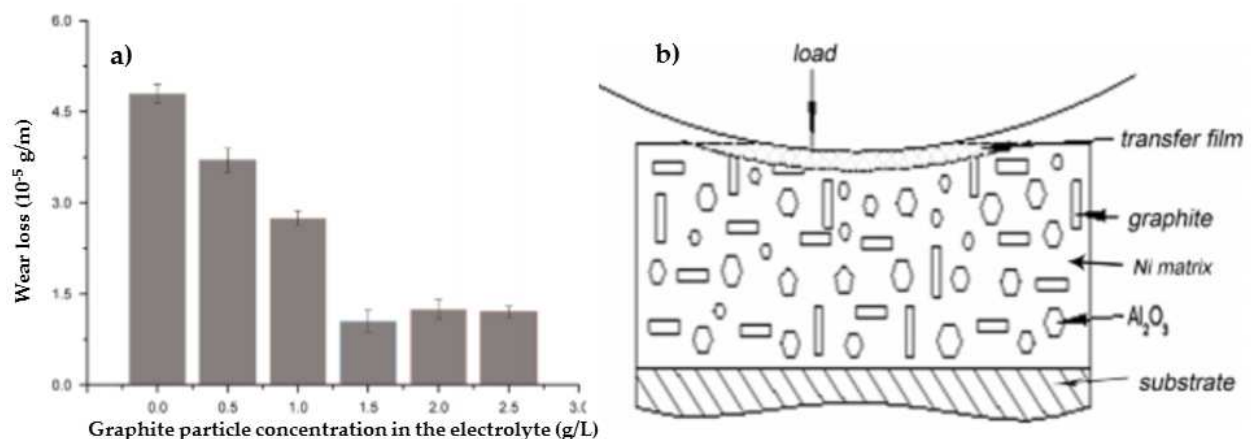


Figure 8. Wear loss versus graphite content in the electrolyte (a) and the schematic illustration of composite friction/wear phenomenon [9]

Friction coefficient and wear loss of composites initially decrease and then increase slowly back with the graphite particle concentration in the electrolyte. The results show an optimum graphite concentration in the electrolyte as 1.5g/L. Under this condition, the lowest friction coefficient, relatively high microhardness, and less wear loss was obtained.

3.2.8. Residual stress

Stress in coatings also adversely affects properties. Nowadays, a variety of options are available for stress reduction of coatings. These include: choice of substrate plating solution, use of additives, and higher plating temperatures. A number of theories have been assumed regarding the origins of stress, however, none of them covers every single situation. Several methods for stress measurement vary from the simple rigid strip technique to complicated methods. Both phase transformations in the composite and additional post-treatment of the coatings can decrease residual stress value in a composite coating [12].

4. In-situ codeposition

Until this section some of the details, advantages and additional performance criterias, related to the properties, were given about electro codeposition technique. When considering this technique, which is applied to metal-ceramic couples for some decades, researchers are tend to deposit the reinforcement and the metal directly. This technique is called *ex-situ codeposition* method. In this method, ceramic particles are suspended in the electrolyte and codeposited together with matrix metal directly. Of course, it brings some disadvantageous situations together because of the surface properties of the particles.

Some of the research groups improved ex-situ codeposition technique in last few years to eliminate the disadvantages. The new technique modified by researchers is called *in-situ codeposition* method and identifies the phase transformation of the reinforcement in the composite structure by various additional treatments such as heat-treatments between elements and/or compounds. Using this approach it is possible to obtain composite structures with wide range matrix metal (aluminium, titanium, iron, nickel, chromium and copper) and second phase particles (borides, nitrides, carbides, oxides and mixture of them) [12].

4.1. Comparison of ex-situ and in-situ methods

There are some advantages of in-situ codeposition technique when compared to the conventional codeposition (ex-situ method) route. These are:

- Reinforcement should be fabricated separately before electro deposition process in ex-situ production method. In this situation, the size of the reinforcement particles limited by the initial particle size and for practical applications size of the particles are rarely in sub-micron scale because of the economic reasons of nano particle production routes.
- Another advantage of in-situ method is particle-matrix interface. Surface structure of second phase particles and contaminants can cause a weak wettability between the particles and the matrix phase and this would be effective for the final properties of the composite structure. Especially the mechanical properties. On the other hand, coherently developed interface between the reinforcement and the matrix can be obtained strongly in in-situ production method.

- Additionally, thermally stable ceramic particles transformed in the composite structure can be distributed homogenously by this method. It is well known that homogeneity in the composite materials bring enhanced mechanical properties with itself.

All the advantageous and disadvantages are summerized in Table 2.

Ex-situ (conventional method)	In-situ (new approach)
X Seperately reinforcement fabrication	√ Phase transformation during process
X Particle size is limited	√ Controllable second phase size
X Weak particle-matrix interface	√ Coherently developed interface
X Possible but hard to achieve homogeneity	√ Homogenous particle distribution
√ Applicable with any oxide, boride, nitride, carbide, and also polymers	X Limited by the matrix metal and chemical affinity between additional
√ No need for additional process	X Generally need additional heat-treatment

Table 2. Comparison summary of two methods

4.2. Post-treatment and transformations

In-situ codeposition method includes phase transformations and these come from additional post-treatments (heat-treatment) generally. There is a major point to be known about heat-treatment processes. It is called the stability of oxidation products such as carbides, nitrides, and oxides under different temperature and atmosphere conditions. Scientific reality that lies down this phenomenon is the change (decrease and increase) in the free energy of these components as a function of temperature (and aslo partial gas pressure). The tendency is important to predict the way of phase transformations according to the heat-treatment processes and defined by using special diagrams called Ellingham Diagrams which show the free energy change versus temperature [35].

4.3. Properties and performance

Traditionally, in electro codeposition technique for fabrication of metal-ceramic composites, ex-situ method is used [36-39]. In this method, ceramic particles are codeposited on cathode directly from the electrolyte (ceramic particle containing suspension). During the last decade, much attention has been paid to the preparation of metal matrix composites by a method that combines several techniques with an in-situ reaction method providing some advantages [40]. Differently, phase transformation of codeposited particles, such as carbon black with an additional heat treatment step has its special attention in this specific production route. It is because carbon is the unique element to compose carbide phase by in-situ transformation. From this perspective, the production route for this kind research includes both the codepo- sition of less studied carbon structures and in-situ phase transformation of metal matrix, such as chromium and various size of carbon black particles. Additionally, many different carbon sources in in-situ method codeposition can be used. To give some examples, they can be

directly carbon based particles, such as carbon black and graphite, or steel substrate itself, and etc.

Based on some former studies [14] the following section discusses fabrication of Cr-C composite coatings on steel substrates by electro codeposition technique and transformation of the layers into chromium matrix, carbide, and/or nitride reinforced composite phase structures with an additional heat treatment process for enhanced corrosive and mechanical applications. The discussion is based on the comparison of the similar research in the sphere.

The present section includes the production of functionally modified hard chromium coatings with a new approach. In addition to this, the observations of the property-performance relation for a specific Cr-C composite coating fabrication are provided. According to the experimental studies researchers fabricated three different coating groups. The identification of these groups are given in Table 3.

Sample-R	Traditional hard Cr coating (reference coating)
Sample-N	Electrodeposited Cr/C _{micro} composite (heat-treated under N ₂ atmosphere)
Sample-A	Electrodeposited Cr/C _{micro} composite (heat-treated under Ar atmosphere)

Table 3. Identification of the samples [15]

XRD patterns are shown by annealing as-deposited Cr–C coatings, crystallization into a crystalline structure would occur. In the same results, it is clearly identified that for the Cr-C composite coatings give peaks that belong to carbide (Cr₂₃C₆), nitride (Cr₂N), oxide (Cr₂O₃) and pure metallic Cr phases after annealing (800°C/3h N₂ or Ar). The results showed that a small amount of Cr₂O₃ and Cr₂₃C₆ phases transformed under inert gas atmosphere (Ar) in some regions. On the other hand, change in heat treatment atmosphere (N₂) formed a new phase structure with the form of Cr₂N.

When compared the surface morphologies micro-cracked structure is visible along the surface for metallic chromium (fabricated by conventional methods). The similar surface structure with cracks is seen for the sample heat treated under Ar atmosphere with an increased crack width and density against the reference sample. Nevertheless, nitride phase formation modifies the surface denser and makes it crack-free with respect to the reference coating (see Figure 9 for details) [15].

Researchers have revealed that nitride formation takes place near the cracks and enlargens nitride-gas interface by the oxidation mechanism as expected [35]. Similarly, an interlayer is formed between the interfaces of coating and substrate. The cross-section of Sample-A gives the same interlayer lying between the coating-substrate interfaces (dark grey contrast). Since atomic carbon in the Cr-C layer can diffuse faster than chromium, the excess carbon atom in the Cr-C layer tends to form carbide phases [41]. The reason for this phenomena is the diffusion of C atoms from the steel substrate to the coating. Carbon atoms diffused from then transform to carbide phase due to the high chemical affinity of C atoms to the Cr atoms [42].

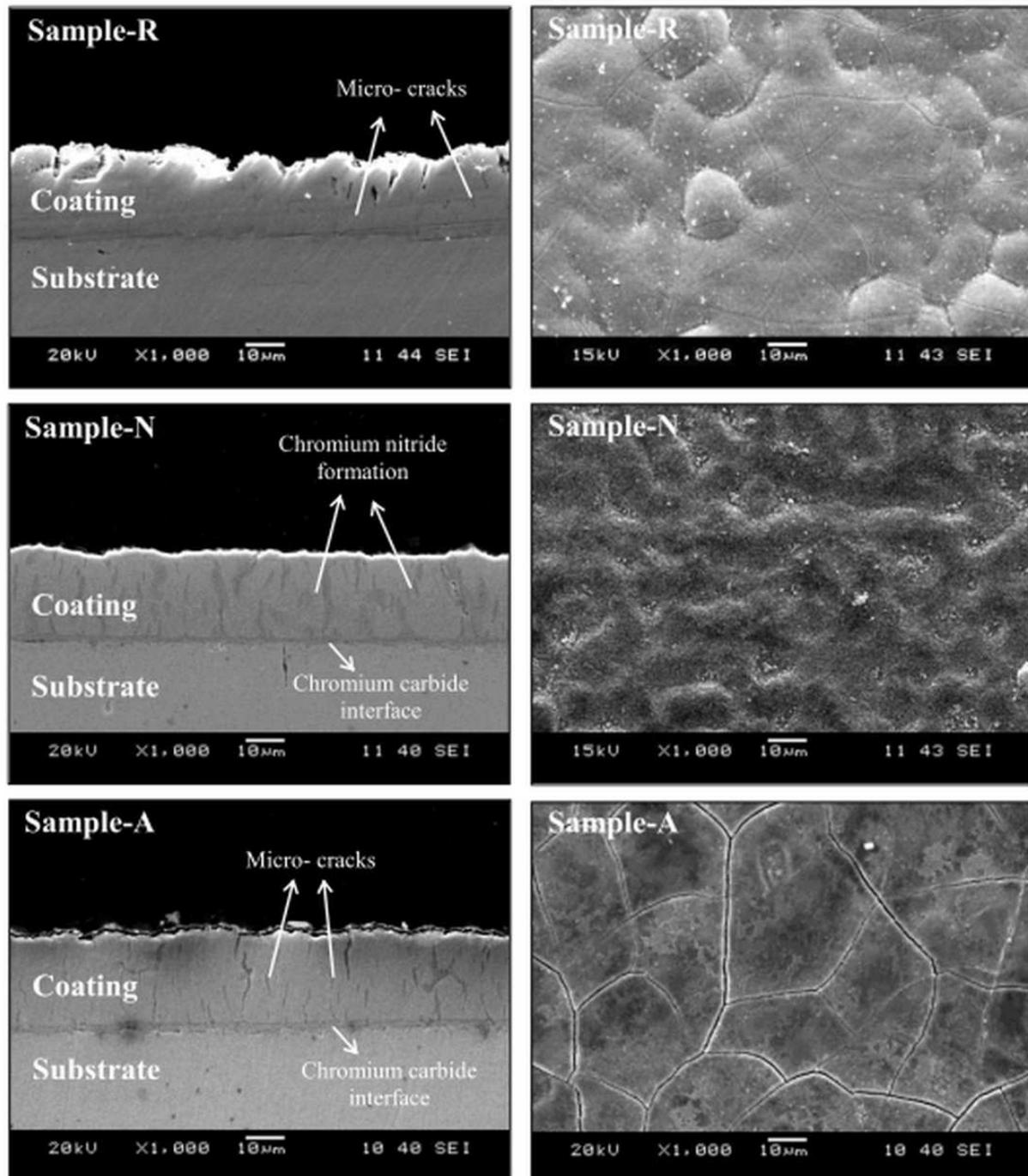


Figure 9. SEM micrographs of Sample-R, -N, and -A from the cross section and the surface

According to the EDS analysis taken, it was assumed that the dark regions are nitride phase for Sample-N and carbide formation occurred in the matrix and also along the interface for the both samples (Sample-N and Sample-A) [42]. Additionally, some of the zones are identified as nitride containing field and some not only nitride phase but also carbide. This is explained

by the N atoms diffusion from atmosphere into the and finally nitride phase formation in the micro-cracks [35].

Until this point, the details which render the study specifically are given about phase structure, transformations, and morphological structure of the composite coatings fabricated by this new method. The technique repeatedly shows its importance when considering the experimental results on both corrosion and mechanical behaviour.

Here are the results summarizing this specific study of the corrosion behaviour of coatings mentioned. Open-circuit potentials and cyclic polarization curves of steel substrate (1040) and, Sample-R, -N, and -A in aerated 3.5wt% NaCl solution are demonstrated in Figure 10 and some quantitative corrosion results are given in Table 4 in details.

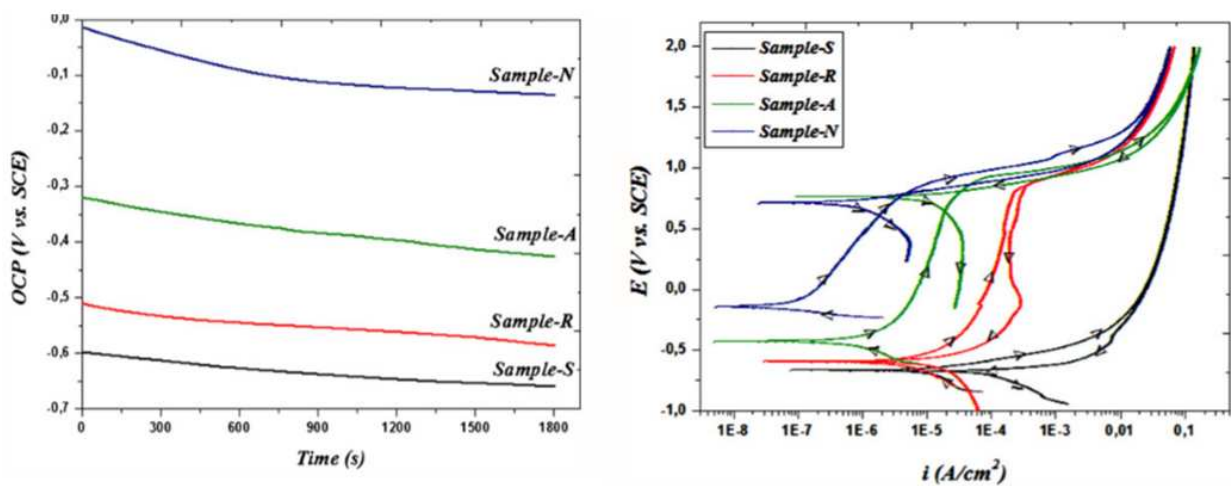


Figure 10. Open-circuit potentials (left) and cyclic polarization curves (right) of steel substrate (1040), and Sample-R, -N, and -A in aerated 3.5wt% NaCl solution [15]

Corrosion test results reveal that the passive current density of the heat-treated samples are lower than those of the untreated samples. That means it is possible to change the corrosion behaviors of the coatings by atmosphere controlled heat-treatments. In addition, Sample-N exhibits the higher polarization resistance and the lower corrosion current density as compared to the others.

	$E_{corr} (mV)$	$I_{corr} (A)$	$R_p (\Omega)$
Sample-S	-635	5.65×10^{-6}	1.99
Sample-R	-587	1.53×10^{-6}	21.40
Sample-A	-394	4.85×10^{-7}	42.28
Sample-N	-124	2.90×10^{-8}	538.77

Table 4. Quantitative corrosion data of steel substrate and, Sample-R, -N, and -A [15]

It is clearly seen from the SEM micrographs of the coatings that countless number of superficial cracks exist all over the surface. Some of them lying from the coating surface through the cross-section. According to the microstructures it becomes clear that the presence of micro-cracks in Cr coating is the main reason on the corrosion resistance decrease. When it comes to the heat-treated samples, it is improved by the crack-filling effect of Cr_2N phase formation as seen in the cross-sectional images.

After the corrosion property, hardness and elastic modulus values are investigated for this study due to the heat-treatment effect on the in-situ phase transformations. It is shown that these phase formations are in a competition with stress relaxation on the hardness of composite coatings. While the relaxation decreases the hardness value, phase formations support the increase in the total hardness. The mentioned hardness values were decreased up to 480H_V level for only carbide formed composite coatings (see Table 5).

	<i>E (GPa)</i>	<i>H (GPa)</i>	<i>H (Vickers)</i>
Sample-R	147	14.1	1381
Sample-A	115	4.9	481
Sample-N	155	6.2	604

Table 5. Hardness and elastic modulus data of Sample-R, -N, and -A [12]

Nevertheless, this value is about 600H_V for the composite coatings which have both carbide and nitride phase. This result can be explained solely by the in-situ nitride formation with a crack filling effect. Similar results are explained on the elastic modulus increase for this specific research.

Two ways to improve the wear resistance of a composite coating were explained previously. One of them is to decrease the friction coefficient. The results of this study showed that the friction coefficient decrease was found to be about 50% for the samples in which nitride formation occurred. As a result of this effect, it is possible to suggest that the need of lubrication, vibrations and over heating can be decreased for engineering machinery applications by using these type functionally modified surfaces [12].

To take into account the adhesion behaviour of these composite coatings, there are no adhesive damage observed up to 30N maximum load for these samples (Sample-N, and -A). Only a little amount of cohesive damage occurred. In contrast, for the nitride formed samples this effect was seen much less. The coherence between the coating and the substrate is explained and supported by the diffusion of C atoms from the substrate to the coating and the formation of carbide interface for the samples.

Finally, as another mechanical result, residual stress values of the coatings were measured for these electro codeposited composites in this research. It is stated that the reference sample, which has only the pure metallic chromium phase, showing tensile stress in a high level as it was expected. Against, residual stresses are compressive and found to be about -380MPa and

-664MPa for the Sample-A and -N, respectively, while it is about +225MPa for Sample-R (reference coating). The reason for the decrease of residual stress is given as the increase in the volume of the in-situ transformed ceramic phase structures (see Figure 11 for details) [12].

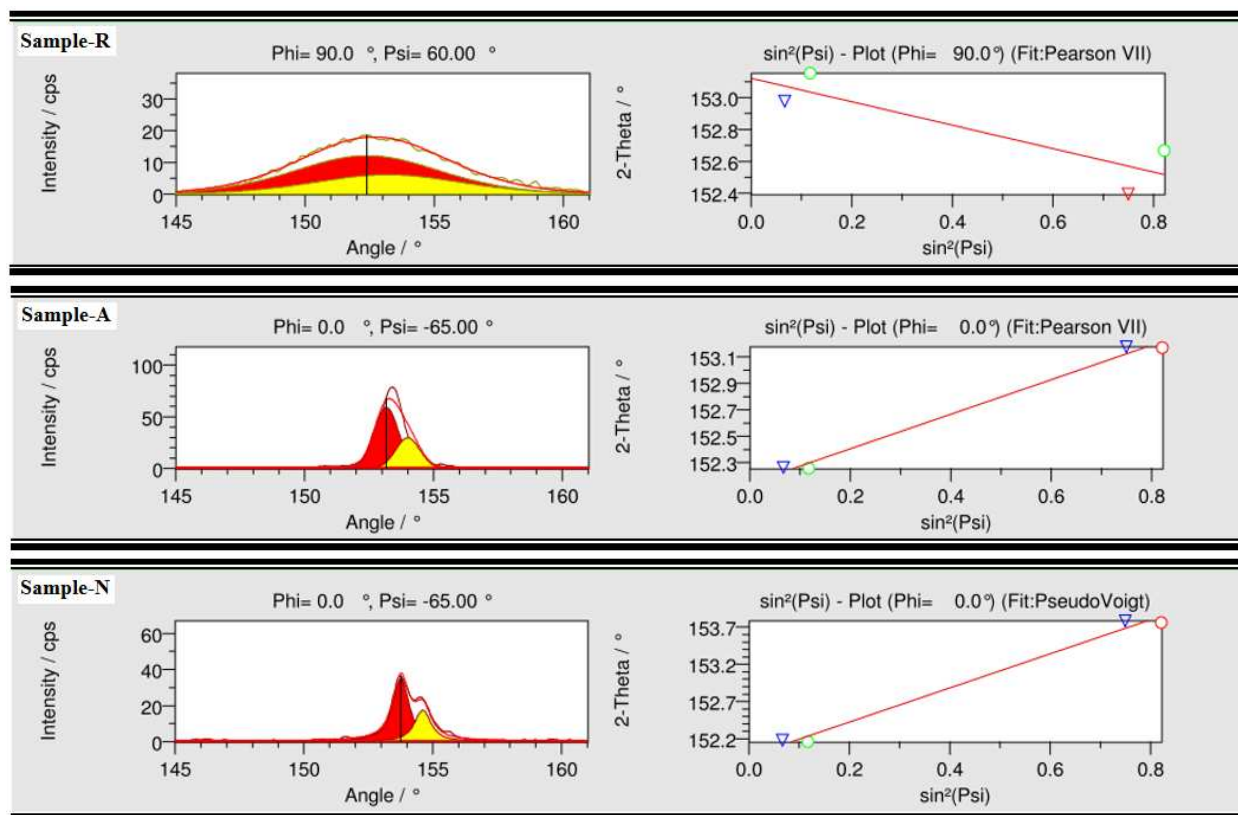


Figure 11. Intensity-angle, intensity- $\sin^2(\Psi)$ fit curves residual stress values calculated from

The coatings are compared with respect to the conventional hard chromium coatings. In regard to the electrochemical behavior, the chromium-carbon black composite coatings heat-treated under nitrogen atmosphere showing a rehabilitated crack-free microstructure, exhibited better corrosion resistance than the conventional hard chromium structures. Therefore, the increase in corrosion potential suggests improvement of corrosion resistance due to the formation of carbide/nitride. Characteristic properties, such as hardness, and modulus of elasticity are determined for carbide and nitride formed composite coatings. It is observed that the following phase transformations support the recovery of friction-wear characteristics and accordance of substrate-coating interface belonging to the material. According to the detailed inspections, it is assigned that the definite results directly correlate with both the magnitude and the direction of the residual stresses. As a result, the corrosion behaviour and the mechanical properties of the in-situ electro codeposited coatings are believed to be controlled by microstructure and surface properties of the metallic chromium layer, which is modified by the formation of carbide and/or nitride phase, and can be used for many engineering applications instead of traditional metallic coatings.

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