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Nanostructure of Materials and Corrosion Resistance

A. A. El-Meligi

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1. Introduction

The application of nanotechnology in the field of corrosion protection of metals and alloys attracts the attention of researchers. Many of these applications require good understanding of the corrosion behavior of the materials as a function of microstructure. Significant progress has been made in various aspects of synthesis of nano-scale materials. In addition, nanostructures promote selective oxidation, forming a protective oxide scale with superior adhesion to the substrate. Nanostructured materials of 1–100 nm are known for their outstanding mechanical and physical properties due to their extremely fine grain size and high grain boundary volume fraction [1]. They are important due to their unique properties that may lead to new and exciting applications [2]. Nanocomposite of polymer coating can effectively combine the benefits of organic polymers, such as elasticity and water resistance to that of advanced inorganic materials, such as hardness and permeability. The nanostructured silica coating showed comparable or better performance than hexavalent chrome passivation [3, 4]. Such behavior of nanostructured materials, which relates to corrosion resistance, relies on materials microstructure. In fact, most properties of solids depend on the materials microstructure. The microstructure includes a number of parameters such as the chemical composition, the arrangement of the atoms (the atomic structure) and the size of a solid in one, two or three dimensions [5]. Comparable variations have been noted if the atomic structure of a solid deviates far from equilibrium or if its size is reduced to a few interatomic spacing in one, two or three dimensions. Nanoporous metals (NPMs) made by dealloying represent a class of functional materials with the unique structural properties of mechanical rigidity, electrical conductivity, and high corrosion resistance [6]. It is stated by Weissmüller et. al, that the prospect of using alloy corrosion as a means of making nanomaterials for fundamental studies and functional applications has led to a revived interest in the process. The quite distinct mechanical properties of nanoporous metals are one of the focus points of this interest, as relevant studies probe the deformation behavior of crystals at

the lower end of the size scale. Furthermore, the coupling of bulk stress and strain to the forces acting along the surface of nanoporous metals provide unique opportunities for controlling the mechanical behavior through external variables such as the electrical or chemical potentials [7]. The relation between chemical architecture of thin (10 and 50 nm) chromium and tantalum oxide coatings grown by filtered cathodic arc deposition (FCAD) on carbon steel and their corrosion protection properties is reported [8]. In fact, the coatings of oxides improve sealing properties of the alloy, but there is an initiation for the localized corrosion. This may be due to the imperfectness of the coats and improper finishing for the alloy surface. The corrosion performance in chloride media of chromium coatings obtained by direct current (DC) and pulse current (PC1 and PC2) was studied [9]. The obtained results show similar hardness values and a superior corrosion performance of PC2 coatings, which is related to their roughness, morphology, wettability and mainly, their crack absence. Silver/silicon oxide core-shell nanoparticles (60 nm) were used in marine antimicrobial corrosion coatings [10]. The results show that the nanoparticles coat could enhance long-term corrosion protection in comparison with the copper biocides. This composite has a strong potential use in environmentally friendly antimicrobial coatings.

2. Properties of nanostructured materials and controlling procedures

Nanostructured materials can be produced by using different synthesis and processing methods. This will lead to variation of their grain sizes or phase dimensions in the nanometer size regime. The interest in these new ultrafine-grained materials results primarily from the special nature of their various physical, chemical, and mechanical properties and the possibilities of controlling these properties during the synthesis and subsequent processing procedures. Since it is now becoming increasingly apparent that their properties can be engineered effectively during synthesis and processing, and that they can also be produced in quantity, nanophase materials should have considerable potential for technological development in a variety of applications [11]. As the properties of solids depend on size, atomic structure and chemical composition, the nanostructured materials exhibit new properties due to one or several of the following effects [12]:

2.1. Effects of size

The effects of size result if the characteristic size of the building blocks of the microstructure is reduced to the point where critical length scales of physical phenomena (e.g. the mean free paths of electrons or phonons, a coherency length, a screening length, etc.) become comparable with the characteristic size of the building blocks of the microstructure [12].

2.2. Dimensionality change

If nanostructured materials consist of thin needle-shaped or flat, two-dimensional crystallites, they become a two- or one-dimensional system with respect to this phenomenon [13]. For example, layered materials MPS_3 , where M is the transition metals, are ordered in layers with

interspacing of 6.4 Å, as shown in Fig. 1 [14]. These materials are crystalline and could be used for many applications, such as, a cathode for the rechargeable batteries, sensors, optical applications, and hydrogen storage [15]. Processing map for hot working of hot extruded AZ31–1.5 vol% nano-alumina magnesium composite (AZ31–NAL) prepared by disintegrated metal deposition (DMD) technique has been developed in the temperature range of 250–500 °C and strain rate range of 0.0003–10 S₋₁ [16]. The nano-alumina composite helps in reducing the preferred orientation in AZ31 alloy. This may increase its corrosion resistance.

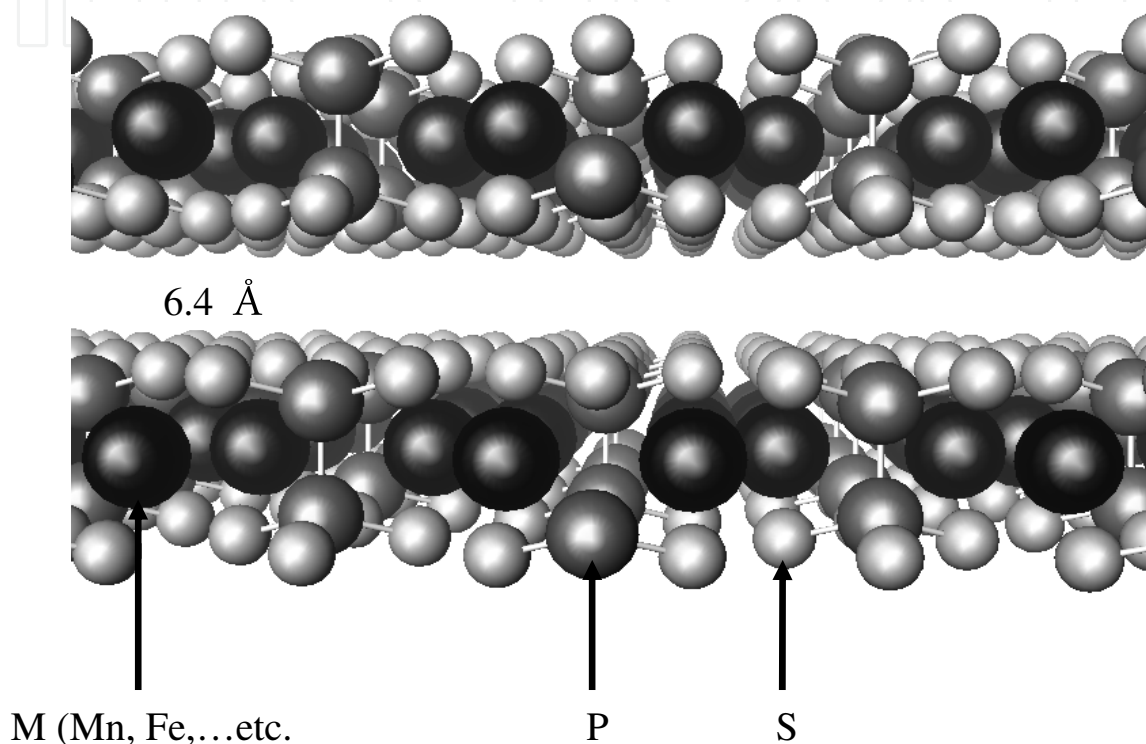


Figure 1. Layered structure of MPS3 [14].

2.3. Atomic structure

A high density of incoherent interfaces or other lattice defects such as dislocations, vacancies, will change the atomic structure [12]. The cores of lattice defects represent a constrained state of solid matter differing structurally from (unconstrained) crystals and/or glasses. As a consequence, a solid containing a high density of defect cores differs structurally from a defect-free solid with the same (average) chemical composition. The boundaries represent an example of this effect: the misfit between adjacent crystallites changes the atomic structure (e.g. the average atomic density, and the nearest-neighbour coordination, etc.) in the boundary regions relative to the perfect crystal. At high defect densities the volume fraction of defect cores becomes comparable with the volume fraction of the crystalline regions. In fact, this is the case if the crystal diameter becomes comparable with the thickness of the interfaces, i.e. for crystal sizes on the order of one or a few nanometers as is the case in nanostructured materials.

2.4. Alloying elements

The alloying elements have great influence on the alloys structure and properties. For example, the addition of alloying elements less noble than iron increases the corrosion resistance in the active region improving the protective quality of the corrosion product film in which the cations of alloying elements are significantly concentrated [17]. The influence of the alloying elements on the interface reactions of zinc coatings during the galvanization process was examined [18]. These reactions affect the crystallization and the structure and properties of the outer layer of the coatings. Depending on the type and concentration of the alloying additions in the galvanizing bath differences were induced in the crystallization process of the Fe-Zn phases. It was found that both the concentration and the distribution of the alloying elements played an important role in the growth of the phases. It has been pointed out for alloys with elements, which are capable of forming passive films, that the atoms of these elements can diffuse easily through the grain boundaries to the surface of the alloy to form the protective passive layer [19, 20].

The following cases of this type of immiscible components in nanostructured may be distinguished: solute atoms with little solubility in the lattice of the crystallites frequently segregate to the boundary cores (e.g. the free energy of the system in several alloys is reduced if large solute atoms segregate to the boundary core). The second case of nanostructured alloys results if the crystallites of nanostructured materials have different chemical compositions. Even if the constituents are immiscible in the crystalline and/or molten state (e.g. Fe and Ag), the formation of solid solutions in the boundary regions of the nanostructured has been noticed [12].

3. Corrosion of materials

Corrosion is the chemical or electrochemical reaction between a material and its environment. It produces deterioration of the material or of its properties. Also, corrosion has different forms of attack [21-23]. The basic corrosion theory is that the corrosion is an electrochemical reaction composed of two half cell reactions, an anodic reaction and a cathodic reaction. The anodic reaction releases electrons (equation 1), while the cathodic reaction consumes electrons (equations: 2-5). Each half-cell reaction has an electrical potential, known as the half-cell electrode potential. The anodic reaction potential, E_a , plus the cathodic reaction potential, E_c , adds up to E , the cell potential. If the overall cell potential is positive, the reaction will proceed spontaneously. The corrosion reactions can be represented as follows:

Anodic reaction:



Where M stands for a metal and n stands for the number of electrons that an atom of the metal will easily release, i.e. for iron and steel:



Cathodic reactions:

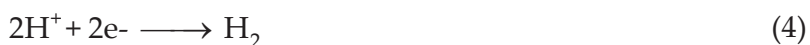
- Oxygen reduction in acidic solution



- Oxygen reduction in neutral or basic solution



- Hydrogen evolution from acidic solution



- Hydrogen evolution from neutral water



The chemical attack or dry corrosion occurs under dry conditions, such as high temperatures in gaseous environments, molten salts and liquid metals. Dry corrosion process is a direct reaction between a metal and the corrosive environment. Dry corrosion is of great importance in a number of petroleum refining processes. It includes the attack of hydrogen sulfide and other sulfur compounds on steel and various alloys at elevated temperatures. Solutions to this type of corrosion generally depend on metallurgical approaches, e.g. variations in composition, heat treatment of the selected metal or alloy. In fact, high temperature corrosion of metals and alloys always involves oxidation process. For example, a metal reacts with oxygen at high temperature by initial adsorption of oxygen, chemical reaction to form the surface oxide, oxide nucleation and lateral growth into a continuous film. Such film may protect the underlying metal [24]. One of the well known oxidation is the iron oxidation in oxygen (as pure metal or in carbon steel alloys) at high temperature [25].

Wet corrosion is an electrochemical process; in practice it limits to nearly 232 °C as an upper temperature. The electrochemical corrosion results from reaction between a metal surface and an ion-conducting environment. This process occurs by metal contact with an electrolyte for transport of electric current. Most cases of electrochemical corrosion proceed in aqueous media such as natural water, atmospheric moisture, rain, and wet soil. Also, other environments enhances the corrosion process e.g. acids, petroleum products, cooling water, chemical solutions,...etc. For example, water presents in refinery by different sources, such as the crude itself, through injection of water of steam to aid in the steam distillation of

various petroleum fractions, water washing or aqueous solution contacting various intermediate and product streams in refining and petrochemical processes [21].

In fact, metal surfaces have corrosion cells in contact with an electrolyte. Different areas on the metal surface could also have different potentials with respect to the electrolyte [26, 27]. These variations could be due to a number of factors: i) metallurgical behaviors, i.e., differences in their composition, microstructure, fabrication, and field installations, and ii) environmental factors. Carbon and low alloy steels are the most widely used material in different industries in corrosive environments and the metallurgical factors have great influence on the corrosion process [28, 29].

3.1. Corrosion resistance of alloys

A number of ways have developed to increase the corrosion resistance of metals such as applying inhibitors, adding passive alloy element, putting protective coating and so on. The application of inhibitors has to follow some regulations such as environmental impact, low toxicity, and structure of inhibitors and alloys. Nanostructure inhibitors are very important in protection metals and alloys. Changing micro-structure of materials will bring surprised results to promote the corrosion resistance of metals/alloys [30-33]. This change occurs by using new micro-structures such as single crystalline, nanocrystalline or microcrystalline and amorphous to replace the traditional cast alloy [34]. Nanostructured materials characterize by their small grain sizes (1-100 nm) and high volume fraction of grain boundaries. These properties improve unique physical, chemical and mechanical properties compared with those of their cast counterparts [34]. The properties are particularly useful in corrosion protection applications.

4. Nanosize and effect on corrosion resistance

Electrodeposition is a versatile technique for producing nanostructured materials. It is a technologically and economically viable production route to metals, alloys and metal matrix composites, both in bulk form and as coatings. Properties of nano-structured electrodeposits such as hardness, wear resistance and electrical resistivity are strongly grain size dependent. Corrosion behaviour of nanostructured-alloys has been assessed by several techniques in various environments [35–39]. Thorpe et al. reported an enhanced corrosion resistance of nanostructured- Fe₃₂-Ni₃₆-Cr₁₄-P₁₂-B₆ than that of its amorphous counterpart [35]. The authors attributed this improved corrosion resistance to the observed greater Cr-enrichment of the electrochemical surface film via rapid interphase boundary diffusion. Bragnolo et al, report improved corrosion resistance with nanostructured-Fe₇₂Si₁₀B₁₅Cr₃ metallic glass wires. In their study, the beneficial effects of nanostructured processing for corrosion resistance were not evident with a non-passivating alloy composition [36]. Zeiger et al, report an enhanced corrosion resistance of nanostructured-Fe-8 wt % Al in Na₂SO₄ solution [37]. The study shows that defect density (density of grain boundaries) promotes metal dissolution. As the diffusion of aluminum is fast enough in

the grain boundaries, it is possible that the oxide film on nanostructured and crystalline-FeAl8 alloy provides better protection than on the same polycrystalline alloy. Weak acid and weak base ease passive film formation of nanostructured-FeAl8 where Al forms stable passive film. The newly developed Ti60Cu14Ni12Sn4Nb10 nanostructured dendrite composite exhibits a particular microstructure that confers outstanding mechanical properties and improves corrosion resistance [40]. It has been reported that the presence of a ductile second phase can significantly improve the mechanical properties of nanocrystalline alloys. Newly developed Ti-base bulk alloy with a dendritic phase dispersed in a nanostructured matrix greatly enhances the usual low ductility of homogeneous nanocrystalline alloy. Polarization tests of Ti60Cu14Ni12Sn4Nb10 copper mould cast specimens indicate good corrosion resistance in acidic media (0.5N H₂SO₄), medium resistance in alkaline (0.5N NaOH) but the alloy undergoes pitting in chloride media. The behaviour of the alloy in H₂SO₄ is similar as the typical behaviour of pure titanium and titanium alloys [41]. It exhibits a wide anodic passive region between 90 mV and 1.5V (SCE), approximately, and passive current densities in the order of 10⁻³ mA due to the formation of highly protective surface films. The voltage range of passivation in NaOH electrolyte is shorter than in H₂SO₄. It finishes when the current increases to 470mV (SCE), approximately. In chloride media, sharp increase in current density interrupts the passivation during anodic polarization. The interruption occurs by a sudden passive film breakdown followed by an excessive pit growth and the subsequent dissolution of the surface of the alloy. The increase of NaCl concentration shifts pitting potentials to more negative values. This behaviour differs from general findings on polycrystalline pure titanium and dilute titanium alloys. The pitting corrosion and localized attack on the alloys don't observe in marine environments [42].

4.1. Corrosion resistance of stainless steel

Stainless steel uses as a structural material in many applications. Corrosion and wear limits its service life. Effective measures are taken to improve its corrosion and wear resistance properties [42–47]. A passive film precludes contact between corrosive environments and the metallic surface. However, weakness of the passive layer can trigger corrosion. The use of inhibitive species constitutes active corrosion protection to decrease corrosion intensity. The use of both strategies jointly could adequately protect the metallic substrate. The conversion coatings such as chromating and phosphating treatments have historically played important role in different industries. It provides corrosion protection to both ferrous and non-ferrous metals. Also in many cases the anticorrosive property of zinc phosphate treatment is insufficient for outdoor exposure. Electroplated Ni and Cr are relatively expensive and Cr(VI) is environmentally unacceptable [48]. As an alternative, siloxane based sol-gel coatings have been suggested as passive corrosion protection. It has the ability to form dense Si–O–Si network adhering to substrate through Me–O–Si bonds. The bonds form good corrosion impeding properties [48–54]. Adding specific organic functional groups such as siloxane improve adhesions on alloys surface. Clusters of metal oxides reinforces silica network during sol-gel synthesis from the respective metal alkoxides [55, 56].

Additionally, sol-gel coatings do not need high process temperature and vacuum conditions are crucial in the case of many of thin layer coating techniques [57–60]. Furthermore, sol-gel is relatively simple, low-cost and applicable to materials having complex geometry. It is considered to have low negative environmental impact. Nevertheless, defects or pores in the sol-gel coating let in the corrosive species and initiate the corrosion processes [61]. The defects indicate the need for additional active corrosion protection. Incorporation of inhibitive species into inorganic fillers enhances corrosion resistance [62, 63]. Many kinds of inhibitors could be used to protect various metallic materials [64–73]; however, very often this negatively influences the stability of the sol-gel matrix [74, 75]. Acetylenic alcohols are considered excellent inhibitors of corrosion [76]. Nanostructure sol-gel impregnated with propargyl alcohol can protect defects of sol-gel [77].

Anticorrosive primers and coatings based on conducting polymers gain momentum Owing to the stringent environmental regulations on the usage of toxic heavy metals in the formulation of corrosion protective coatings [78, 79]. The recent advancements in nanotechnology have hastened the development of high performance nanostructured coatings. They have a broad spectrum of anticorrosive activity under a wider range of hostile environments. Inhibitor coatings based on conducting polymers are either chemically or electrochemically deposited on the metal substrate [80–87].

4.2. Surface modification

ZrO₂, a bioceramic, coats stainless steel 316L to insulate the needles and improve their biocompatibility. Three types of stainless steel 316L specimens were used in the experiment: an untreated specimen, an electropolished specimen and an electropolished and plasma treated specimen. The effects of electropolishing and plasma treatment on coating strength and the relationship between coating thickness and electrical conductivity were investigated. The result showed that the coating strength of the plasma treated sample was 130% greater than that of the untreated sample and 40% greater than that of the electropolished one. The electrical insulation characteristic of ZrO₂ coating on stainless steel 316L was superior to that of uncoated stainless steel 316L. The appropriate thickness of ZrO₂ coating is 500 nm for the electrical insulation. Compared to untreated specimens, the surface roughness of treated specimens decreased by as much as 80% after 5 min, and thus, this was the most effective time to carry out the electropolishing, as shown in Fig. 2 [88].

The high-current pulsed electron beam (HCPEB) technique has been proven to be an efficient method for surface modification of alloys [89–91]. Modifications improve the overall performance of alloys such as microhardness, corrosion resistance, and wear resistance. The structure and phase transformations in the near-surface layers of a low carbon steel (0.2 wt.% C) subjected to a high-current pulsed electron beam (HCPEB) treatments have been investigated by using electron microscopy and X-ray diffraction (XRD) [92]. A nanostructure consisting of cementite and C-supersaturated austenite is formed in the near-surface region after multiple bombardments. This is confirmed by the XRD patterns shown in Fig. 3. According to the peak profile analysis, the average grain sizes of the γ phase (austenite) in the surface layer after the 5- and 10-pulse bombardments by the HCPEB are about 6.5 and 4.2 nm, respectively.

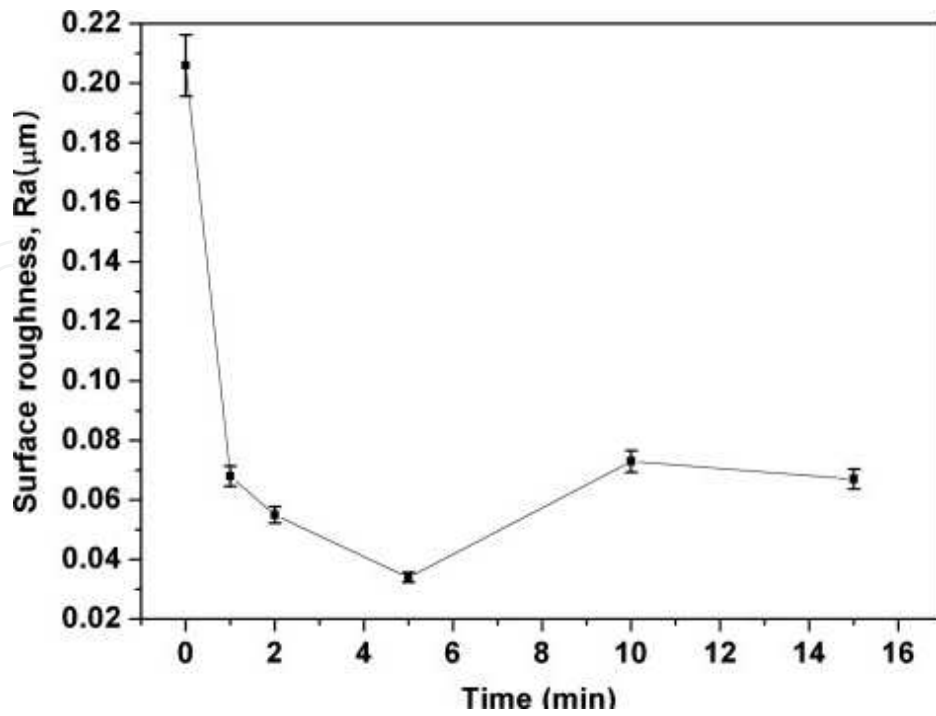


Figure 2. Variation of surface roughness as a function electropolishing time [88].

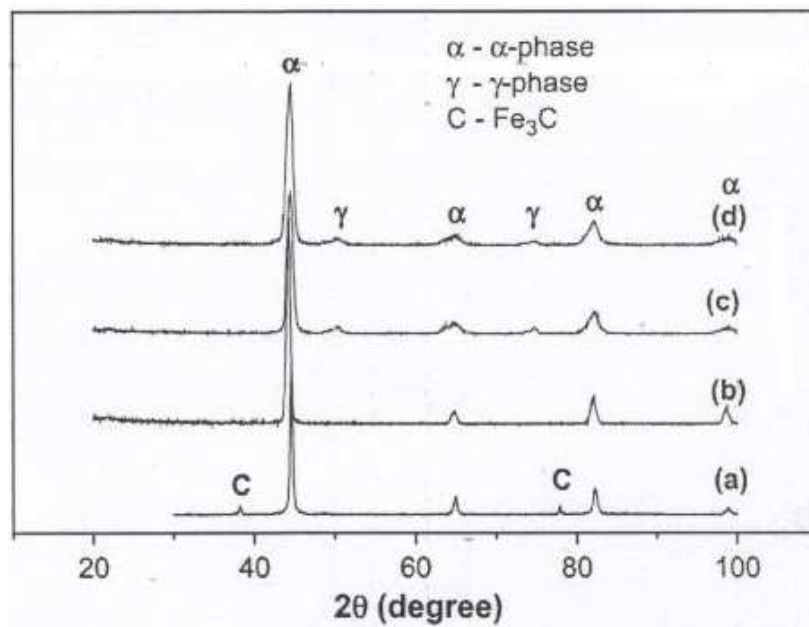


Figure 3. XRD patterns collected from the surface of the initial no. 20 steel (a), irradiated with 1 pulse (b), 5 pulses (c), and 10 pulses (d). The energy density of HCPM is 4 J cm² [92].

4.3. Stainless steel corrosion and nanostructure

The family of stainless steels (SS) is large and varied; in fact, there are more than 100 registered types. Each of these was originally designated for some specific use. For example, SS316 is used for severe environments. Of course, there are many industrial processes that require a higher level of resistance to corrosion. Carburizing has been applied to austenitic stainless steel to promote increased wear and corrosion resistance [93]. Nanometric-sized carbide-based crystallites have been synthesized successfully through the pulsed nanocrystalline plasma electrolytic carburizing method on the surface of 316 austenitic stainless steel [94]. It was found that the corrosion resistances of coated samples have a direct relationship with the average size of complex carbide-based nanocrystallites. The synthesized carbide-based crystallites exhibit average sizes at around 37–80 nm. The minimum average size of nanocrystals was found to be 37.7 nm in 600 V of peak of applied cathodic voltage, 10 kHz of frequency of pulsed current, 40 °C of temperature of electrolyte, 10 min of treatment time.

Polarization resistances of different samples found through the potentiodynamic corrosion tests performed after surface hardening treatment. The polarization resistances due to corrosion in specimen groups treated at different conditions varied between 153.4 kΩ/cm² and 635 kΩ/cm². The figure explains which specimen has maximum or minimum corrosion resistance. From the above results, it can easily be said that a high corrosion resistance has been obtained with higher applied voltages and treatment times of carburizing. These results indicate that the corrosion resistances of the obtained layers are a direct function of the average size of the nanocrystallites [94].

Improvement in the surface layers' properties by changing their structure remains actual due to the fact that the destruction of the materials, including fatigue failure, wear and corrosion depends usually on the surface structural state [95]. The surface nanostructure, which is formed in the surface layers with thickness of about of 30–50 nm, plays a main role in the enhancement of properties [96–99]. At the same time, only a few recent studies have paid attention to the corrosion behavior of stainless steels with nanograined surface structure [100–102]. These studies have shown that the corrosion resistance can also be markedly improved, particularly by shot peening [103] or sandblasting with subsequent low-temperature annealing [104, 105]. For example, a nanocrystalline surface layer was produced on an AISI-321 stainless steel by severe plastic deformation via ultrasonic peening (UP) [106]. The nanostructured surface layer formed after straining already contains mainly the martensite nanograins characterized by an average size of about 10 nm. Grain size increased gradually up to 60 nm within the layer containing both austenite and martensite phases at a depth of about 30 nm from the treated surface. Both the microhardness behavior of the stainless steel surface and its corrosion performance in 3.5% NaCl solution can be enhanced by the UP. They are shown to be in correlation with: (i) the grain refinement process and (ii) the increase in the volume fraction of strain-induced martensite.

4.3.1. Effect of nanostructure on passive film

Nanostructure changes the thickness of passive film. XPS Cr spectra from the passive films in 3.5% NaCl solution on nanostructure (NS) coating and the cast alloy are shown in Fig. (4) [107]. After 40 s bombardment using the same bombardment parameters, the Cr³⁺ peak disappeared in the passive film on the NS coating but was still present in the film on the cast alloy. This indicates that the passive film on the NS coating was thinner than that on the cast alloy in normal NaCl solution. However, nanostructure increased the thickness of passive film on the magnesium alloy with rare earth elements [108]. It is well known that the passive film on the magnesium alloy is mainly the corrosion product layer on the sample, which blocks the dissolution of the material and inhibits the corrosion. Therefore, nanostructure promotes the dissolution of alloy and forms more products on the sample. Finally, the film layer was much thicker than that of the cast alloy. Nanostructure also changes the compact property of the passive film. After cathodic reduction, the variation of current with time could be measured at a fixed potential. If the contribution of the double layer charge is neglected, the initial drop of current density should be related to the growth of a protective film on the electrode surface. The current decreases with time as follows [109]:

$$I = 10 - (A + kg t) \quad (6)$$

where I represents current density, t is time, A is constant and k represents the slope of the double-log plot for potentiostatic polarization. $k = -1$ indicates the formation of a compact, highly protective passive film, while $k = -0.5$ indicates the presence of a porous film, growing as a result of a dissolution and precipitation process. A porous passive film presents on the 309 stainless steel and nanostructure improves formation of a compact film [110].

4.4. Patents of corrosion inhibition

It has been found that low levels of molybdate in combination with low levels of various phosphorous containing compounds controls corrosion in ferrous metals [111, 112]. In addition, foaming, sludge formation, and/or focused or localized corrosion has not been observed in connection with the use of the molybdate with certain phosphorous containing compounds. Additionally, the use of molybdate in combination with phosphorous containing compounds prevents or reduces the formation of precipitates, including iron and other potential precipitates [113]. A composition and method is disclosed for inhibiting the corrosion of metals in contact with an aqueous system capable of corroding the metal. The inventive composition contains a substantially water-soluble polymer of an acidic amino acid and at least one water-soluble salt of molybdenum or zinc. The composition is substantially non-toxic and environmentally acceptable and is supplied in a corrosion-inhibition amount to the otherwise metal-corrosive aqueous system [114]. A corrosion inhibitor for use with Urea Ammonium Nitrate solutions is disclosed, comprising a blend of molybdate and one or more of the inorganic phosphates (including phosphates,

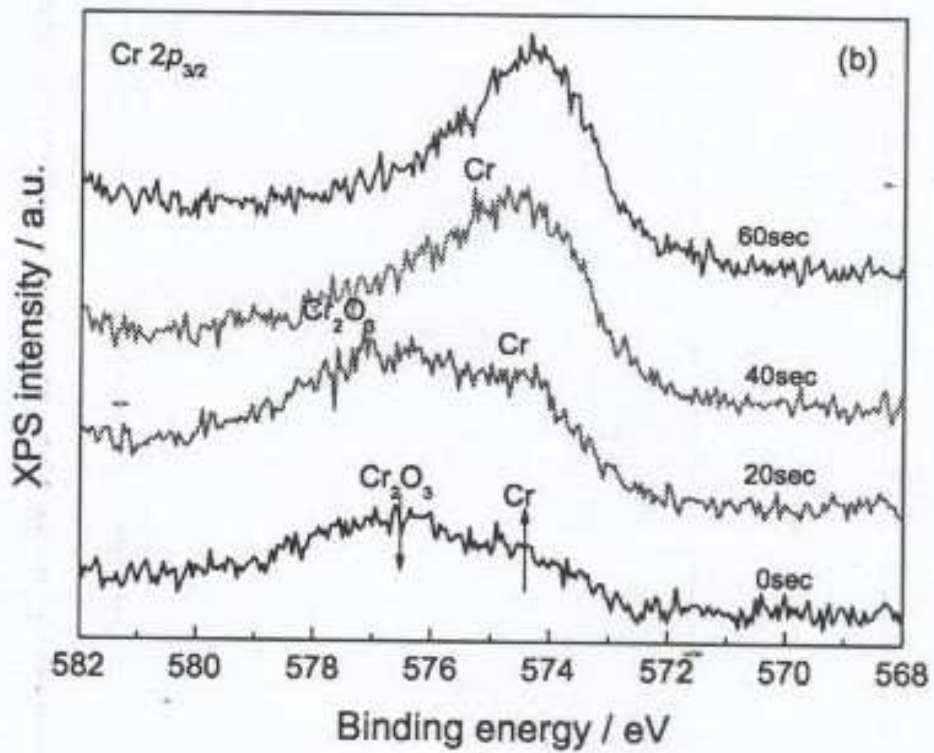
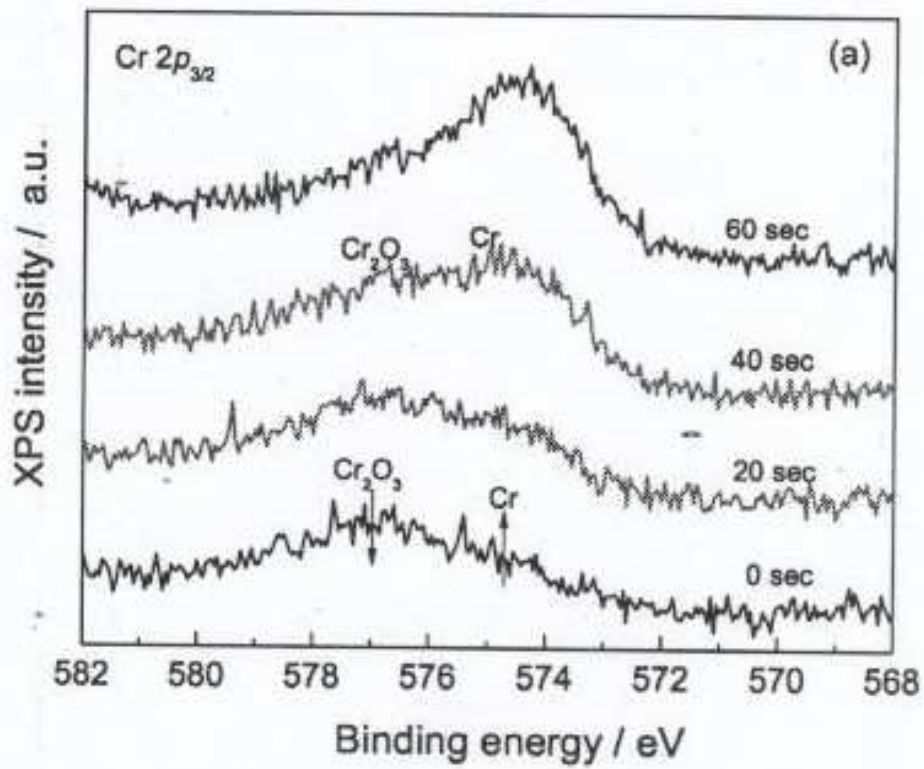


Figure 4. Cr 2p XPS depth profile spectra from the cast alloy (a) and the NC coating (b) after passivation 30 min at 0 V in 3.5% NaCl solution. The depth is indicated in spectrum[107]

polyphosphates, and pyrophosphates) and organic phosphates or phosphonates. Inorganic phosphates include, but are not limited to, SHMP (Sodium Hexametaphosphate) and TKPP (Tetra-Potassium Pyrophosphate) [115]. A corrosion inhibitor composition for a fuel, comprising a plurality of nanoparticles formed of an inorganic composition having an average longest dimension of 1 nanometer to 100 nanometers, wherein the inorganic active composition is insoluble in the fuel and is adapted to react with a corrosion causing contaminant [116]. Catalytic layers for use in the electrodes of fuel cells including a non-noble metal substrate layer coated with one or a few monolayers of noble metal, such as Pt. These thin, highly porous structures with large catalytically active surface areas, should exhibit a significantly higher power output per mg of Pt and per cm² of the membrane than the current Polymer Electrolyte Fuel Cells catalytic layers. [117]. Nanoparticles comprising molybdenum, methods of manufacturing nanoparticles comprising molybdenum, and nanotechnology applications of nanoparticles comprising molybdenum, such as electronics, optical devices, photonics, reagents for fine chemical synthesis, pigments and catalysts, are provided [118]. The present invention relates to methods and compositions for reducing damaging oxidation of metals. In particular, the present invention relates to nanoparticle surface treatments and use of nanoparticle surface treatments to reduce the damaging oxidation and corrosion of stainless steel and other alloy components in oxidizing and corrosive conditions [119-121].

5. Conclusion

Properties of nano-structured electrodeposits such as wear resistance, electrical resistivity and hardness depend strongly on grain sizes of metals and alloys. Nanocrystallization decreases grain size and changes surface condition. The surface condition significantly influences the electrochemical corrosion behaviors of metals/alloys in liquid system. There are a number of advanced techniques have been developed to attain the nanostructure. Many applications of the nanomaterials made to improve the devices and industries. The application of nanotechnology in the field of corrosion prevention of metals is very important. Nanometric-sized carbide-based crystallites have been synthesized successfully through the pulsed nanocrystalline plasma electrolytic carburizing method on the surface of 316 austenitic stainless steel. The corrosion resistance of coated samples has a direct relationship with the average size of complex carbide-based nanocrystallites. Significant corrosion resistance attained with higher voltages and treatment times of carburizing. These results indicate that the corrosion resistances of the obtained layers are a direct function of the average size of the nanocrystallites. In local corrosion, nanocrystallization increases the unstable points on the surface of the materials, which increases the possibility of local corrosion. However, the excellent ability of element diffusion helps to heal the local corrosion points. These points inhibit the growth of the local corrosion. The research continues to develop nanostructure of inhibitors and alloys. This will reduce the corrosion of metals and alloys.

Study (reference number)	Main Findings
[16]	The nano-alumina composite helps in reducing the preferred orientation in AZ31 alloy. This may increase its corrosion resistance.
[34]	Nanostructured materials characterize by their small grain sizes (1-100 nm) and high volume fraction of grain boundaries. These properties improve unique physical, chemical and mechanical properties compared with those of their cast counterparts. The properties are particularly useful in corrosion protection applications.
[88]	The appropriate thickness of ZrO ₂ coating is 500 nm for the electrical insulation. The electrical insulation characteristic of ZrO ₂ coating on stainless steel 316L was superior to that of uncoated stainless steel 316L.
[92]	A nanostructure consisting of cementite and C-supersaturated austenite improve corrosion and wear resistance for low carbon steel.
[93]	Carburizing has been applied to austenitic stainless steel to promote increased wear and corrosion resistance.
[94]	Nanometric-sized carbide-based crystallites have been synthesized successfully through the pulsed nanocrystalline plasma electrolytic carburizing method on the surface of 316 austenitic stainless steel. It was found that the corrosion resistances of coated samples have a direct relationship with the average size of complex carbide-based nanocrystallites.
[100-105]	Only a few recent studies have paid attention to the corrosion behavior of stainless steels with nanograined surface structure. These studies have shown that the corrosion resistance can also be markedly improved, particularly by shot peening or sandblasting with subsequent low-temperature annealing.
[108]	Passive film on the nanostructure increases the thickness of passive film on the magnesium alloy with rare earth elements. The passive film on the magnesium alloy is mainly the corrosion product layer on the sample, which blocks the dissolution of the material and inhibits the corrosion.
[110]	A porous passive film presents on the 309 stainless steel and nanostructure improves formation of a compact film.
[119]	Nanoparticle surface treatments use to reduce the damaging oxidation and corrosion of stainless steel and other alloy components in oxidizing and corrosive conditions.

Table 1. Main findings of some studies presented in the text.

Author details

A. A. El-Meligi*

Address all correspondence to: aemeligi@amaiu.edu.bh, ael_meligi10@hotmail.com

Head of Research and Publication, AMA International University-Bahrain, Bahrain

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