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Methods for Corrosion Protection of Metals at the Nanoscale

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Abstract

There was a lack of literature related to the corrosion and its prevention at the nanoscale. Recently, the nanotechnology based protective methods could offer many advantages over their traditional counterparts, such as protection for early-stage, higher corrosion resistance, better corrosion control, and controlled release of corrosion inhibitors. This review explores how metals can be protected at nanoscale by using both nanotechnology and nanomaterials. It covers the advanced methods using nano-alloys, nano-inhibitors, nano-coatings, nano-generators, and nano-sensors.

Keywords: Corrosion protection; nano-alloys; nano-inhibitors; nano-coatings; nano-generators; nano-sensors.

Introduction

In 2016, the global cost of corrosion is estimated to be US$2.5 trillion (~ 3.4 % of the global Gross Domestic Product -GDP). In case of conventional metallic structures, the acceptable value of thickness lost due to the metal degradation is about ~100 µm/year. Nowadays, with the development of nanoscience and nanotechnology, the small metallic parts (or nanostructure materials) have been widely used in many products, such as print electronics, contact, interconnection, implant, nano-sensors, display units, ultrathin layers, drug delivery systems... Thus, their thickness loss should be controlled with acceptable values in range from 10 to 100 nm.

Traditional methods for protection of metals include various techniques, such as coatings, inhibitors, electrochemical methods (anodic and cathodic protections), and metallurgical design. In practice, effective corrosion control is achieved by combining two or more of these methods. Usually, highly corrosion resistant materials are associated with a high cost factor. Even then, such materials can undergo degradation in severe environments/stress.

The use of cheaper metallic materials along with proper corrosion control strategies is therefore economic for many applications. Nanomaterials and nanotechnology based protective methods can offer many advantages over their traditional counterparts, such as protection for early-stage, higher corrosion resistance, better corrosion control, and controlled release of corrosion inhibitors.

This mini review explores how metals can be protected at nanoscale by using both nanotechnology and nanomaterials (nano-alloys, nano-inhibitors, nano-coatings, nano-generators, nano-sensors).

Nano-Alloys

Nano-alloys (nanostructured alloys) are constructed from at least two different metallic nanomaterials, in order to overcome the limits of single components, to improve properties, to achieve new properties, and/or to achieve multiple functionalities for single metallic nanoparticles. Nano-alloys can also refer to the formation of nanocrystalline metal phases within the metallic matrices.

It was reported in literature that nano-alloys can offer many advantages over their conventional counterparts, such as higher corrosion resistance [1-7], high oxidation resistance [8,9], strong ductility enhancement [10], high hardness [11], and wear resistance [12].

To improve the corrosion resistance of Ti–6Al–4V alloy without modifying its chemical composition, Kumar et al [1] fabricated the surface nanostructure for this alloy by using ultrasonic shot peening (USSP) method. Similarity [7] used USSP method to fabricate the surface nanocrystallized AISI 409 stainless steel, for higher corrosion resistance.

For high-strength aluminum alloys [10] used the thermo-mechanical treatment to impart them the nanocrystalline structures and to control their strength and ductility [13] prepared the 3D honeycomb nanostructure-encapsulated magnesium alloys. In their study, graphene oxide (GO) was incorporated into AZ61 alloy (at 1 wt.%) to form the honeycomb nanostructure-encapsulated Mg alloys, which have the higher corrosion resistance and mechanical properties than the pure AZ61 alloy. The authors proposed 4 mechanisms: (i) GO promoted the nucleation of α-Mg grains, reduced their interconnections, thus refined their sizes; (ii) high anti-permeability of GO acting as the tight barrier against corrosion; (iii) GO reinforced the corrosion layer on the surface of Mg matrix; (iv) GO facilitated the formation of bone-like apatite due to its oxygen-containing groups.

Nano-Inhibitors

For smart anticorrosion coatings, nano-inhibitors (nano-sized inhibitors) might refer to the inhibitor loaded nanocontainers. These nanocontainers exhibited the smart releasing property for their embedded inhibitors, by external or internal stimuli (such as pH-controlled release, ion-exchange control, redox-responsive control of release, light-responsive controlled-release, and release under mechanical rapture [14]). In addition, the smart nanoshells could prevent the direct contact between the inhibitors with both coating matrices and adjacent local environments. All nanocontainers can be divided into two category of polymer nanocontainers (core-shell capsules, gels) and inorganic nanocontainers (porous inorganic materials). Polymer nanocontainers require multi-step technology for their fabrication. Besides, their fabrication needs several equipment. On the other side, available porous inorganic materials can be directly applied as inorganic nanocontainers for self-healing coatings. Inorganic nanocontainers could be mesoporous silica or titania, ion-exchange nanoclays and halloysite nanotubes [15].

For organic coatings, various inhibitors have been loaded into nanocontainers, such as benzotriazole [16], mercaptobenzothiazole [17, 18], mercaptobenzimidazole [19], hydroxyquinoline [20], dodecylamine [21], molybdate salts [22], cerium salts [23], fluoride salt [24], zinc salts [25].

Nano-inhibitors can quickly respond to the local environmental changes associated with corrosion processes, such as local pH, ionic strength, and potential, and release encapsulated corrosion inhibitors to retard the corrosion process [26]. This kind of system can: (i) prevent contact of inhibitor with coating, (ii) provide controlled release of inhibitor after initiation of corrosion, (iii) decrease the amount of consumed inhibitor, (iv) improve the durability of coating, and (v) provide the possibility of installing triggering mechanisms for releasing self-healing agents [27]. Nanocontainers/microcapsules for self-healing coatings are expected to be featured with the following characteristics: (a) mechanical and chemical stability, (b) compatibility with coating material, (c) sufficient loading capacity, (d) impermeability of the shell wall, (e) ability to sense corrosion in early stages, and (f) the ability to release corrosion inhibitor on demand. The application of containers (capsules) is one of the most promising approaches for the development of stimuli-responsive coatings with self-healing/active protection functionalities [28].

In case of metal coating, recently we reported the use of cerium load nanosilica for electroplating of Zn-Ni alloy coating on steel substrate [29]. In our study, the electrochemical measurements suggested that inhibitor could be released from nanocontainer in the early electrodeposition of alloy coating on steel substrate. Whereas, the salt spray test indicated that inhibitor was released during the corrosion of coated steel, thus increased the protective duration of coating by two times.

Nanocoatings

Nanocoatings (nanocomposite /nanostructured coatings) refer to the use nanomaterials and nanotechnology to enhance the coating performance. Nowadays coating should not only serve as the decoration with physical barrier, but also act as the smart multifunctional materials.

For anticorrosion, in general, the barrier performance of coatings can be significantly improved by the incorporation of nanoparticles, that decreasing the porosity and zigzagging the diffusion path for deleterious species. At the interface coating/metal, nanoparticles are expected to enhance the coating adhesion and reduce the trend for the coating to blister or delaminate [30-32]. Besides, nanoparticles or nanostructured coatings could act as a barrier against corrosive species [22].

It was reported in literature that nanomaterials could be used as nanofillers to reinforce both organic and metallic coatings. Various organic matrices have been used to fabricate the polymeric nanocomposite coatings, such as epoxy [30, 31], polyurethane [33], chitosan [34], polyethylene glycol [35, 36], polyaniline [37, 38], rubber-modified polybenzoxazine [39], ethylene tetrafluoroethylene [40], polyester [41], polyacrylic [42], polydimethylsiloxane [43], polypyrrole [44], and alkyds [45]. For metallic nanocoatings, two main matrices have been used for anticorrosion: Ni matrix [46-50] and Zn-Ni matrix [29].

Nano-Generators

Nano-generators refer to the uses of nanosized devices/materials to convert the mechanical/thermal/light energies into electricity. It was reported in literature for the self-powered cathodic protection using nanogenerators [51-55].

"Guo et al. [51] reported the use of the disk Triboelectric Nanogenerator (TENG) to provide a self-powered cathodic protection for stainless steels. Their TENG's output transferred charges and short-circuit current density were 0.70 C/min and 10.1 mA/m^2, respectively, at the rotating speed of 1000 rpm. By coupling the negative pole of this TENG with stainless steels in the 0.5 M NaCl solution, the cathodic polarization potentials were in range from–320 mV to –5320 mV. Similarity [52] used the flexible TENG to harvest the mechanical energy of wind and raindrops for cathodic protection of iron in 0.1M $NaHSO_3$+0.1M $NaNO_3$ solution. Kinetic wave energy also could be harvested by using the flexible TENG [53].Zhang et al. [54] reported the use of flexible hybrid nanogenerator (NG) for simultaneously harvesting thermal and mechanical energies. In their hybrid NG, a triboelectric NG was constructed below the pyro/piezoelectric NG. Recently Cui et al. [55] reported the use of polyaniline nanofibers to construct a wind-driven TENG. Their TENG exhibited a high output values: maximum output voltage of 375 V, short current circuit of 248 µA, and 14.5 mW power, under a wind speed of 15 m/s.

In other direction, other approach of photo generated cathode protection, had been reported by coupling the nano-TiO_2 photo anode with metal electrode using simulated solar irradiation [56], white-light irradiation [57] or under UV light [58]. Recently, the hybridization of noble metals (Au, Ag, Pd) nanoparticles and nano-TiO_2particles are the most promising approach not only to enhance the visible light sensitivity of TiO_2, but also to reduce the recombination of photo generated electron–hole pairs [59].

Nano-Sensors

Nano-sensors (or nanomaterials based sensors) can offer many advantages over their microcounterparts, such as lower power consumption, high sensitivity, lower concentration of analytes, smaller interaction distance between object and sensor. Beside, with the supports of artificial intelligence tools (such as fuzzy logic, genetic algorithms, neural networks, ambient-intelligence…), sensor systems nowadays become smarter.

For corrosion protection at the nanoscale using smart coatings, the early detection of localized corrosion is very important, with regard to the economy, safety, and ecology. The most promising approach is to embed the smart nano-sensors, which are sensitive to the changes of environmental pH values, into the protective coating. Recently, Exbrayat [60] developed the new nano-sensors for monitoring early stages of steel corrosion in NaCl solution. Their nano-sensors were constructed using silica nanocapsules, with the hydrophobic liquid core containing a fluorescent dye. In case of steel corrosion, these nano-sensors were able to detect iron ions and low pH values. [61] used the phenolphthalein loaded mesoporous nanoparticles to detect the active cathodic zones in aluminum and magnesium alloys. This pH indicator changed color at the high pH values.

Conclusion and Future Scope

To protect metals from corrosion at the nanoscale, various methods could be used effectively, such as by using nano-alloys, nano-inhibitors, nano-coatings, nano-generators, nano-sensors… These advanced methods can not only protect metals at the early-stage, but also provide the structural health monitoring and self-healing.

Besides the methods for corrosion protection at the nanoscale, there are several important studies should be carried out, such as (i) Mathematical modeling and simulation of corrosion at the nanoscale, (ii) Methods for testing and measurement of metal corrosion at the nanoscale, (iii) Nanoscale simulation of cathodic protection…

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