Nanomaterials for corrosion control

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Nanomaterials are important due to their unique properties that may lead to new and exciting applications. Current scenario of application of nanotechnology in the field of corrosion prevention of metals is reviewed here. Recent research and developments in this area are discussed in designing efficient coating materials and alloys, which provide superior resistance to corrosion.

NANOSTRUCTURED materials (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]. Significant progress has been made in various aspects of synthesis of nano-scale materials. The focus is now shifting from synthesis to manufacture of useful structures and coatings having greater wear and corrosion resistance. Existing PVD and CVD processes for preparing microcrystalline coatings can be used to produce nano-structured coatings by modifying the process parameters or using feedstock powders having nano-grained structure. Deposition of coatings by thermally activated processes like high velocity oxy-fuel thermal spraying (HVOF) has been successfully used for producing nanocrystalline (nc) coatings[2,3]. Nanostructures promote selective oxidation, forming a protective oxide scale with superior adhesion to the substrate. A polymer nanocomposite 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[4]. Improvements in environmental impact can be achieved utilizing nanostructure particulates in coating and eliminating the requirement of toxic solvents. Nano-sized silica has proved to be an alternative to phosphate–chromate pretreatment that is hazardous due to toxic hexavalent chromium[5]. Nano cobalt–phosphorus is compatible with most existing electroplating equipment and positioned as an effective replacement for the hexavalent chromium[6]. Medical benefits of nanostructured diamond, hydroxyapatite and metalloceramics coatings are well reviewed[7]. Nanocomposite coatings based on hydroxyapatite nanoparticles can provide better corrosion pro-

tection of titanium that can be utilized for fabrication of advanced biomedical implants[8]. Development of paints and finishing materials with self-cleaning properties, discoloration resistance, graffiti protection and high scratch and wear resistance caused a major revolution in the concrete world[9]. Work is in progress for developing nanoparticle-based organic corrosion inhibitors, biocidal coatings and non-skid coatings[10]. Wear-resistant protective coatings based on nc-materials show considerable promise as a result of the combination of strength and ductility that can be achieved. However, the viability of protective nc-coatings will ultimately depend upon the general corrosion resistance exhibited by these materials over extended periods of service.

Corrosion behaviour of nc-alloys

Electrodeposition is a versatile technique for producing nc-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 nc-alloys has been assessed by several techniques in various environments[11–15]. Thorpe *et al.*[11] reported an enhanced corrosion resistance of nc-Fe_{32}-Ni_{36}-Cr_{14}-P_{12}-B_6 than that of its amorphous counterpart. The authors attributed this improved corrosion resistance to the observed greater Cr-enrichment of the electrochemical surface film via rapid interphase boundary diffusion. Bragagnolo *et al.*[12] reported improved corrosion resistance with nc-$Fe_{72}Si_{10}B_{15}Cr_3$ metallic glass wires. In their study, the beneficial effects of nc processing for corrosion resistance were not evident with a non-passivating alloy composition. Zeiger *et al.*[13] reported an enhanced corrosion resistance of nc-Fe-8 wt% Al in Na_2SO_4 solution. The study showed 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 nc-FeAl8 alloy provides better protection than on the same polycrystalline (pc) alloy. The passive film formation of nc-FeAl8 is distinctly eased in the pH range (weakly acidic to weakly basic) where Al forms stable passive film. The study indicates that nc-materials can be more easily passivated in

weakly acidic medium compared with the corresponding pc-material; whereas the situation is opposite in a strongly acidic medium, where higher dissolution rates are measured. Barbucci et al.[14] investigated corrosion behaviour of $Cu_{90}Ni_{10}$ alloy in neutral media containing chlorides. They reported a decrease in the protective properties of the passive layer in the nanostructured alloy that was found to depend on the oxygen concentration. The passive oxides, which grow on the nanostructured metal surface, are found not as compact as expected and detected in coarse-grained alloys. According to the authors, the increased amount of grain boundary in the nanostructured alloy could justify the loss of oxide compactiveness as a result of its irregular growth on the surface. Alves et al.[15] found that nc-$(Ni_{70}Mo_{30})_{90}B_{10}$ alloys are less sensitive to corrosion in alkaline solutions than the coarse-grained material.

Corrosion behaviour of nc-metals is investigated in different environments[16–18]. Rofagha et al.[16] investigated corrosion behaviour of nc-nickel (99.99%, 32 nm grain size) in 2N H_2SO_4 in de-aerated media and found that the corrosion potential of nc-nickel was shifted about 200 mV to the positive than that of pc-nickel. The study also showed that nc-processing of nickel catalyses hydrogen reduction processes, reduces kinetics of passivation, and compromises passive film stability. According to the authors, the excellent corrosion performance typically observed with conventional pc-Ni and Ni-based alloys appears to be retained in the nc-state, providing considerable promise for the development of protective (wear, fracture and corrosion resistant) nc-coatings. Youssef et al.[17] compared corrosion behaviour of nc-zinc produced by pulse current electrodeposition with electro-galvanized steel in de-aerated 0.5 N NaOH electrolyte. The estimated corrosion rate of nc-zinc (90 $\mu A/cm^2$) was found to be about 60% lower than that of electro-galvanized steel, and the passive film formed on the nc-zinc surface seems to be the dominating factor for this. The nc-structure enhances both kinetics of passivation and stability of the passive film formed. Anodic and cathodic Tafel slopes of nc-zinc (~40 and 107 mV/ decade) are found to be lower than that of electro-galvanized steel (~59 and 128 mV/decade), indicating higher activation energy for dissolution for nc-zinc. The corroded surface of nc-zinc shows discrete etch pit morphology, while uniform corrosion was observed on the electro-galvanized steel surface. Mishra and Balasubramaniam[18] compared corrosion behaviour of nc-nickel of different grain sizes (8–28 nm) in 1 mol H_2SO_4 electrolyte with that of bulk nickel. Zero current potential, passive current density and breakdown potential were found to increase with decrease in grain size. The increase in passive current density indicates defective nature of passive film formed on nc-nickel. Tendency for localized corrosion was lower in the case of nc-nickel as indicated by an increased breakdown potential. The corrosion rate of freshly exposed nc-nickel was found to be lower com-

pared to bulk nickel, indicating a higher hindrance to anodic dissolution from the nc-nickel surfaces. XRD analysis indicated that the nc-nickel deposits were compressively strained, with microstrain increasing with decreasing grain size.

The reported studies on corrosion resistance of nc-alloys showed mismatching results. It can be noticed that both in weakly acidic and alkaline media the nc-material maintains a more effective passive layer, whereas in media containing aggressive ions, the passive film stability is decreased compared to the pc-material. As the defect density is high, it can be assumed that the corrosion resistance of the pc-material is better than that of the nc-material. However, the diffusion rate of alloying atoms in nc-alloys will be higher compared with pc-alloys. For nc-alloys, where corrosion resistance originated from the formation of passive films (oxide films), it can be expected that their corrosion resistance is higher compared to conventional pc-alloys. It should be noted that corrosion resistance depends on the electrode, the aggressiveness of the electrolyte and also how effective is the passive layer formed. In conventional plating, unavoidable impurities in metal alloys spread throughout a coating, migrating naturally to grain boundaries and precipitating. In nano-coatings, the size of the grains is much smaller and their number is increased exponentially. As a result the impurities are super-diffused; homogenization by segregation. Such a coating is stronger and more resistant to stress and corrosion cracking[6].

Ceramic coatings

Ceramic coatings are attractive as they possess good thermal and electrical properties, and are more resistant to oxidation, corrosion, erosion and wear than metals in high-temperature environments. Nanoparticles of diamond as well as chemical compounds used for hard coatings (SiC, ZrO_2, and Al_2O_3) are commercially available[19], with typical particle sizes in the range 4-300 nm. Within tribology, a new development has been to deposit nanocoatings from colloids, e.g. of graphite. Nano-sized silica has proved to be an alternative to toxic chromate conversion coating[5]. Metal precoat based on the combination of a nanostructured metallic oxide of ceramic-type, with metals like Ti and Zr produces nanometre-range conversion coating, while the conventional phosphate layers are within micron range[20].

Incorporation of suitable nanoparticles in paints for improved properties is well commercialized. During the painting process, e.g. of automobiles, the ceramic nanoparticles float around freely in the liquid paint. When the automobile body is baked at a higher temperature, the ceramic nanoparticles crosslink into a dense network instead of the long molecular chains found in conventional paint. This allows the lacquer to provide a much more effective

scratch protection against normal wear and tear and allows the paint to retain its gloss.

Shen et al.[21] have re-emphasized the importance of nano-TiO_2 in the development of high corrosion resistance and hydrophobic coatings. Hydrophobic coatings with low wet ability are possible to effectively prevent the water on the substrate surface, and exhibit excellent corrosion resistance in wet environments. Hydrophobicity of the porous coatings is attributed to air trapped in the nanopores that limits water accessibility and concentration of corrosive species in the stainless steel holes, and hence causes a retardation of the anodic dissolution process. The corrosion potential of the nano-TiO_2 and fluoro alkyl silanes/nano-TiO_2-coated electrodes is found much nobler than that of the 316L stainless steel substrate in Ringer's solution.

Co-deposition of ceramic nano-scaled particles during the electroplating process brings improvements in technical properties at reasonable cost. However, the corrosion resistance deteriorated when the particles were co-deposited. Euler et al.[22] produced a series of nickel nano-ceramic composites, with co-deposition of particles of Al_2O_3 and TiO_2 as a single primary particle in the nanometre range (10–30 nm) at one end of the scale and as agglomerates up to a size of a micrometre at the other. Successful incorporation of particles up to 2-volume % has been established despite the problem of possible agglomeration. The decrease in corrosion resistance is explained by an accelerated diffusion of chloride ions along the interface between nickel and the incorporated particles. The high surface energy and agglomeration tendency of the nanoparticles in highly conductive metal electrolytes will tend to impede uniform distribution of the particles.

Polymer coatings

Conducting polymers have evoked a great deal of interest due to their electrochemical properties and their mixed ionic/electronic conductivity properties[23]. They have been used as host matrices in various composite films. Organic or inorganic particles can be mixed with or incorporated in the conducting polymers to modify their morphology, conductivity and different physical properties depending upon the application, such as corrosion protection. Polycrystalline nanocomposites that consist of conductive polymers were found to display novel properties. Nano-particulate dispersions of organic metal polyanilines in various paints at low concentrations can cause tremendous effects in corrosion protection[24]. Melt dispersion of polyaniline leads to fine particles, which self-organize into complex ultra fine networks. Some specific nanoconducting polymers which enhance corrosion resistance are polyaniline, polythiophene and polypyrrole. To enhance the oxidizing power of the polymers, incorporation of strong oxidizing species in the polymer has been envisaged. Polypyrrole nanocomposites with oxides, especially with

Fe_3O_4 have prospects for use in corrosion protection of iron[25]. Polypyrrole nanocomposites with montmorillonite clay showed better corrosion protection compared to undoped polypyrrole[26].

Nanostructured materials engineering extends the possibility of engineering 'smart' coatings that can release corrosion inhibitors on demand when the coating is breached, stressed or an electrical or mechanical control signal is applied to the coating[27]. Inherently conducting polymer (ICP) films containing inhibiting anions as the dopant anions can release them when the film is coupled to a breach in the coating. Research has developed chromate-free corrosion inhibiting additives in which organic corrosion inhibitors are anchored to nanoparticles with high surface areas that can be released on-demand[28].

Self-assembled nanophase coating

In the traditional sol–gel method, hydrolysis–condensation processes are followed by condensation polymerization upon film application. However, the evaporation process results in voids and channels throughout the solid gel and cannot provide adequate corrosion protection due to the high crack-forming potential. Sol–gel technology has an important limitation related with the maximum coating thickness attainable; typically lower than 2 mm. Studies showed that incorporation of nanoparticles to the sol can make it possible to increase the coating thickness, without increasing the sintering temperature[29]. Electrophoretic deposition of commercial SiO_2 nanoparticles suspended in an acid-catalysed SiO_2 sol on AISI 304 stainless steel substrates leads to coatings as thick as 5 mm with good corrosion resistance[29].

Incorporation of nanoparticles in the hybrid sol–gel systems increases the corrosion protection properties due to lower porosity and lower cracking potential[30]. Incorporation of inorganic nanoparticles can be a way to insert corrosion inhibitors, preparing inhibitor nanoreservoirs for self-repairing pre-treatments with controlled release properties[30,31]. Studies showed that sol–gel films containing zirconia nanoparticles present improved barrier properties. Doping this hybrid nanostructured sol–gel coating with cerium nitrate brings additional improvement to corrosion protection. Zirconia particles present in the sol–gel matrix act as nanoreservoirs providing a prolonged release of the cerium ions[32].

The recent discovery of a method of forming functionalized silica nanoparticles in situ in an aqueous sol–gel process, and then crosslinking the nanoparticles to form a thin film, is an excellent example of a nanoscience approach to coatings. This self-assembled nanophase particle (SNAP) surface treatment based on hydrolysed silanes, containing a crosslinking agent substantially free of organic solvents and Cr-containing compounds promotes adhesion of overcoat layers more effectively. Unlike chromate-

based treatments, SNAP coatings provide barrier-type corrosion resistance but do not have the ability to leach corrosion inhibitors upon coating damage and minimize corrosion of the unprotected area[30]. The SNAP surface coating could replace the currently used chromate containing surface treatment and can provide the basis of long-lived coating for aluminium alloys[5,33]. The ability to design coating components from the molecular level upward offers potential for creating multifunctional coatings. Molecular simulation approaches have been used to enhance the understanding of complex chemical interactions in coatings-related processes[34].

Self-cleaning paints and biocidal coatings

There is a great interest in the design and development of surfaces that not only provide biocidal activity but are also easy to clean and even self-cleaning. Most of such coatings acquire their biocidal/self-cleaning capacity by incorporating specific nanoparticles: basically silver (Ag) and titanium oxide (TiO_2)[35,36]. Nano TiO_2 is used for developing anti-UV, anti-bacterial and self-cleaning paints. This possesses self-cleaning hydrophobic properties, which causes water droplets to bead-off of a fully cured surface picking up dirt and other surface contaminants along the way. This self-cleaning action helps clean and maintain important surfaces and to accelerate drying, leaving the surface with minimal spotting. A recent study by Cai *et al.*[37] utilizes corona treatment technique, inert sol–gel coating and anatase TiO_2 layer. With the corona treatment, an organic surface was activated to allow a uniform TiO_2 sol–gel coating. Nanoparticles of surface-treated Al_2O_3 molecules help increase hydrophobicity and increase scratch resistance.

Microbial evolution on a wide variety of surfaces can cause corrosion, dirt, bad adour and even serious hygiene and health problems. AMBIO (Advanced Nanostructured Surfaces for the Control of Biofouling), a European Union research project[38] is investigating how to prevent the build-up of organisms on surfaces under marine conditions to avoid biofouling. The project aims to use nanostructuring to significantly reduce the adhesion of organisms to surfaces in aquatic environments, and thus control the fouling process without the use of toxic biocides such as copper and organotin compounds that prevent fouling by killing organisms. Nanostructuring of the surface alters the wetting properties and is intended to signal that the site is not suitable for the organisms to settle. The project aims to synthesize new nanostructured polymers that are stable under marine conditions. Although no alternatives to the use of biocides are available at present, creation of nanostructured surfaces could offer an innovative and environment-friendly solution to the problem of biofouling[38]. Research has developed new biocidal coating systems that prolong biocidal activity by immobilizing such additives on nanoparticles; the embedded biocides are designed to be released into the environment only when needed, thus extending the lifetime of the biocidal activity[10].

Nanostructured alloy and composite coatings for high-temperature applications

Nanostructures form protective oxidation scales with superior adhesion to the substrate[39]. The high density of grain boundaries provides fast diffusion paths, promoting selective oxidation of protective oxide scales. The fine-grained coatings and/or the fine-grained oxide scales show a fast creep rate at high temperatures, which can release the stresses accumulated in the scales, therefore reducing the scale spallation tendency. The oxides formed on nanocrystalline coatings are micro pegged onto the grain boundaries to form a complex interface that results in better scale adhesion to the metal substrate. Nanocrystalline alloy coatings, oxide-dispersive alloy coatings and metal-oxide composite coatings show superior high-temperature corrosion resistance.

Engineering alloys rely on the formation of protective oxide films such as Al_2O_3 and Cr_2O_3 to resist high temperature and corrosive environments. Unfortunately, relatively large concentrations of Al or Cr are needed to form a complete Al_2O_3 or Cr_2O_3 scale. In the Ni-20Cr-Al alloy system, for instance, greater than 6 wt% Al is required to form a complete Al_2O_3 scale. With nc-alloy coatings, the Al content that is required to form a complete protective oxide scale can be substantially reduced. Experimental results indicate that when the grain size of Ni-20Cr-Al coatings was ~60 nm, alloys containing ~2 wt% Al could form a complete α-Al_2O_3 scale at 1000°C in air. This concentration is only one-third of the required Al% for the Ni-20Cr alloy with normal grain size[39].

Ti alloys and Ti–Al intermetallics having advantages of high strength, lightweight and high melting point have lower oxidation resistance at elevated temperatures. They have potential applications in the aerospace and automotive industry due to their excellent mechanical properties at high temperatures and corrosion resistance. Nano- or sub micro-alloy coatings produced by electro-spark deposition provide a powerful tool for Ti–Al intermetallics to be used as high temperature structural materials[39].

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