



CORROSION RESISTANCE OF NANOPARTICLE - INCORPORATED NANO COATINGS

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Nano coatings are materials that are produced by shrinking the material at the molecular level to form a denser product. Nano coatings have several advantages such as better surface appearance, good chemical resistance, better thermal and electrical conductivity and better corrosion resistance. Incorporation of nanoparticles enhance the corrosion resistance of zeolite coatings, epoxy coatings and antimicrobial coatings.

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Introduction

Nanoparticle based coatings

Nano particle based coatings have been used to protect corrosion of various metals and alloys. Zeolite coatings, epoxy coatings, self-cleaning paints and antimicrobial corrosion coatings have been used to protect metals and alloys from corrosion. Their corrosion protection efficiency is enhanced, when nanoparticles are incorporated into these coatings.

Nano coating

Nano-coatings are materials that are produced by shrinking the material at the molecular level to form a denser product. The appearance and usefulness of nanoparticles brings many advantages and opportunities to paint and coating industry. Coating industry is among the first to tap the potential of nanotechnology. Addition of nanoparticles to coatings can upgrade many properties of coating system and can produce multipurpose coatings with a little cost difference. Such coatings, sometimes made of self-assembling monolayers are applicable in many ways : from scratch resistant coatings on glass to self-cleaning surfaces to moisture absorbing to anti-graffiti and corrosion resistance coatings. Further, unique composition, better strength and flexibility along with excellent gloss and transparency makes nano-coatings even more effective. Many of the nanoparticles like nano-ZnO are non-toxic in nature and thus add another advantage to coating industry.

Nano-coating can be applied in many ways including chemical vapor phase deposition, physical vapor phase deposition. Electrochemical deposition, Sol-gel methods, electro-spark deposition, and laser beam surface treatment.

Main Advantage of Nano-coatings¹

- Some of the main advantages of nano-coatings are
- Better surface appearance.
- Good chemical resistance.
- Decrease in permeability to corrosive environment and hence better corrosion properties.
- Optical clarity.
- Increase in modulus and thermal stability.
- Easy to clean surface.
- Anti-skid, anti-fogging, anti-fouling and anti-graffiti properties.
- Better thermal and electrical conductivity.
- Better retention of gloss and other mechanical properties like scratch resistance.
- Anti-reflective in nature
- Chromate and lead free.
- Good adherence on different type of materials.

Nanoparticle – based coatings for magnesium alloys with thermal and mechanical stability

Magnesium alloys have an excellent strength to weight ratio and are attractive materials in cars, aircrafts and high end portable devices. Nevertheless they are also very reactive and require excellent corrosion protection. Inorganic coatings offer good protection especially under mechanical and thermal strain. However, due to the low temperature stability of most magnesium alloys, dense inorganic coatings cannot be applied using conventional techniques.

Purely inorganic, transparent coatings have been developed for the corrosion protection of magnesium alloys, based on commercially available, aqueous SiO₂ nano-dispersions. These coatings can be processed under mild conditions, but are permeable for aggressive anions. The permeability can be decreased by sealing with inorganic polymeric sols. Despite their low thickness the resulting coatings show remarkable protective properties.

With decreasing particle size the sintering temperature decreases. Commercial water based silica dispersion with suitable sintering additives can be applied onto AZ31 and AZ91 (grinded, degreased with acetone and activated with Nital) by dip coating. Small particles, slow withdrawal and low dispersion viscosity result in thin (~300 nm) defect-free and transparent coatings. Thicker crack-free coatings can be achieved by multiple coating application (up to 5 layers = 1.5 μm). The coating resistance (R_{po}) increases with each additional layer and localized corrosion becomes inhibited.

Zeolites

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. The term zeolite was originally coined by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Based on this, he called the material zeolite, from the Greek meaning boiling stone.

About 194 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known. Zeolites are widely used in industry for water purification, as catalysts, and in nuclear reprocessing. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture.

Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na⁺, K⁺, Ca²⁺, Mg²⁺ and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite. An example mineral formula is: Na₂Al₂Si₃O₁₀•2H₂O, the formula for natrolite.

Structure of Zeolites

Like most silicates - the zeolites are based on TO₄ tetrahedra, where T is an aluminium or silicon atom (phosphorus in aluminophosphates). The vast 3-dimensional networks are a result of all four corners for the tetrahedra being shared, producing low density microporous materials. Zeolite structures can be thought to exist of finite or infinite (chains, layers etc..) component units. An important class of materials is the pentasil zeolites, named so because they are constructed of five-membered rings. The most important example is that of ZSM-5 - which is shown in Fig 1. ZSM-5 is used in a variety of catalytic applications, including the catalysis of methanol into fuel hydrocarbons.

The individual pentasil units are shown in Fig. 1. They combine to form long chains, (Fig 2), which then join together to form layers, (Fig. 3).

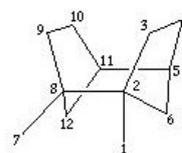


Figure 1. Secondary building units (SBU) in pentasil zeolites.

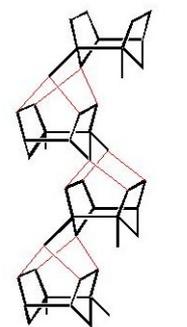


Figure 2. SBU linked chains

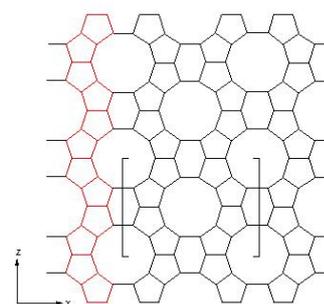


Figure 3. Layer formed from linked chains in ZSM – 5 structure

Zeolite Molecular Sieves

Zeolite molecular sieves are characterized by the following properties:

- Selective adsorption due to the uniform pore size of the zeolite structure.
- High adsorption capacity for polar substances at low concentrations.

Zeolite - Structure and Properties

Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of aluminosilicates. These crystals are characterised by a three-dimensional pore system, with pores of precisely defined diameter. The corresponding crystallographic structure is formed by tetrahedras of (AlO₄) and (SiO₄). These tetrahedras are the basic building blocks for various zeolite structures, such as zeolites (Fig 4 and Fig 5), the most common commercial adsorbents.



Fig 4. Molecular Sieve Type A



Fig 5. Molecular Sieve Type X

Due to the presence of alumina, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics. For instance, the sodium form of zeolite A has a pore opening of approximately 4 Ångstrom (4×10^{-10} m), called 4Å molecular sieve. If the sodium ion is exchanged with the larger potassium ion, the pore opening is reduced to approximately 3 Ångstrom (3Å molecular sieve). On ion exchange with calcium, one calcium ion replaces two sodium ions. Thus, the pore opening increases to approximately 5 Ångstrom (5Å molecular sieve). Ion exchange with other cations is sometimes used for particular separation purposes. The pore opening of the sodium form of zeolite X (13X) is approximately 8 Ångstrom.

The ability to adjust the pores to precisely determined uniform openings allows for molecules smaller than its pore diameter to be adsorbed whilst excluding larger molecules, hence the name “molecular sieve”. The different pore sizes of synthetic zeolites open up a wide range of possibilities in terms of “sieving” molecules of different size or shape from gases and liquids.

Zeolite Coatings

Zeolites are microporous crystalline aluminosilicates with uniform and molecular sized pores. They are non-toxic and have been explored for medical applications. The application of zeolite films as chromium-free protective coatings on aluminum alloys have been investigated. It has been shown that as-synthesized organic template containing high-silica-zeolite (HSZ) MFI coatings on AA-2024-T3 are non-porous and have excellent corrosion resistance in strong

acids, bases, and pitting aggressive media. High silica coatings including MFI, BEA and MTW are all good corrosion resistant coatings. The in-situ crystallization coating deposition process can coat surfaces of complex shapes and in confined spaces. Beving et al., successfully expanded their investigations to include other aluminum alloys (6061-T4, 5052-H32, 7075-T6) and steels (SS304-2b, S1008, S4130). They were able to use one simple pretreatment and a single zeolite formulation on all aluminum alloys and steels to synthesize MFI coatings. Corrosion protection was measured by DC polarization in several corrosive media. DC polarization in 5 wt% NaCl is used as a screening diagnostic prior to salt-fog testing. Salt-fog accelerated weathering tests were performed according to ASTM 117-B on scribed and non-scribed HSZ MFI coated 2024-T3. The non-scribed HSZ MFI coated 2024-T3 panels had no observable corrosion after more than 2000 hrs continuous salt fog exposure.

The scribed HSZ-MFI coated 2024-T3 panels exhibited no delamination of the zeolite coating after 1000 hrs continuous salt fog exposure and corrosion was limited to the scribe. The compatibility between zeolite coatings with primer and topcoat systems has been investigated. A coating system of zeolite-primer (chromated) and zeolite-primer (chromated)-topcoat passed 3100 hrs continuous salt fog exposure with no observable corrosion and delamination.²

Corrosion resistant zeolite coatings

For over one hundred years, hexavalent chromium compounds, mainly chromates, have been widely used as a corrosion inhibitor to protect high strength Al alloys used in aerospace and defense applications, as well as other materials in a wide range of applications.³⁻⁵ Chromate can be applied to a surface as a chromate conversion coating or added to paint as a pigment. Unfortunately, chromate has become stringently regulated because it is highly toxic and carcinogenic; hence, a chromium-free alternative with equivalent or superior corrosion performance is critically needed.

Zeolites are a class of crystalline oxides with uniform channels and/or cages ranging from 0.3 to 2 nm. They are extensively used as adsorbents, catalysts, and ion exchange agents. The idea of corrosion-resistant zeolite coatings takes advantages of several well-known facts about zeolite.

i) Most zeolites are non-toxic, and some compositions are even used in food and drug applications.

ii) High-silica and pure-silica zeolites are thermally and chemically stable. For example, many high-silica zeolites (HSZ) are thermally stable up to 1000°C, and pure-silica zeolites are stable in all mineral acids except hydrofluoric acid. Thus, the framework of zeolites contains the needed corrosion resistance. (As used herein, HSZs have a Si:Al ratio greater than 50, while the ratio for low-silica zeolite (LSZ) is less than 2.)

iii) Most HSZ syntheses use structure-directing agent (SDA) molecules, which are eventually trapped inside the zeolite pores.

For separation and catalysis applications, these molecules are normally removed before use. However, for anticorrosion applications, it is better to retain the SDA since it was recognized that defect-free as-synthesized zeolite can be gastight, and some SDA molecules, such as amines, have already been used as corrosion inhibitors. These facts all suggest that as-synthesized zeolite films can be corrosion resistant. Recent technological advances of Zeolite corrosion resistant coatings have been reported.⁶⁻¹⁰

Epoxy coatings-influence of nanoparticles on the anti corrosion and mechanical properties of epoxy coatings

Epoxy has been widely used as a coating material to protect the steel reinforcement in concrete structures,¹¹⁻¹³ because of its outstanding processability, excellent chemical resistance, good electrical insulating properties, and strong adhesion/affinity to heterogeneous materials. Epoxy coatings generally reduce the corrosion of a metallic substrate subject to an electrolyte in two ways. First, they act as a physical barrier layer to control the ingress of deleterious species. Second, they can serve as a reservoir for corrosion inhibitors to aid the steel surface in resisting attack by aggressive species such as chloride anions.

Nonetheless, the successful application of epoxy coatings is often hampered by their susceptibility to damage by surface abrasion wear.^{14,15} They also show poor resistance to the initiation and propagation of cracks.¹⁶ Such processes introduce localized defects in the coating and impair their appearance and mechanical strength. The defects can also act as pathways accelerating the ingress of water, oxygen and aggressive species onto the metallic substrate, resulting in its localized corrosion. Furthermore, being hydrophilic in nature, epoxy coatings experience large volume shrinkage upon curing and can absorb water from surroundings,^{17,18} The pores in the cured epoxy coating can assist in the migration of absorbed water and other species to the epoxy-metal interface, leading to the initiation of corrosion of the metallic substrate and to delamination of the coating.

The barrier performance of epoxy coatings can be enhanced by the incorporation of a second phase that is miscible with the epoxy polymer, by decreasing the porosity and zig zagging the diffusion path for deleterious species. For instance, inorganic filler particles at nanometer scale can be dispersed within the epoxy resin matrix to form an epoxy nano composite. The incorporation of nanoparticles into epoxy resins offers environmentally benign solutions to enhancing the integrity and durability of coatings, since the fine particles dispersed in coatings can fill cavities¹⁹⁻²¹ and cause crack bridging, crack deflection and crack bowing.²² Nanoparticles can also prevent epoxy disaggregation during curing, resulting in a more homogenous coating. Nanoparticles tend to occupy small hole defects formed from local shrinkage during curing of the epoxy resin and act as a bridge interconnecting more molecules. This results in a reduced total free volume as well as an increase in the cross-linking density.^{23,24} In addition, epoxy coatings containing nanoparticles offer significant barrier properties for corrosion protection^{25,26} and reduce the trend for the coating to blister or delaminate.

Homogeneous epoxy coatings containing nanoparticles of SiO₂, Zn, Fe₂O₃ and halloysite clay were successfully synthesized on steel substrates by room-temperature curing of a fully mixed epoxy slurry diluted by acetone. The surface morphology and mechanical properties of these coatings were characterized by scanning electron microscopy and atomic force microscopy, respectively. The effect of incorporating various nanoparticles on the corrosion resistance of epoxy-coated steel was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy. The electrochemical monitoring of the coated steel over 28 days of immersion in both 0.3 wt.% and 3 wt.% NaCl solutions suggested the beneficial role of nanoparticles in significantly improving the corrosion resistance of the coated steel, with the Fe₂O₃ and halloysite clay nanoparticles being the best. The SiO₂ nanoparticles were found to significantly improve the microstructure of the coating matrix and thus enhanced both the anticorrosive performance and Young's modulus of the epoxy coating. In addition to enhancing the coating barrier performance, at least another mechanism was at work to account for the role of the nanoparticles in improving the anticorrosive performance of these epoxy coatings.²⁷

Nano Particle incorporated 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 (TiO₂).^{28,29} Nano TiO₂ 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.³⁰ utilizes corona treatment technique, inert sol-gel coating and anatase TiO₂ layer. With the corona treatment, an organic surface was activated to allow a uniform TiO₂ sol-gel coating. Nanoparticles of surface-treated Al₂O₃ molecules help increase hydrophobicity and increase scratch resistance.

Microbial evolution on a wide variety of surfaces can cause corrosion, dirt, bad odour and even serious hygiene and health problems. AMBIO (Advanced Nanostructured Surfaces for the Control of Biofouling), a European Union research project 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.³¹ 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.³²

Nanoparticle based antimicrobial corrosion coatings

Marine microbiological corrosions are responsible for considerable damages to all devices and vessels immersed in seawater, and this induces serious economic problem to maritime activities.³³⁻³⁵ Coating is the most convenient method for preventing the corrosion/fouling of steel surfaces, storage tanks, ship bottoms and their super structures. Employing effective antifouling marine paints, containing booster biocides at non-toxic levels is one approach to solve the issue of fouling.³⁶⁻³⁸ Copper and its oxides are common biocides in a large number of commercial antifouling marine paints. Commercially available antifouling coatings have cuprous oxide (Cu₂O) as the primary biocide, which typically varies from 20% to 76% copper content.³⁹ However, recent reports have shown that 26% sampling locations/year in UK exceeded the concentration of current Environmental Quality Standard (5 µg / L)⁴⁰ for copper⁴¹ and marine microalgae were able to take up copper very quickly in natural coastal seawater.⁴² These data suggest that monitoring of concentrations of copper is important so as not to cause ecological damage in marinas.

Besides Cu, other metals such as zinc and silver exhibit antifungal and antibacterial properties, which have been widely utilized in advanced coating technologies.⁴³⁻⁴⁷ Especially, silver has long been known to have strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities, even at low concentrations in the ppb range.⁴⁸ Meanwhile, silver has a remarkably low toxicity compared to other heavy metal ions,⁴⁹ which make it possible to be more environmentally friendly antimicrobial painting additives instead of copper.

One important function of paints containing biocides or inhibitors is to obtain optimal release rate of the actual active substance into the sea. The leaching rate of biocides should not be too fast, resulting in rapid and premature depletion of the antifouling activity of marine coatings and unnecessarily high concentration in the sea. However, the release rate should not be too slow since this would undoubtedly result in fouling.⁵⁰ In order to deal with both issues, application of core-shell structured materials should be one of the best alternatives since the shells offer protection to the cores and introducing new properties to the hybrid structures.⁵¹⁻⁵³

Up to date, there are only some reports exploring the marine corrosion protection based on core-shell structures. White et al. demonstrated the application of micrometer-scale capsules loaded with oligomers for self-healing of the cracks in polymer coatings^{54, 55} and Shchukin et al. developed corrosion protection coatings with halloysite nanotubes as nanocontainers loaded with the corrosion inhibitors.⁵⁶ However, there are still challenges such as stability of core-shell particles, uniform dispersity in a matrix, and control of the release rate. Ke et al., have

successfully prepared monodispersed Ag/SiO₂ core-shell nanoparticles with facile pathway.⁵⁷

Ag/SiO₂ core-shell nanoparticles within the size of 60 nm were applied in marine antimicrobial corrosion coatings. TEM and XRD results indicated silver was completely covered by silica and its crystal form was not affected after coated by silica. Effects of Ag/SiO₂ nanoparticles in the microbial corrosion of acrylic-coated steel were studied by means of electrochemical noise analysis (ENA). ENA results reveal that 1 wt% Ag/SiO₂ nanoparticles exhibit better antimicrobial corrosion activity than that of conventional 40 wt% Cu₂O biocides. Inductively coupled plasmaoptical emission spectrometry (ICP) showed very lower amount of Ag ions leaching from the matrix resin, whereas a higher amount of copper ion leaching from the resin in the same period. It was concluded Ag/SiO₂ core-shell nanoparticles could enhance long-term corrosion protection in comparison with the copper biocides. This composite has a strong potential use in environmentally friendly antimicrobial coatings.⁵⁸

Summary

Incorporation nanoparticles enhance the corrosion protection efficiency of zeolite coatings, epoxy coatings and biocidal coatings.

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