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Effect of various nanomaterials used in coatings to resist corrosion -A Detailed Review study

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Abstract : In many industries, various types of metals are used for the construction of Reactors, Pressure vessels, piping's, etc. So, depending on environmental conditions, the property of process fluid, different temperature, and pressure suitable MOC. (Material of construction) is used. If proper material is not selected then fluids may be liquids like water, Oil, Nacl, and some gases like CO2, H_2S, etc. will Corrode the vessel and this is problematic factors were most of the industries are lacking behind for finding the solution. So, the solution behind this corrosion is to apply a layer of coating which has different properties to that of metal and which can sustain on the metal under aggressive conditions. But only a simple layer of coating is not enough to avert corrosion because fine properties (Fine size and High density) might form active sites for corrosion attack. So, in that case, nanoparticles should be added/Mixed to the coating to improve the property of coating. A nanocoating is a coating that either has constituents in the nanoscale or is composed of layers that are less than 100 nm. By applying this layer, not only the life of the reactor is enhanced but also it prevents contamination of inner fluids. So, different types of nanomaterials can be used for coatings like Graphene coating, Nickel-P Coatings, Al, Silver, TiO_2, etc. This review has studied, Effect of different nanomaterials coatings at the different corrosive environments and the different synthesizing and analyzing techniques used by research scholars to conclude their evidence.

Keywords : MOC., Corrosion, nanoparticles, nanocoating, active sites and synthesizing and analyzing.

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Introduction

Corrosion is the common destruction of pure metal that occurs when it reacts with the environment that contains oxygen, hydrogen, etc. and gets converted to a more stable form such as oxides, hydroxides, sulfides. Corrosion also happens when metal is under severe stress causing the metal to crack. Various forms of corrosion observed are pitting corrosion, intergranular corrosion, stress corrosion, etc. [1] Corrosion being the loss of energy can be countered by using conversion coating, sacrificial anodes, and by the use of some conducting polymer coatings. There is a growing need to prevent metals from the attack of corrosion to increase their life span. The corrosion rates are usually measured in mils per year (mpy) and are determined with various methods. The role of the anti-corrosion coating is to serve as a barrier between the corrosive electrolyte and the metal surface by inhibiting chemical compounds formed on the surface that promote corrosion. Phosphating is the frequently used and effective industrial surface treatment for corrosion protection of metallic surfaces because phosphate coatings are insoluble in nature and can be deposited either by chemical or electrochemical methods. Corrosion can be prevented by the formation of an oxide layer over the metal surface. We have reviewed a process where the metal oxide layer was formed with the help of plasma electrolytic oxidation (PEO) also called as micro-arc oxidation (MAO). This process is similar to anodizing but it deals with higher potential that causes discharges and the plasma formed modifies the structure of the oxide layer. [6]

The use of nanotechnology in preventing them has been one of the promising advancements in this field. Use of carbon-based nanofillers such as carbon nanotubes and graphene, addition of titanium dioxide, magnesium nanoparticles, zirconium nanoparticles, etc. in coatings and inhibitors have shown a significant increase in the prevention of corrosion. Nano-fluids are emergent technology that can offer superior corrosion resistance. Nano-fluids include colloidal nanoparticles (nominally 1–100nm in size) stabilized in conventional base fluids such as water. [1] The performances of these nanostructures are determined by a detailed study of shape, geometry, and morphology of nanostructures. Electroless deposition method is sometimes used for coating metals. In this method, a uniform coating of metallic layer on the surface of fibers through chemical reduction of metal ions in an aqueous solution and thereafter, metals are deposited without using electrical energy. [7] The sol-gel method was used in many processes reviewed to modify the surface of the substrate to get a high surface area. Erkan Yilmaz,et al. stated that the process is also called chemical solution deposition and it involves several steps, in the following chronological order: hydrolysis and polycondensation, gelation, aging, drying, densification, and crystallization. [10]

CORROSION DETERMINATION METHODS: Potentiodynamic polarization (PDP) technique as described by J. Telegdi et al. is one of the most commonly used DC electrochemical methods in corrosion measurements. Oxidation and reduction reaction happen on the metal surface due to applied potential on the test electrode and current is generated. The polarization curve plotted is used to determine the corrosion potential and rate of corrosion of metal. [2] Another method used for studying the corrosion of metal and alloys is electrochemical impedance spectroscopy (EIS). It is a very complex and nondestructive method where impedance is measured as a function of frequency.

NANOPARTICLES DETERMINATION METHODS: Electron microscopy is one of the famous instruments used to view the high-resolution image of the nanoparticle by using electron as a source of illuminating radiation. It’s two main types are TEM and SEM. Transmission electron microscopy (TEM) is also used to observe the characteristics of very small samples by using an accelerated beam of electrons, which passes through a very thin specimen through which features such as structure and morphology can be observed. [4] Scanning electron microscopy (SEM) is a method where an electron beam is used to scan the samples and enlarged images are obtained. The signals generated during SEM analysis produce a two-dimensional image and provide information about the specimen such as external morphology, chemical composition. To find the chemical composition of materials Energy Dispersive X-ray Spectroscopy (EDS or EDAX) can be used to a spot size of a few microns and to create element composition maps over a much broader raster area. [3] EDS is applied along with SEM to determine the element compositions on the surface of the sample and also detects the presence of any foreign substance that are nonorganic and the coatings in metal.

X-ray powder diffraction (XRD) is also used for studying morphology, crystal structure, the orientation of grains by constructive interference of monochromatic X-rays, and crystalline samples. Similar layers of nanoscales can be created by the Nanosphere lithography (NSL) technique. NSL is a bottom-up technique for the creation of large-area two-dimensional nanopattern arrays on material surfaces. Typical feature sizes of the patterns reach from 100 nm to 2000 nm. It gives planar ordered arrays of nanomaterials. [5] Another instrument used for high resolution under nanoscale is atomic force microscopy (AFM). The presence of an organic and inorganic compound or any specific molecular group in the sample can be estimated by Fourier transform infrared spectroscopy (FTIR). It uses the mathematical process (Fourier transform) to translate the raw data (interferogram) into the actual spectrum. The bonds between different elements absorb light at different frequencies [8].

Literature Review

1. GRAPHENE COATINGS

Seyed Ali Hosseini Khorasani, et al. presented Ni-graphene composite coating which is a high corrosion resistance coating on a copper substrate. So, the method used for fabrication was co-electrodeposition (nickel electroplating was used to increase the resistance against corrosion). They had used improved hummers method graphene oxide was synthesized and then to Ni watt's bath different concentration of graphene oxide (GO) aqueous solution was introduced. And Ni & Go ions were reduced simultaneously to form a composite coating. For analysis, the surface topography of coating AFM was used and for the study of synthesis of GO & reduction of the coating during the plating process, Raman spectroscopy, FTIR & EIS and to compare the corrosion resistance between pure Ni-coating and Ni-graphene coating PDS method was used. So, they resulted that with the increasing (0.44-0.6mg/lt.) of Go in solution to the coating bath, leads to more corrosion resistance about 100 times more compared to pure Ni. So, to change the growth direction of Ni, the compositing of Ni coating by RGO was useful.[11]

R.K. Singh Raman, et al. has studied some of the factors like resistance against degradation in an aggressive environment, permeation of corrosive fluid through it, and also according to the life of the coating, it is used for mechanical applications. Graphene has some properties like a very thin layer possess a very high toughness, chemical inertness, and also impermeable that was the purpose of using this material for coating. The chemical vapor deposition (CVD) method was used to deposit multilayers graphene on copper under vacuum. An examination of the layer was done by Raman spectroscopy (RS) that was IG/ID= 1.36 which means 4 to 5 layers of graphene on copper. When the pure copper and the graphene-coated copper were exposed to a corrosive environment i.e. immersed in 0.1m NaCl for experimental comparison, the multilayer-coated copper decreases the dissolution 5 times lower than uncoated copper and it was examined by EIS technique. Therefore, to prevent copper from corrosive fluids 1.5 order of magnitude should be applied. And for nickel less is expected.[12]

Ahmed Khalid Hussain, et al. reviewed to protect the metals from corrosion by using graphene-based polymer composite coatings. The pure graphene has anti corrosion mechanisms such as prevention of electron at anodic site from reacting cathodic site, formation of impermeable passive layer of graphene on metal surface making tortuous path of corrosive material to reach graphene metal interface. But if defects are present, then graphene coating promote corrosion due to its conductive nature. Thus, hybrid coating such as carbon nanotubes, carbon nanofiber, graphene with ceramic, metal, etc. Graphene and graphene oxide (GO) nano sheets were dispersed in waterborne polymer matrix like epoxy resin by insitu polymerization to prevent agglomeration. Polyvinyl alcohol (PVA) polymer coating containing immersed graphene showed corrosion resistance by decreasing the pin hole defects. When graphene was embedded in polyurethane (PU) matrix to form nano composite they showed improved corrosion performance. Conducting polymers (CP) also show high anticorrosion properties due to their environmental stability and when they are reacted with graphene nano platelets, they form nanocomposite coating that provide double layer protection and it was proven by Tafel curves. But CPs are costly and hence are limited in use. A hybrid of graphene and polypyrole epoxy composite depicted high electric conduction and improved corrosion protection. inorganic nano particles such as magnetic Fe_3O_4 were also used between graphene layers to prevent reagglomeration. EIS results showed enhancement in anticorrosion properties. Silica nanoparticles with excellent chemical stability, lanthanide nanoparticles with low toxicity are also good corrosion inhibitors.[13]

2. NICKEL-PHOSPHORUS COATINGS

S.M.A. Shibli, et al. had investigated physiochemical, electrochemical characteristics, topographical, morphological characteristics, and studied pure tetragonal 10-20 nm size zirconia-based Ni-P composite to prevent corrosion. It was studied that due to low surface roughness, dense compact morphology, high wear resistance, abrasion resistance, hardness, and corrosion resistance property Ni-P was more extensively used in mild steel tubular articles. To gain chemical stability and to prevent corrosion from halides ceramic oxide is used. And Ni-P matrix is used as a second phase composite to improve mechanical and physical properties. Nano-tetragonal Zirconia was prepared by using Zirconium Oxychloride as the precursor by wet decomposition to enhance the corrosion resistance of Ni-P coatings in NaCl medium. As they concluded that Ni-P-nano-tetragonal zirconia coating has retained under high aggressive conditions with high polarization resistance and has excellent physicochemical characteristics with enhanced corrosion resistance.[14]

Anna malai jegan, et al. had investigated the feasibility of enhancing the mechanical properties of Al_2O_3 coatings on AISI304 SS Specimen. As per there study Ni metal and alloy show good mechanical properties and Al_2O_3 has a low price, and at higher temperature shows good chemical stability, high microhardness, and wear resistance. so, they had used as a coating material. The pulsed electrodeposition method was used to deposit (Watts bath Ni-nano-Al_2O_3 composite coating) Ni-nano-Al_2O_3 composite coating over AISI304 S.S. specimen and Taguchi's orthogonal array concept/Method was used to optimize the microhardness. An analysis was done by using XRD and EDX to check the deposition of composite over the specimen, and also to check the corrosion resistance. So, when Ni-Al_2O_3 was applied specimen, it prevents the specimen from corrosion and also bears high heat and becomes highly abrasive and can be used as an alternative to chromium coatings. They concluded from there experiment that Al_2O_3 particle was completely embedded in the Ni matrix, coating thickness was about 15 µm, Hardness value was maximum, the pulse frequency is foremost 40.40% and for about 0 to 408 hr. the specimen was under a corrosive environment and no corrosion has appeared.[15]

Ankita Sharma, et al. has study corrosion and wear resistance of mild steel substrate to protect MS against corrosive environment. They had used Ni-P and Ni-P-Al_2O_3 as nanocomposite coating with Alumina particles with various contents from 5 to 20 gm/lt. in a bath were co-deposited. The method used for deposition was the EL deposition technique. Ni-P-X (Ni-P-matrix) coatings were categorized into two parts i.e. coatings incorporating soft particles and coating contains hard particles. And wear resistance was examined by using the Pin-on-disc method. They had used SEM for morphology, X-ray, and EDAX for energy dispersive analysis under 3.5 wt. % NaCl solution for less than 10 days. So, after experimental results, they came to the point that the Ni-P coating provides less hardness than that Ni-P-Al_2O_3 coating and was more superior to pure MS against corrosion. The coating vanishes if the amount of Al in the coating is less than or equal to 2.7 % but show wear resistance, hardness, and high friction coefficient as compared to Ni-P coating. [16]

Ankit Sharma, et al. had investigated the corrosion and wear resistance of MS after applying Nanocomposite coating. Ni-P and Ni-P-PTFE nanocomposite coating were deposited on the surface of MS. The method which was used for deposition was electroless plating technique. An analysis of the coating was done by using SEM, EDAX, and XRD under 3.5 wt. % of NaCl. And for wear resistance tests they had used the Pin-on-disc method. The thickness was about 7 and 23 µm and after electrolysis, they found that Ni-P-PTFE is nodular as compared to Ni-P deposits was smooth. For around 20 days of continuous exposure to the corrosive environment, both coatings were observed to be superior against corrosive conditions to that of pure MS whereas Ni-P-PTFE coatings exhibited less wear resistance than Ni-P coatings. PTFE gives lubricated effects results in a lower friction coefficient than that of Ni-P coating and because of Adhesive wear, both coatings won't last long. [17]

3. ALUMINIUM COATINGS

Mojtaba vakili-azghandi, et al. had studied the improvement of corrosion resistance of 6061 Al alloy having silicate electrolyte containing Al_2O_3 nano-particles. They had used the plasma electrolyte oxidation (PEO) method based on an anodic oxidizing technique to coat Al_2O_3 on the surface which has a similar crystalline structure and phase composition. To modify the corrosion behavior, they had used silica alkaline electrolyte. They had added low, medium, and high concentrations of KOH, and Na_2SiO_3 were added to the PEO electrolyte in the presence or absence of Al_2O_3 nanoparticles. To study the coating and thickness they had used Electron microscopy and X-ray diffraction under 3.5 wt. % of the NaCl solution. As a result, they found that because of the presence of KOH, Na_2SiO_3, and Al_2O_3 nanoparticles in low, high, and medium concentrations chance of corrosion becomes less due to low porosity and thickest coating. And they conclude that due to surface oxidation, incorporation, and co-deposition of Al_2O_3 nano-particle (were more than SiO32- ions due to electron discharge force) different layers of alpha and Gamma Al_2O_3 and mullite ($Al_2O_3.nSiO_2$) was detected within PEO coatings.[18]

Mala M. Sharma and Constance W. Ziemian studied the pitting and stress corrosion cracking (SCC) susceptibility of nanostructured Al-Mg Alloys in natural and artificial sea water environments. Two nanocrystalline 5083 alloys were developed with varied composition and processing condition and their test results were compared with commercial aluminum AA5683(H111) Alloy. Very few pits were observed in both AA5083 and nano Al-7.5mg alloys for non-immersed and fully immersed condition. The conventional alloy had irregularly shaped pits (0.5 to 1.7mm^2) whereas the nano alloy had few finer pits (0.05-0.07mm^2 for Al-7.5mg and 0.04-0.06mm^2 for Al-8.6mg alloy) that were uniformly distributed. Unlike the conventional AA5083 alloy, the nano crystalline alloys were subjected to intergranular corrosion. Lower the percentage of residual strength, more the susceptibility to corrosion attack. The nano Al-8.6mg alloy maintained 91% of its residual strength during 6 months of testing which show that there was less effect from corrosion cracking. Whereas the conventional AA5083 retained more than twice percent of residual strength after 6 months. The nano Al-7.5mg alloy have improved resistance to stress corrosion than the AA5083 but more significant pitting damage compared to nano Al-8.6mg alloy.[19]

Sriganesh gandham, et al. had studied corrosion and erosion rates of nanofluids at a particular operating temperature on different metals like cast Al, cast iron, steel, brass, solder, and copper which makes work easier for selection of nanoparticle according to their property for dispersing into coolant fluid. So as a coolant they had used water – ethylene glycol and they had dispersed Ag and Al_2O_3 of about 0.5 wt.%. After anti-corrosive testing, they had found that Ag and Al_2O_3 were dangerous in nature whereas, for the automotive system Multiwalled carbon nanotubes were suitable. Because, MWCNT's can be oxidized with acids to attach more functional groups with the wall structure which leads to good stability, shows good dispersion when dispersed with coolant, and displays good anti-corrosive and anti-erosive properties. But Silver nanoparticle failed in corrosion test whereas Al nanoparticle failed in erosion test. Therefore, they found that Al nanoparticle resulted in good and stable additives after dispersion into nanofluid in the automotive coolant.[20]

4. SILVER COATINGS

V.J. Keast, et al. has study degradation of triangular silver nanoparticles (AgNP) in the presence of air as it is used in many applications like in biosensing, plasmonic and antimicrobial field. TEM was used to monitor the dissolution of a single- crystal triangle. When it was exposed to a corrosive environment having O_2 and H_2S, a new thick layer of Ag_2S of about 20-50 nm was formed on the surface after 21 days. In their study they observed that within 3 days, the triangle stared to lose their regular shape because of the formation of Ag_2S on the surface. And after 14 days the triangle was fully corroded and after 21 days some regions of uncovered Ag remains. So, they concluded that there is a photoinduced conversion of AgNP into small clusters and oxidation of Ag to Ag^+ ions take place and move away from AgNP and it transforms into Ag_2S. These were the important factors controlling these corrosion and antimicrobial properties.[21]

Jose luis elechiguerra, et al. had study some of the metal nano partial and nanowires was used in electro fabrication and nanoelectronics so there was a huge chance of corrosion, so the capping agent should be used to prevent such type of corrosion. In their paper, they had also covered some caping agent covering techniques like solution phase technology and Nanosphere lithography (NSL). An examination of the layer was done by TEM. NSL was used to form noble arrays on the surface. The polyol method using polyvinyl pyrrolidone (PVP) for the deposition of silver nanoparticles on the surface. The nanoparticle after synthesis remains as crystal while nanowire becomes multi-wined. They observed that silver sulphide nanocrystals were formed on the surface and after 24 weeks the structure of nanowire was not clearly recognized. And when TEM was done to monitor the deposition and they observed that the size (< 5 nm) metal particle excitation at room temperature and fluctuation of the structure was observed i.e. with the decrease in size of nanocrystals, fluctuation rate increased. And to clean the sulphides Hydrogen plasma reduction is adopted. So, depending on the type of surface and the environment, a different capping agent is used and silver as a nanomaterial can be synthesized on many materials by different techniques. [22]

5. TITANIUM DIOXIDE COATINGS

K. Indira, et al. reviewed a study of influence of TiO_2 Nanotubes (TNT) on corrosion behavior. TNT is also one of the widely used nanotube in corrosion resistance due its enhanced properties, cost effective construction, high specific surface area, ion exchangeable ability and high surface to volume ratio. Anodization, sol-gel methods, etc. are some of the methods used for TNT synthesis. Their study revealed that Sr and Zr ions were engulfed onto TNT. Inclusion of Sr and Zr ions in TNT depicted better corrosion resistance than the TNT without these ions. Thick calcium phosphate layer was formed on surface when TNT was not incorporated with Sr and Zr ions. Nanoporous titania was developed and examined and excellent corrosion resistance was observed when the nanoporous titania was immersed in hank's solution (it is composed of inorganic salts and supplemented with glucose.) for 7 days.[23]

Nilesh.S. Bagal, et al. studied the deposition of zinc phosphate coatings on low carbon steel (LCS) with incorporated nano-TiO_2 particles by chemical phosphating method. The corrosion performance of LCS was analyzed using EIS and PDP in 3.5% NaCl solution. EM and EDS were used to analyze morphology and chemical composition of coatings. The phosphate coating was uniform and more homogeneous in presence of nano TiO_2 particles with very few defects, higher coating weight and improved corrosion resistance as compared to the normal zinc phosphate coating. The color of coating was dark grey and grey for normal phosphate coating and phosphate coating with nano TiO_2 respectively. The corrosion rate of nano-TiO_2 was 3.5 milli inches per year which was less than the normal phosphate coated sample that had 8 milli inches per year. The nano TiO_2 coating had insulating nature that was proved by polarization resistance values that was more for nano coatings (487.9 ohms) than normal coating (240 ohms). Nano TiO_2 coating decreases the porosity and it was reduced to 50% thus improving the corrosion resistance of phosphate coating.[24]

Vaibhav S. Kathavate, et al. experimented the corrosion protection performance of nano-TiO2 containing zinc phosphate coatings obtained by anodic electrochemical treatment and deposited on low carbon steel AISI1015 (LCS). LCS act as anode and graphite rod act as cathode. The corrosion protection performance was characterized by PDP curve, EIS in 3.5% NaCl electrolyte. Morphology was investigated using SEM, EDS, XRD. The porosity was reduced due to presence of nano TiO_2 in phosphate bath and homogeneous coating was formed. The nano TiO_2 in electrodeposited coating sample had less porosity than chemically deposited nano TiO_2.The performance of coating was expected to improve on addition of nano TiO_2. Taguchi technique was used for corrosion protection performance of electrodeposited nano TiO_2 incorporated zinc phosphate coating. The electrochemical phosphating method yielded better corrosion resistance than chemical phosphating at room temperature. The corrosion rate of electrodeposited phosphate coated specimen were 8 times less than bare LCS in 3.5% NaCl solution.[25]

Suning Li, et al. did a detailed study on cerium-doped nano-TiO_2 coatings that were developed by sol-gel method for corrosion protection of 316 L stainless steel. Surface morphology, structure and properties of prepared coatings were analyzed by X-ray diffraction, X-ray photoelectron spectroscopy, SEM. They used electrochemical technique to evaluate the corrosion resistance performance of their coating in 3% NaCl solution in both presence and absence of stimulated sunlight illumination and the cerium doped coating showed excellent corrosion resistance in both the cases as compared to undoped coating. It works on the principle of photocathodic protection that states that when a metal coated with thin TiO_2 is exposed to UV irradiation, electron hole pairs are generated TiO_2 coating. This recombination of electron hole pair can be reduced by doping. Doping reduces the crystal size of nano TiO_2 and the distribution of nanoparticles become compact. Cerium nitrate acts as corrosion inhibitor in an aqueous aggressive medium and it conceals the corrosion reactions. Under illumination, the open circuit potential (OCP) drop immediately to more negative value than the corrosion potential of 316 L stainless steel which is not in case of undoped TiO_2. [26]

U. Kamachi Mudali, et al. reported about the nanostructured coatings for corrosion protection in reprocessing plants. Highly oxidizing nitric acid from dilute to concentrated solution containing fission product from room temperature to boiling condition were the main process medium. The plant carried out various development works such as double oxide coating on Ti for reconditioning (DOCTOR)and nanostructured Ti, TiO_2, TiN and ZrN coating for corrosion protection. In nitric acid, improved corrosion resistance was shown by nanostructured Ti, TiO_2 and ZrN coating deposited on type 304L stainless steel by magnetron sputtering technique and Zr-based bulk metallic alloy(Zr34Ti3Cu20Al10Ni8) deposited on type 304L SS by pulsed layer technique. Presence of nanocrystalline oxide particles of Ti on DOCTOR coating exhibited superior corrosion resistance. In nanocrystalline TiO_2 coated type 304L SS, TiO_2 exhibited good passivating surface with low anodic dissolution rate making it one of the best material for corrosion protection. in nanocrystalline ZrN coated type 304L SS, the electrochemical corrosion result stated that corrosion resistance of ZrN was much better than the uncoated 304L SS in 8M HNO_3. [27]

6. ZINC COATINGS

Murat Ates has studied the improvement of corrosion resistance of stainless-steel type 304 by using Methylcarbazole (MCz) and its nanocomposites with Montmorillonite nano clay and Zn nano- particles. Stainless steels are increasingly utilized in various industries due to their relatively high strength, high chemical stability, low gas permeability, and low corrosion rate. Nano clay and Zn nanoparticles were chemically synthesized under vigorous stirring followed by in situ polymerization of methylcarbazole, which caused the incorporation of nano clay and Zn nanoparticles into the P(MCz) matrix. To study the behaviour of coating by using Tafel polarization curves, as well as electrochemical impedance spectroscopy under 3.5 wt. % of Nacl solution. Studies of P(MCz), P(MCz)/nanoclay, and P(MCz)/nanoZn confirmed that they provide good anticorrosion protection. So according to their study chemically synthesized SS/P(MCz), SS/P(MCz)/nanoclay, and SS/P(MCz)/nanoZn nanocomposite film coating have high corrosion protection efficiency (PE=99.56%, 99.89%, and 99.67%, respectively). Thus, they concluded that nano clay and Zn nanoparticles possess acts as a barrier, which can be employed in order to achieve improvements in chemical corrosion protection through P(MCz) coating.[28]

Joshua Olusegun Okeniyi, et al. studied the effects of dialium guineense based zinc nanoparticle material on the inhibition of microbes inducing microbiologically influenced corrosion (MIC). Zinc nanoparticle were synthesized from the extract of leaf from the natural plant and was characterized by SEM and EDS. The microbes found on metal surface do not cause metallic corrosion directly, but the physical presence of their colony like methanogen, sulphate and nitrate reducing bacteria can accelerate corrosion process through the byproduct of their metabolic activities. Since microbes interact with the metallic surface, they hinder the formation of films. Thus, prevention of further corrosion on metallic surface is prohibited. The positive control of 10µg Gentamicin was used for comparison with the inhibition results evaluated by the use of the zinc bio-nanoparticle and it was found that dialium guineense based zinc nanoparticle material exhibited higher sensitivities than gentamicin. The Zn ion undergoes a mechanism that would lead to cell death of microbial stains and thus protect metals from cause of MIC. [29]

V.S.Kathavate, et al. worked on electrodeposition of nano ZnO blended phosphate coatings for the corrosion protection performance of low carbon steel (LCS). Electrochemical characterization results depicted that nano zinc incorporated phosphate coating show lower corrosion rate(1.89mpy) in 3.5% NaCl solution against normal zinc phosphate coating (5.68mpy). The 2 stages of electrodeposition of zinc on LCS which include nucleation (change in potential from zero to maximum) followed by the growth of phosphate layer (change in potential from maximum to stable value). During electro deposition, hydrogen evolution take place at cathodic site (graphite rod) and metal dissolution take place at anode. Electrodeposition at various current densities (2-8mA/cm^2) were performed and they observed that the porosity increases as a function of current density and nano ZnO exhibit less porosity than the normal coating. The presence of nano ZnO particles helps in activation of more nucleation site on steel substrate and forms more compact and dense coating that provide the better crystalline coverage; they also help in occupying more surface area and more coating weight. The color of normal phosphate coating was greenish grey and nano ZnO phosphate coating was white grey color. The corrosion rate of nano coating was found to be 3 times less than the normal zinc phosphate coating and 8 times less than the bare LCS.[30]

7. ZIRCONIUM COATINGS

Sherif Elbasune, et al. reported the study of the significant role of stabilized colloidal ZrO_2 nanoparticles for corrosion protection of AA2024 in artificial sea water. An average of 10mm particle size were illustrated using TEM. XRD diffractogram demonstrated high crystalline structure. Traditionally chromate coatings were employed to protect aluminum alloy but dye to its carcinogenic effects, eco-friendly inhibitors became necessary development to be made and thus nano ZrO_2 came into picture. This new approach of using colloidal ZrO_2 particles as corrosion inhibitor ushered an extensive surface area and reactivity. The effectiveness of the process was evaluated using PDP in aerated 3.5% NaCl corrosive solution at room temperature and EIS. The corrosion resistance of nano ZrO_2 was improved by blocking the intermetallic sites on the metal surface and thus the corrosion current density of AA2024 was reduced sharply. The electrochemical reaction occurred due to local alkalinity of ZrO_2 cause the precipitation of ZrO_2 at the intermetallic sites. Thus, the cathodic area was reduced decreasing the corrosion rate $Zr^{4+} + H_2O \rightarrow ZrO^{2+} + 2H^+$; $ZrO^{2+} + H_2O \rightarrow ZrO_2 + 2H^+$. SEM results depicted that after 5 days of immersion of AA2024 in 3.5% NaCl solution with ZrO_2, there was no sign of corrosion around the intermetallic particle.[31]

8. SILICA COATINGS

Naghmeh Amirshaqaqi, et al. researched the corrosion behavior of aluminum/silica/polystyrene (PS) nanostructured hybrid flakes. The surface of Al flakes that were produced by grinding Al foil in ball mill with white spirit and fatty acid as solvent and lubricant respectively, was encased by silica nanolayer by hydrolysis and polycondensation of tetraethyl orthosilicate through sol-gel process to obtain Al/Si flakes. Fourier transform infrared spectroscopy; energy dispersive X-ray spectroscopy and SEM were conducted to show that silica and PS nano layer were formed on aluminum flakes. This hybrid coating act as an outstanding protective film and thus corrosion protection results were acceptable in both acidic and alkaline solution. The organic layer was combined with inorganic layer because the inorganic silica had a limitation of “brittle structure” that caused gassing. The addition of organic PS nano layer made the surface hydrophobic. They found that the evolution of hydrogen for the samples dispersed in aqueous NaOH solution at pH 12 and aqueous HCl solution at pH 1 started after specific amount of time from immersion and this time is called incubation period. The morphology study stated the thickness values of silica and PS layers as 10-15 and 25-30nm respectively.[32]

Samire Sabagh, et al. has studied the effect of corrosion when epoxy coating containing SiAlON nanoparticles at different loadings (0-12 wt.%) was successfully coated on steel substrates. Their purpose of using epoxy coating because it acts as a physical barrier layer and also serves as a reservoir for corrosion inhibitors to aid the steel surface in resting attack by aggressive species such as chloride anions and also inorganic fillers were used to prevent diffusion. To increase the adhesion between the polymer matrix and material various ceramic particles were used. They ng Bisphenol A with polyamine hardener as a curing agent. To analyse the behaviour of corrosion for around 35 days they had used electrochemical impedance spectroscopy against 3.5 wt. % NaCl solution at room temperature. So as per there experimental result, high-performance nanocomposite coating sustains in all chemical conditions. Hence, applying a small amount of filler content improves chemical properties. Therefore, they had added 5 wt. % of SiAlON nanopowder that increased charger transfer resistance up to 10,000 times compared to net coating.[33]

9. IRON COATINGS

Javed Alam, et al. has strongly highlighted their investigation on corrosion resistance performance of soya oil alkyd, containing polyaniline/ferrite nanocomposite by studying corrosion rate, Physio-mechanical properties, and SEM studies. To prevent corrosion of iron and Al-based metals, polypyrrole, polyaniline, and there derivates as a conducting polymer can be used. As per their previous years study the Monsanto variation is working on (ICP)- based paint but the design and production of PANI- based coating systems with commercial viability requires paint formations with a minimum possible agglomeration of ICP and acts as a prolong protective layer under different corrosive conditions. After observing of PANI/ ferrite in UV visible spectra nano compounds shows maximum absorption of wavelength up to 350 nm to 600 nm. Which means there is a polaronic transition peak. Therefore, they confirm the emeraldine doped state of Cl- doped PANI in a Fe_3O_4/PANI nanocomposite. They concluded that PANI/ferrite/alkyd nanotechnology is efficient to protect steel from corrosion because they act as an inhibitor, it is more malleable and dispersed uniformly and can be used for many applications.[34]

10. COPPER COATINGS

Maria Trzaska, et al. came with a straight forward and energetic approach to study the electrochemical corrosion behavior of nano-copper thin layer coating on metal surface. This method followed the analysis of the appropriate loops on energy phase plane. The loop area was used to calculate the corrosion phenomenon. The nature and extent of corrosion reaction was governed by its potential to transfer the anodic and cathodic charges. The electro-crystallization method was used to deposit layers on polycrystalline copper substrate. Platinum foil with large area was used as auxiliary and a saturated calomel electrode was used as reference electrode. Even though nano-structured copper and microcrystalline copper were exposed to same corrosive environment for experimental comparison, nano-structured copper showed lower corrosion resistance than the microcrystalline material. The microcrystalline copper encountered pitting corrosion at grain boundaries whereas, the nano-structured copper experienced uniform corrosion. The one period energy (amt. of energy delivered by the source in 1period) evaluated showed that nanocrystalline copper layer absorbs 3 times less energy than microcrystalline one.[35]

11. MAGNESIUM COATINGS

Giovanna Poggi, et al. investigated the use of hydroxide nanoparticles for deacidification and collateral inhibition of iron-gall ink corrosion of paper. Magnesium hydroxide nanoparticle dispersed in alcohols were used to hinder 2 different and collaborative degradation process that affect historically valuable manuscripts and other papers. During the preparation of gall ink, tannins that were extracted from gall-nuts was hydrolyzed and gallic acid was formed and was made to react with iron (II) and sulfuric acid. Two free radical mechanism fenton reaction (Fe^{2+}+H_2O_2 → Fe^{3+}+OH^- +$OH^\bullet$) involving iron ions and fenton like reaction (Cu^++H_2O_2 → Cu^{2+}+OH^- +$OH^\bullet$) involving copper ions were observed during the catalysis of cellulose oxidation by transition metal ions. The pH value of paper is lowered in presence of metal gall-ink due to sulfuric acid. The nanoparticles deacidifies it by forming an alkaline reserve that prevents further degradation of paper and maintains the pH range between 6.5-7.5. Bookkeeper method (dispersion of mainly micro-sized particles of MgO in fluorinated solvents) was used in their experiment that was one of the best non-aqueous mass deacidification treatment. Unlike nanoparticles, the micro sized particles required surfactant to disperse. Thus, it is considered to be better and safer than bookkeeper. Samples deacidified with nanoparticles had a color change after 48h of aging whereas untreated sample showed sever diffuse browning just after 24h. Mg $(OH)_2$ nanoparticles showed mechanical strength similar to that of unaged samples.[36]

Anees A. Khadom, et al. studied use of MgO nanoparticles in retardation of high-temperature fuel ash corrosion of fireside boiler tubes and turbines. The surface morphology was studied by EM. Corrosion rate was evaluated by weight loss technique as a function of inhibitor concentration, time and temperature in presence and absence of fuel ash and it was found that the corrosion rate increased with time and temperature but decreased when inhibitors were added. Steel alloys are oxidized when heated to higher temperature in oxidizing media such as combustion atmosphere with excess air and the oxide film formed controls the corrosion. With increase in oxide layer thickness, the high temperature corrosion decreases with increase in time due to increase of diffusion distance of ion. Inhibitors of high temperature corrosion increases the melting point of fuel ash impurities and change the structure of corrosive agents. The mass loss technique showed the order of inhibition from best to worst as: nano MgO > nano MgO –MgO blend > MgO. The maximum inhibitor efficiency was 81% using nano MgO at mixing ratio of 2:1 at 600^{O}C. and the lowest was 3.5% for normal MgO at 1:1mixing ratio at 900^{O}C. Injection of nano MgO reduced the corrosion rate by 50-75%.[37]

12. OTHER COATINGS

M.Leleh, et al. has studied the effect of corrosive environment on AZ91D magnesium alloy at two different temperatures 150^{O}C and 350^{O}C. They had used Oxidative coating as a barrier and the pores between them is filled by using the sol-gel layer by dipping it. The method used was Micro-arc Oxidation (MAO) for deposition. And for analysis electron microscope and X-ray diffraction under 3.5 wt. % NaCl solution. Electrochemical impedance spectroscopy and potentiodynamic polarization test (to measure porosity) was also included by them for analysis. So, they resulted that sol-gel layers significantly increased the corrosion resistance of the substance by reducing the presence of porosity. They concluded that after heating sol-gel at 350^{O}C has 50 nm average grain size with a rough surface than that at 150^{O}C. [38]

Hryhoriy Nykyforchyn, et al. experimented the formation of surface corrosion-resistant nanocrystalline structures (NCS) on steel. Mechanical pulse friction treatment (MPT) was used to generate surface nanocrystalline structure on middle carbon steels by severe plastic deformation. But use of severe plastic deformation method in corrosion environment would be complex as there would be decrease of corrosion resistance of the metal because the dispersion of the structure would increase general activity of metal. This treatment also includes high temperature phase transformation and alloying. The boundaries of NCS were not in equilibrium and was denoted by high dislocation density. The surface activation after MPT could intensify the corrosion process. They further specified the negative impact of carbon content in steels on corrosion rate by the observation that the steel 45 containing more carbon content experienced higher corrosion rate than steel 35. The specimens were alloyed with various elements such as carbon, silicon, nitrogen, and the results were noted. Corrosion current decreases as: untreated> MPT with carbon alloying> MPT with silicon alloying> MPT with nitrogen alloying.[39]

Habib Ashassi- Sorkhabi, et al. has studied by using polyaniline/nano diamond (PANI/ND) having high-electrical conductivity, unique electrochemistry, chemical, and physical properties, FT-IR studies, good environmental stability and ease of synthesis on mild steel. So, they had improved the characteristic property of PANI by combining with the polystyrene latex. They had used chemical polymerization using the cyclic voltammetry technique for synthesis. And for effective dispersion of ND particles, Ultrasonic Irradiation was used. And for investigation, they had used electrochemical impedance spectroscopy and polarization method under 0.5 m H_2SO_4 solution (as corrosive environment). As a result, they came to a point that because of the unique properties of PANI and ND it can be used against 0.5M H_2SO_4 solution as it improves corrosion resistance which is nothing but the formation of nano colloidal adherent and compact PANI coating in the Presence of ND'S.[40]

Ahmed A. Farag had briefly reviewed on improving the chemical, mechanical and optical properties of a coating by adding nanoparticles in it depending on the properties of nanoparticles and also depending on the application to produce corrosion inhibitors and corrosion-resistant coatings. So that nano-coating has constituents in nanoscale or made up of numbers of layers up to 100nm. He has also given information regarding organic and inorganic composite coatings which gives protection and reliability with long-term performance. So environmental impact can be reduced by using nanomaterials as inhibitors, Ti oxide, nanocoating, Alumina nanocoating, Nano conductive PTH, ceramic coating, Nano conductive ppy, Nano conductive PANI as anti-corrosive coating and corrosion inhibitors. Therefore, nanocoatings have significant potentials to offer superior enhancements in the corrosion performance of surfaces compared to micromaterial coatings.[41]

Conclusion:

This paper has reviewed various sorts of coatings to avoid corrosion with their applications in different fields. From the detailed literature review following points are found

- Among various method of corrosion protection, nanotechnology turned into a promising method to prevent them.
- Various nanoparticles were used either as a binder or inhibitors to improve the corrosion resistant properties. Besides these corrosion resistance properties, the nanoparticles also enhance other physical and chemical properties of the coatings.
- nanoparticles reduce the porosity of the coatings and increases the life span of the metals.
- SEM, TEM, FTIR, sol-gel analysis were the commonly used techniques to study the morphology, chemical properties and structures of the coatings.
- PDP, EIS methods were frequently observed to be used in all the processes studied to determine the extent of corrosion. And as reviewed, these analyses were performed mostly in 3.5% NaCl solution.

Hybrid coatings of graphene were used for corrosion resistance whereas nickel phosphate nanocoating's was used in mild steel specimens. Aluminum nanoparticles had good resistance towards stress corrosion but experienced pitting corrosion. They act as stable additives in nanofluids. Silver nanomaterial can be synthesized by various methods and they were used depending on required conditions. TNTs were widely used with phosphate coatings and they showed an outstanding corrosion resistance. Doping TiO_2 with cerium or Sr and Zr ions greatly increases its properties. Further the performance of zinc, silica, iron, magnesium nanoparticles were also studied and all of them helped in reducing the corrosion to a great extent.

Future scope:

As we saw earlier nanomaterials are used not only in the chemical industry but also in medical sectors, Mechanical areas, etc. In the future, we will see more applications and it will be used in every sector like manufacturing materials and devices:- Faster computers, advanced pharmaceuticals, controlled drug delivery, biocompatible materials, nerve and tissue repair, crackproof surface coatings, better skincare and protection, more efficient catalysts, better and smaller sensors, even more, efficient telecommunications, these are just some areas where nanomaterials will have a major impact. New nano-materials and ideas are at present being built up that show potential for producing energy from development, light, variation in temperature, glucose, and different sources with a high conversion effectiveness.

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