Nanocomposite coatings on steel for enhancing the corrosion resistance: A review

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Abstract
Steel is known for its low cost of fabrication, high mechanical strength and hence is extensively used for drilling equipment, pipelines, ship building and offshore structures. Corrosion of steel is a costly problem in many applications especially in oilfield and marine environments which are known for the high temperature, high pressure and corrosive conditions. In this paper, nanocomposite coating is being explored as the preferred strategy to improve corrosion resistance for steel. Here, we will give details on the various coating materials, deposition techniques and the challenges involved in realising the most suitable coating on steel based on results of recent research. In addition, we also detail the filler specifications for getting high performance nanocomposites.

Keywords
Nanocomposites, corrosion, coating, steel, challenges

Introduction
Coating to enhance mechanical strength and corrosion resistance is one of the best practical and cost effective methods for metallic components.¹,² Steel is an indispensable metal alloy for a number of applications in railways, building, bridges, appliances, oil and gas, and other infrastructures. Two kinds of steel called mild steel and stainless steel are commonly used by utilising their mechanical strength and corrosion resistance characteristics respectively. However, even stainless steel is susceptible to corrosion under extreme environments³,⁴ which requires replacement of damaged parts and results in a huge loss of time and money for the maintenance. Hence, the issues related to protection and durability of the steel-based components deserve attention and research.⁵ Development of new materials and surface modification of corrosive system are some of the ways to prevent corrosion. Looking for an alternative material like titanium (Ti) and other alloys can lead to a higher cost of fabrication than that of steel. Hence a more cost effective way to prevent the corrosion for new and existing steel structures is coating. An economic study has shown that internal coating on pipelines or other structures is more cost effective than that of bare carbon steel plus inhibitors.⁶

Corrosion due to marine atmosphere results in almost 30% of the total equipment failure which require in either repair or replacement of equipment entirely or partially. In a marine environment, steel corrosion is influenced by parameters such as salinity (concentration of dissolved salt), alkalinity (concentration of hydrogen ions) and hardness of sea water.

Corrosion of steel is basically an electrochemical reaction which occurs in the presence of water, O₂, and ions such as Cl⁻ or F⁻ ions⁷,⁸ (Figure 1). In addition, gases such as CO₂, CO, SO₂, and NO₂ speed up the corrosion process. When metals which differ in their standard electrode potentials are contained in an electrolyte, electrons get transferred from metals with greater negative potential and the corrosion occurs at the point from where the electrons leave. Commonly used methods to prevent corrosion are (i) passive barrier protection: protective coating to prevent exposure
to atmosphere, e.g. epoxy coatings, (ii) active protection: A primer containing reactive chemical which disrupts the anode formation directly applied on steel, e.g. is $\text{Zn}_3(\text{PO}_4)_2$ wherein $\text{Zn}^{2+}$ ion acts as a cathodic inhibitor and $(\text{PO}_4)^{3-}$ ions act as an anodic inhibitor, and (iii) sacrificial protection: method of protecting steel via oxidation of another metal. Zinc is the most widely used metal. It acts as a sacrificial agent to steel, as it corrodes by protecting steel with less corrosion rate.9

Organic polymer coating or paints with epoxy resins polyurethane (PU) and acrylic are widely used to prevent corrosion.10 Resins act as a barrier which physically prevents metal to contact the corrosive ambient environment. However properties of resin are found insufficient in many cases for preventing the penetration of aggressive ions through the resin pores.11 Pristine polymer alone is insufficient in effectively preventing corrosion and new strategies such as nanocomposite coatings are being explored.12–14 Super hard nanocomposite material coatings play a major role in enhancing hardness (>40 GPa), oxidation resistance (>800°C) and thermal stability (Up to 1200°C).15–17 Transition metal nitrides in combination with amorphous silicon or boron nitride for example, nc (nanocrystalline)TiN/a-Si$_3$N$_4$ or nc TiN/a-BN are found to be a good choice for coating low mechanical strength alloys or forming tools.18 Tribological properties of these materials determine their industrial applications.

**Nanocomposite coating**

Many disciplines of science and technology are being influenced by nanotechnology.19–21 Polymer-based nanocomposites in which an organic polymers reinforced by an organic/inorganic fillers have become a prominent research area recently.22,23 Size, shape, morphology and the weight percent of the fillers greatly influence the intrinsic properties of composites. Synergic contributions from thermally and mechanically stable inorganic/organic materials and lightweight, flexible and ductile organic polymers make the composites superior in properties compared to their pristine counterparts. To prevent steel from corrosion, nanostructured hydrophobic and super-hydrophobic coating of primers were explored.24–26 They are found to act as a good water barrier and hence effectively blocks water absorption and enhance the service life of metals and their alloys. In a typical nanocomposite coating, specific nanoparticles (NPs) are added to enhance the overall performance. NPs of alumina, titania, silica are well-known materials used in coating formulations.27–29 NPs were observed to modify the surface energy of the inherently hydrophobic siloxane polymers and hence improve the performance of nanocomposite coating immersed in aggressive media.30

There are a number of ways to improve the properties of nanocomposites by incorporating NPs, fibers, glass beads, etc. Reinforcements are found to improve thermal resistance, corrosion resistance and mechanical properties of metal matrix due to their unique properties. However the main challenge in getting the optimum properties from composites is the non-uniform dispersion of NPs in the matrix. Research is in progress to overcome this problem to enhance the nano-fillers and polymeric matrix interactions. Functionalisation of materials such as GOs or CNTs with a high surface area and van der Waals’ force of attraction is found to improve the dispersion and hence improves thermal stability and mechanical properties.31 Development of a hybrid composite coating in which the dispersion of hybrid material i.e., combination of two or more different materials into a polymer or metal matrix was found to give enhanced mechanical properties and corrosion resistance. Hybrid coatings have the potential to open up a new scope especially in epoxy-based coatings.32

Nanocomposite coatings are useful for a number of applications in different fields. Figure 2(a) is a pie diagram which shows the number of publications on nanocomposite coating in some of the major research areas and Figure 2(b) is a histogram which shows the publications on steel in marine environment since 2000 to till 2018.

A good corrosion resistant material is characterised by (i) good durability and adhesion, (ii) excellent gloss, (iii) high barrier properties, and (iii) cost-effectiveness. Corrosion studies are usually carried out using an electrochemical cell in three electrode configurations. In a typical experiment, the sample which is to be tested act as the working electrode, Ag/AgCl as reference electrode and platinum rod as counter electrode. A number of parameters which determines the extent of corrosion can be determined by using an electrochemical workstation. Some of them are open circuit potential (OCP), polarization resistance, and corrosion rate. In addition to the above tests, surface energy test of the coated material, adhesion properties, water absorption

![Figure 1. Schematic of the corrosion process in steel.](image-url)
measurement, \(^{33}\) coefficient of thermal expansion (CTE), scratch test, and cathodic disbondment test \(^{34}\) are very useful in exploring the complete performance of coated material.

### Coating materials explored

Anti-corrosion coatings can be broadly classified into (i) organic coating (ii) inorganic coating and (iii) metallic coating as shown in Figure 3. Advantageous and disadvantageous of materials in each category are also listed.

Organic coatings are mostly used for protecting carbon steel structures/pipe lines from outdoor corrosion. Organic coating normally acts as a physical barrier and prevents \(O_2\), \(H_2O\) and other corrosive ions in reaching the metal surface. Two major drawbacks of organic coatings are coating permeability and weak adhesion. \(^{35}\)

Many methods have been proposed and NPs can play a major role in mitigating the above issues.

A combination of organic and inorganic coating is getting explored to make use of both their properties. Organic-inorganic hybrid composites combine two or more phases with at least one phase in nanoscale. The final properties of composite are hence not just the sum of contributions from each phase but with unique properties. If the interphase interactions between organic and inorganic phases are van der walls or ionic or hydrogen bond hybrid composite is called type I, while for covalent bonding force, hybrid is type II. \(^{36}\) The nature of interaction among different phases determines the final performance of the composite.

Given below are some of the recent works on corrosion resistant coatings with a brief analysis on each nanocomposite. Knowledge on these nanocomposites gives an overall idea on the process of corrosion, corrosion protection, characterisation techniques, and future material requirements. This further helps in finding a suitable material for coating on steel in marine environment.

**Figure 2.** (a) Number of publications pertaining to nanocomposite coating from some of the major areas of research for the last 8 years, and (b) histogram shows the number of publications from 2010 to 2018 using a key word ‘nanocomposite coatings on steel in marine environment’ in Scopus search database.

**Figure 3.** Broad classification of anti-corrosion coatings, and examples along with their pros and cons.
Enhancement in corrosion resistance

Epoxy paint blended with TiO₂ NPs. Epoxies are very extensively used as coating material due to their superior material properties and low cost. Epoxies are a class of reactive pre-polymers and polymers which contain epoxide functional group. A wide range of epoxies are produced industrially for different technological applications. Mardare et al. experimented with the effect of pristine and TiO₂ incorporated epoxy paint on the corrosion properties of naval steel plates immersed in sea water. A two component polyamide with glossy acrylic PU was coated at a thickness of ~80 μm on steel. OCP for uncoated samples was found to decrease from −488 mV to −705 mV vs. Ag/AgCl during immersion (Figure 4(a)). The shift in potential to more negative value indicates the easiness for oxidation reaction in marine ambient.

Observation shows that a constant OCP of −599 mV for polymeric primer coated E32 steel implies the improved resistance to corrosion. When the polymeric primer was coated with TiO₂ NPs, the OCP value was found even more positive (~483 mV) which gradually changed to −442 mV. However the values did not settle to a constant value which was an indicator of non-uniform protection even though corrosion performance was improved. The same was evident from the corrosion rate plots (Figure 4(b)). Polarization studies (Figure 4(c)) revealed that polarization resistance of primer plus TiO₂ coated steels were 1000 times higher than uncoated steel. Specific hysteresis loop of uncoated steel in cyclic voltammogram shows the susceptibility for localised corrosion. In case of primer plus TiO₂ NPs coated steel does not show any specific hysteresis corresponding to localised corrosion (Figure 4(d)). The TiO₂ NPs showed significant influence on the corrosion properties of epoxy. The corrosion rate of nanocomposite of TiO₂ and epoxy was 0.141 μm/year while that of uncoated steel is 386.79 μm/year. Hence, TiO₂ dispersed polyamide adduct cured epoxy can increase the lifetime of naval steel which can reduce the cost of replacement and maintenance cost.

Uniform dispersion of nanofillers in polymer matrix is the main challenge for making polymer-based nanocomposites. To get the desired performance either TiO₂ or another nanofiller has to be uniformly dispersed in the metal matrix. Duong et al. came up with a solution to this problem.

Figure 4. A comparison of corrosion parameters of uncoated steel (E32) and coated steels (a) open circuit potential, (b) corrosion rate, (c) polarization resistance and (d) cyclic voltammetry (reproduced with copyright permission from Benea et al.).
with a method for the mono-dispersion of TiO\textsubscript{2} nanotubes in the polymer epoxies by modifying them with 3-aminopropyl triethoxysilane (APTS). The mechanical, thermal and corrosion resistant properties of APTS grafted TiO\textsubscript{2} nanotubes are greatly enhanced compared to the unmodified TiO\textsubscript{2}-based coating. Amine groups on TiO\textsubscript{2} further helped in improving the bonding with epoxies and contributed to the overall performance enhancement.

Recently, many epoxy-based nanocomposites have been explored. Atta et al.\textsuperscript{43} investigated magnetite nanohybrid epoxy as a protective marine coating for steel. Porous iron oxide NPs doped with iodine and capped with surfactant was used to repair the cracks present in epoxy coats. Improved corrosion and mechanical properties were observed due to the formation of stable thin films on the cracks and holes present in epoxy coats. By filling the cracks, NPs act as a strong barrier which can prevent penetration of aggressive ions to the metal surface. El Faham et al.\textsuperscript{44} used silver embedded epoxy nanocomposites as an organic coating to steel. Silver NPs are found to enhance the anticorrosion properties of epoxies. They have further identified the effect of sea water, and pH of solutions on the performance of Ag NPs.

**Polybenzoxazine/SiO\textsubscript{2} nanocomposite coatings.** Polybenzoxazine (PB) is a material with low surface free energy, zero shrinkage, low water absorption, and good dielectric properties which make it outperform epoxies and phenolic resins for many applications.\textsuperscript{45} PB has many advantageous over conventional novolac and resole type phenolic resins.\textsuperscript{46} Surface hydrophobicity can minimise the chance for corrosion while addition of coating on the parent material can eliminate the delamination. Zhou et al.\textsuperscript{47} investigated a nanocomposite coating on mild steel consisting of PB and SiO\textsubscript{2} NPs. They studied the influence of silica content, surface chemistry of NPs and bonding between polymer and NPs on corrosion resistance. Silane functionalised benzoxazine (PB-TMOS) was prepared by a traditional thermal curing method without hydrolytic process. The surface energy of fluorinated silane functional benzoxazine (TFP-TMOS) film was 15.5 mJ/m\textsuperscript{2} which was much lower than that of pristine Teflon by 21 mJ/m\textsuperscript{2}.\textsuperscript{48}

FTIR and NMR techniques were utilised to understand the dual cross linking structure of coating. Finally, corrosion resistance properties of the coating on mild, stainless steel alloys and pure Ti were explored. Corrosion resistant properties of pure and coated steel were tested in 3.5 wt% NaCl solution at 25\textdegree{}C. Figure 5(a) shows Tafel’s plots of pure steel and coated steel. The corrosion current density I\textsubscript{corr} of various samples was found by extrapolation method. The lower the polarisation current, the better is the corrosion resistance.\textsuperscript{49} I\textsubscript{corr} of pristine and coated mild steel are 2.95±0.28 μAcm\textsuperscript{-2} and 0.59±0.08 μAcm\textsuperscript{-2}, respectively. Thus it can be concluded that the corrosion resistance of coated mild steel increased four times compared to pristine steel. For stainless steel, I\textsubscript{corr} reduced from 0.12±0.02 μAcm\textsuperscript{-2} to 1.55±0.35 nAcm\textsuperscript{-2}, which is two orders of magnitude reduction in corrosion resistance. For the Ti sample, I\textsubscript{corr} is observed to be 44.70±5.40 nA cm\textsuperscript{-2}. The weight loss of the samples in 6% FeCl\textsubscript{3} solution shows considerable improvement of corrosion in coated samples (Figure 5(b)). Contact angle measurement reveals the increased hydrophobicity after coating (Figure 5(b) inset). The electrochemical impedance spectroscopy (EIS) was measured and Nyquist diagrams were plotted which shows a single capacitive semi-circle as shown from Figure 5(e) to (e). In general, diameter of the semicircle corresponds to the charge transfer resistance (R\textsubscript{ct}) which indicates the corrosion resistance.\textsuperscript{50} The higher the R\textsubscript{ct} value, the better is the corrosion resistance and all the coated samples have higher values compared to their pristine counterpart. Authors attribute the reason for the reduced water intake to the dual cross-linking between PB and Si-O-Si.

Many combinations of PB with nanomaterials have been tried.\textsuperscript{51} Recently, Caldona et al.\textsuperscript{52} investigated corrosion protection of elastomer modified PB/GO composite coating. Rubber modified PBZ protects carbon steel from corrosion attack while GO provides enhanced protective attributes. Protective property was tuned by varying the amount of GO. The optimum concentration for enhanced corrosion resistance was also determined.

**ZnO-polysiloxane coating.** High surface energy of PU and epoxy demands the use of alternative material to decrease the affinity towards water and microorganisms.\textsuperscript{53,54} NPs based polysiloxane appear to be promising. However, they have been studied scarcely. Among the NP family, ZnO gained a huge attention in making anticorrosive coating formulations due to its antimicrobial properties, high thermal stability, high electron mobility and high refractive index.\textsuperscript{55,56} ZnO-incorporated polysiloxane (PDMS) coating has been explored by Arukalam et al.\textsuperscript{57} They optimised the size and the concentration required for the highest anticorrosion performance. Surface morphology, liquid repellency and roughness of the coating were studied and performance was found to be a major function of size and PDMS:ZnO ratio. The authors recognised the optimised condition as 30 nm sized ZnO and polymer to ZnO ratio as 1:1. Impedance of the nanocomposite was \(\sim 10^9\) Ωcm\textsuperscript{2} and remained constant throughout the exposure of coating in 3.5 wt% NaCl solution. This work gives the scientific community a new formulation
chemistry which has the potential on industrial design of polysiloxane-based nanocomposite coating. The ZnO NPs helped in improving the surface properties of polymer coating.

Siloxane is a compound with short repeating unit of Si and O atoms with organic side chains. Polysiloxane is derived from siloxane having siloxane as repeating units and many polymer composites find potential improvement with the addition of siloxane in it. epoxy-siloxane-silica nanocomposite was explored by Torrico and group as a coating material for corrosion protection. Structure and properties of coating is determined by the fraction of silica/siloxane phase. Structural analysis revealed the covalent bonding of silica-siloxane domains to the epoxy phase. NPs incorporation resulted in a low surface roughness of <5 nm and high thermal stability >300 °C, strong adhesion and excellent barrier properties with high corrosion resistance (~50Ωcm²).

**Epoxy-nanochitosan coating.** Nanochitosan (NCH) is a linear polysaccharide composed of acetylated and deacetylated unit and has many commercial and biomedical applications. Ma et al. studied the anticorrosive properties of mild steel coated with epoxy resin with different NCH loading ratios.

Figure 6(a) i.e., first day immersion data shows poor corrosion resistance of all the coated systems due to the electrolyte penetration. It was inferred that corrosion has been initiated in the coated films while it was not observed to reach the coating/substrate interface. The impedance plot after 30 days is given in Figure 6(b). As can be seen, pure epoxy coated steel was found to undergo significant degradation. However, the resistance of coated samples improved. Corrosion inhibition of coated films is due to the prevention of corrosive species to reach the coating/metal interface by NCH. High corrosion resistance of ECH0.5 (epoxy + 0.5 wt% NCH) and ECH1.0 (epoxy + 1.0 wt% NCH) is due to the uniform dispersion of NCH in the epoxy matrix. In the higher loading case, ECH1.5 shows lowest resistance and may be due to the aggregation of NCH caused by the strong hydrogen bonding which further weakened the bonding between NCH and epoxy. In this way, small pores were generated at the matrix vicinity allowing corrosive agents to reach the coating/metal interface.

**Amino-functionalised NPs functionalised epoxy.** Performance of epoxy materials can be enhanced via compositing with nanomaterials. Saliba et al. synthesised and characterised novel organic-inorganic composite
coating material. Amino functionalised silica NPs were incorporated into epoxy-based powder by sol-gel process. In this way, development of interfacial reaction between organic-inorganic and inorganic-inorganic components resulted in improved mechanical properties such as hardness and elastic modulus against under water corrosion. Even though direct evidence for increment in corrosion resistance is not carried out in their present studies, superior integration between NPs and epoxy matrix is expected to improve the overall performance with a future scope for suitably coating this material on various graded steels.

Many combinations of epoxies with one or more NPs were tried by different researchers and some of them are given in subsequent subsections. For example, corrosion properties of epoxy coating based on silane functionalised graphene quantum dots (f-GQDs) were explored by Pourhashem et al. They have prepared f-GQDs by a cost-effective hydrothermal process and modified further by (3-aminopropyl) triethoxysilane. Spray coating technique was used to coat a mild steel substrate and corrosion studies shows improvement in corrosion resistance due to high barrier performance of f-GQDs in polymer coating.

Clay plus zirconia-based epoxy coating. Weight percent of the filler materials plays an important role in determining the overall performance of the composite. Behsadnasab et al. varied the ratio of clay to zirconia content in epoxy polymer matrix to understand the barrier properties and ohmic resistance.

Nanocomposite coating was prepared by slurry method. EIS studies on pristine metal, polymer and composites were performed in 3.5 wt% NaCl electrolyte solution and representative Nyquist plots are shown in Figure 7. An inductive loop at low frequencies in case of bare mild steel (Figure 7(a)) shows adsorption of intermediate product in the corrosion process. Resistive component in the low frequency region was found to be large (~MΩ cm²) (Figure 7(b)) when compared to the bare steel. With clay and zirconia in the weight ratio 2:1 in epoxy gives better corrosion resistance (~GΩ cm²) (Figure 7(c)). Simultaneous use of clay and ZrO₂ was found very effective for long period of protection. It is claimed that combination of layered clay and ZrO₂ promoted the exfoliation of clay NPs which improves the corrosion performance via enhancing the barrier properties and ohmic resistance. ZrO₂ is known for its high hardness, wear resistance and high thermal stability (~2400°C). Its CTE is similar to that of Fe. Zirconia was used in combination with hydroxyapatite (HA) and TiO₂ to enhance the overall coating performance. Electrodeposition of HA-ZrO₂-TiO₂ coating on 316 stainless steel was found to enhance the corrosion resistance due to the synergistic contribution from corrosion resistant HA and titania, mechanically strong zirconia. NPs addition reduces porosity of HA coating from 46% to 6%.

GO-ZrO₂-epoxy coating. Graphene oxides consist of hydroxyl, carboxylic, and epoxide functional groups on edges and basal planes. Polymer-GO composites gained attention in the recent years. However, the reason for poor composite properties is the agglomeration of GO sheets due to their high surface area and van der Waals' interaction. Functionalization of the graphene sheet with organic components is one way to reduce the agglomeration and can act as a good reinforcement material for polymer matrices. Di et al. have functionalised GO and ZrO₂ before
incorporating them into the epoxy matrix. The GO-ZrO2-epoxy hybrid composite enhanced corrosion properties of epoxy coatings on metal substrates. Enhancement in corrosion can be attributed to sheet like structure, dispersion homogeneity, and absence of exposed tiny pores and exfoliation of GO-ZrO2 hybrid within epoxy matrix. The as-prepared composite coatings can open up new scope in the field of corrosion protection. Pourhashem et al.72 used solvent-based epoxy coatings filled with GO sheets for the corrosion protection on steel. Their study confirms the distribution of GO plays a crucial role in determining the coating performance. Dispersion of GO depends on the viscosity and GO weight percent in the polymer matrix. Among various GO concentrations, the one with 0.1 wt% GO has lower viscosity, good dispersion, and adhesion with superior corrosion protection in NaCl electrolyte.

**CNT incorporated Zn-rich epoxy nanocomposites.** It is essential to recreate the oilfield gaseous environment during experiment for more realistic corrosion analysis of coating materials. For example, to pump high pressure oil-brine mixtures through pipelines, CO2 is used as carrier fluid.73 In the process, CO2 dissolves in water to form carbonic acid and causes internal corrosion of steel pipelines.74 Low carbon steels are more susceptible to corrosion due to the corrosive gases such as CO2. Hence, cost effective corrosion resistant coatings can play an important role to mitigate the issue. Cathodic protection on low carbon steel using Zn-rich epoxy coatings has been carried out in 1940.75 Corrosion under static sea water conditions is a method for lab scale evaluation. Valencia et al.76 investigated corrosion resistant behaviour of Zn-rich epoxy nano-coating primer (ZREP) and CNT incorporated ZREP coating on steel substrate under dynamic conditions. Equipment for corrosion studies consists of a rotating cylinder electrode (RCE) and an electrolyte of CO2 saturated 3 wt% NaCl. Anti-corrosion properties of nanocomposite can be attributed to the combined effect from Zn and C elements. Authors have adopted damage evolution concept to analyse the experimental findings and to propose the mechanisms.

CNTs are known to be one of the best reinforcement materials for many metal-polymer matrices.77 A two-layer coating structure was developed by TabkhPaz et al.78 on steel substrate and the corrosion properties were investigated. In the first layer, immediately on the top of steel substrate MWCNTs, GNP and Zn particles were added. Graphene NPs decrease CTE mismatch, gas permeation and increases anticorrosive nature. Zn particles act as sacrificial material and to enhance the galvanic protection and mechanical properties of first layer MWCNT was added. In the second layer, hexagonal boron nitride was added to the polymer to enhance the gas barrier effect and mechanical properties. In this way, composites layers filled with nano-particulates gave an overall protection to the metal surface.

**Graphene reinforced Zn-rich nanocomposite coatings.** Zn-rich coatings for metal substrates have been used in marine and industrial environment since 1930 as a protection from aggressive corrosive environments.79 In a polymer matrix, when polymer acts as a barrier against aggressive ions, Zn gives cathodic protection to steel. To ensure the electrical conductivity required for galvanic protection, conductive fillers are required as (i) polymers are not good conductors and (ii) high Zn loading affects the coating flexibility, adhesion and paint viscosity. Many fillers have been explored such as CNT,80 aluminium pigments,81 Zn NPs,82 and GOs.83 However, ultimate goal to achieve long term protection remains to be a challenge and needs further experimentation. The incorporation of graphene into Zn-rich epoxy matrix has been rarely studied. Hayatdavoudi et al.84 have optimised the graphene concentration for the optimal protection of steel substrates. Graphene was found...
to enhance the percolation structure of coating in addition to uniformly activating sacrificial Zn particles. Potential-time measurement (Figure 8(a)) shows that for an immersion time of 25 days, HG-ZRE offers a higher barrier to corrosion compared to that of pristine and low graphene ones. A low amount of graphene results in more corrosion and this implies the importance of graphene loading. Zn and carbon steel have a corrosion potential of \(E_{\text{corr}} = 1.05\) V and \(E_{\text{corr}} = 0.65\) V, respectively. Zinc particles in ZRE coatings are electrically connected to steel substrate and hence the interface becomes polarised to a mixed potential of that of immersed Zn and steel. Interface potential or degree of cathodic polarisation is a function of surface area of Zn particles and steel substrate. For Zn to be considered as a sacrificial material, it has to be electrically connected to steel in the electrolyte solution. A high graphene content sample has a low percolation resistance while a low graphene sample has nearly similar percolation path as that of pristine Zn-rich epoxy (Figure 8(b)). A schematic of the percolation structures in various samples is shown in Figure 8(c) to (e). Addition of 0.4 wt% graphene found to give optimum protection for Zn-rich coating while low graphene content showed a reverse effect. The effect of graphene content on the properties of coating material is due to the low percolating resistance and electrochemical activity of Zn particles. From their studies it can be inferred that addition of optimum amount of graphene sheets is one of the promising strategies to enhance the corrosion resistance of Zn-rich epoxy coatings. Proper amount of graphene sheets give rise to enhanced barrier protection against aggressive species and hence less corrosive environment to Zn.

**Zn-rich epoxy primer via single layer graphene.** Anticorrosion properties of zinc-rich primers (ZRP) occur through two different protection mechanisms: (i) cathodic protection by sacrificial anodic dissolution, and (ii) barrier protection via stable layer of zinc oxide products, which fills the pores in coating and prevents the electrolyte penetration in steel. To ensure cathodic protection effectively, Liu et al. investigated the effect of a single layer graphene on the corrosion barrier properties of Zn-rich epoxy primer. From various structural studies, researchers have confirmed that...
addition of graphene facilitated settling of ZnO at the interface of steel and coating. It was observed that both cathodic and barrier protection are enhanced at an optimum graphene concentration of 0.6 wt%. Zinc corrosion products were mainly consists of ZnO and Zn\textsubscript{5}(CO\textsubscript{3})\textsubscript{2}(OH)\textsubscript{6} on the steel surface, whose quantity increased over time which was evident from impedance spectra (semicircles with larger diameters) and could be attributed to the barrier protection effect. Graphene was found to promote cathodic protection of Zn-rich epoxy, in the presence of artificial scratch on surface coatings.

Graphene-Ceria nano-fillers in PU. PU is superior to many other polymers in adhesive strength, corrosion resistance, abrasion resistance and UV protection. It consists of a soft segment (polyol) which contributes to elastomeric properties, and a hard segment (diisocynate) which controls mechanical properties. The intrinsic properties of PU in combination with various fillers improved its performance. Among various metal oxide fillers, CeO\textsubscript{2} is known for its corrosion resistance at harsh conditions. Rahman et al. have reported graphene and CeO\textsubscript{2} NPs are efficient filler materials in a PU matrix used for composite coating. Corrosion studies were carried out by exposing the coating at natural ambient of kingdom of Saudi Arabia for 30 days. Corrosion resistance of composite coating on a steel substrate were found to be better than that of pure polymer coating or polymer with graphene alone or with CeO\textsubscript{2} alone. Optimised CeO\textsubscript{2} and graphene concentration gave rise to enhanced performance and coated mild steel was used for short term field test. This multifunctional hybrid coating appears to be a new strategy to solve the corrosion issues on mild steel in industrial applications.

Polystyrene-graphene-based composites. Many graphene-based polymers were explored for corrosion protection however vinyl/polymer-based ones are rarely found in literature. Yu et al. reported the first successful application of polystyrene/GO composites via in-situ miniemulsion polymerisation. Corrosion resistant efficiency (Figure 9(a)) of polystyrene (PS) increased from 37.9 % to 99.53% by nano-compositing with 2 wt% of functionalised GO in PS matrix. In the figure ‘pv-GO’ represents functionalised GO. Thermal decomposition temperature of pure PS enhanced by 24.8 % and storage modulus was found to increase from 1800 to 2800 MPa. EIS of pristine and GO incorporated samples are shown in Figure 9(b) with the equivalent circuit at the inset. An increase in charge transfer resistance with pv-GO content reveals the improvement in anti-corrosion properties. Figure 9(c) shows the proposed mechanism on how the metal surfaces were protected by nanocomposites. A polymer coating acts either as a barrier or active material that takes part in the reaction for protecting the metal surface. Functionalised graphene sheets with flexible property helped to increase the gas barrier properties. They have also observed that graphene sheets enhanced the diffusion pathways for the O\textsubscript{2} and H\textsubscript{2}O by preventing them from reaching the metal surface.

In addition to the above nanocomposites, various combinations of nanomaterials, polymers, and metal matrices were fabricated with the aim of enhancing corrosion protection. Following works give a quick glance on a few recent works on nanocomposite coatings. Electrodeposition of polyaniline/zeolite nanocomposite coating on 304 stainless steel surface was investigated by Shabani et al. Corrosion properties were studied in 0.5 M HCl solution and parameters such as deposition time and current densities were optimised for a uniform coating. Corrosion rate of coated 304 SS was observed to be 36 times lower than that of uncoated 304 SS. Corrosion potential changed to more positive value (from $-0.411$ to $-0.279$) for
coated samples. Polyaniline/zeolite coating offered protection efficiencies of \(\sim 97\%\) at a current density of \(2.5\,\text{mA/cm}^2\) for SS in acid medium. Research outcome of the present paper shows that polyaniline/zeolite has significant potential in preventing corrosion of 304 SS in an acid environment.

Nano metal oxide mixtures of Fe, Ce and Ti were used by Ashraf et al.\(^9^5\) to understand the coating performance on BIS 2062-grade steel which is mainly used for boat construction. They have observed that optimum concentration of nano-mixtures \((0.005\%\,\text{Fe}_2\text{O}_3 + 0.01\%\,\text{CeO}_2 + 0.005\%\,\text{TiO}_2)\) are very effective in corrosion protection with a passivation resistance of \(\sim 6043\,\Omega\text{cm}^2\) and low corrosion current density of \(3.53\times10^{-6}\,\text{Acm}^{-2}\). The nanomaterials in coating show semiconducting behaviour and hence enhanced the electronic conductivity over the metal surface.

Corrosion studies on waste ferrochrome (FeCr) slag/polyaniline hybrid coating on carbon steel have been investigated by Khan et al.\(^9^6\) NPs of FeCr slag obtained after milling for 4 h was used to make nanocomposite with polyaniline via in-situ polymerisation process. Anticorrosion performance of nanocomposite of FeCr-slag with polyaniline was evaluated by incorporating them with commercial Zn-rich epoxy phosphate primer system. Their results reveal a significant improvement in anticorrosion properties due to FeCr/PANI.

A new composite coating made up of alkyd@lanthanide bis-phthalocyanine was studied for its corrosion protection properties for carbon steel pipelines\(^9^7\) and observed significant corrosion resistance in of steel in 0.5 M HCl solution. Performance of alkyd-based resin was greatly enhanced by lanthanide compound incorporation by reducing water permeability, improving physico-mechanical properties and adhesion strength.

The above examples show that there is no limit to the possibility for exploring the materials in finding their performance to any specific applications.

Some of the coating materials described above along with their property enhancement and dispersion method adopted, etc. are summarised in Table 1.

Table 2 shows that for many coating materials either corrosion properties or mechanical properties were only investigated. It is very essential to understand both characteristics when they are using as a coating material for steel in marine environment.

### Current challenges

(i) **Uniform dispersion**: In many cases, filler or dispersing material used for reinforcing metal or polymer matrix failed to give expected reinforcement due to agglomeration of fillers. Uniform dispersion of fillers guarantees enhanced coating properties and methods for the same need to be explored further especially when the concentration of fillers is high.

(ii) **Novel coating material**: Coating material with high mechanical strength and corrosion resistance is yet to be explored. A material which has a high corrosion resistance may have low mechanical strength and vice versa. Development of hybrid nanocomposite coatings with promising properties is very much required to solve the existing corrosion issue without losing the surface mechanical properties of the coating.

(iii) **In-situ corrosion**: There are only a few reports on the in-situ corrosion studies\(^1^0^4,1^0^5\) and more information about the corrosion process can be obtained via in-situ studies. Hence, electrochemical corrosion studies have to be combined with existing surface analysis techniques\(^1^0^6\) for deeper understanding of corrosion and localised chemical behaviour.

(iv) **Advanced tools**: Correlations between microstructure of coating materials and their properties can be completely known only through advanced characterisation techniques such as high temperature nano-indentation, atom probe tomography, and synchrotron X-ray nanodiffraction, etc.\(^1^0^7\)

(iv) **Field test**: Many corrosion inhibitors and corrosion resistant alloys with enhanced performance have been explored in the recent years. However, various approaches need to be commercially demonstrated to be viable. Furthermore, new techniques have to

---

**Table 1**

<table>
<thead>
<tr>
<th>Coating Material</th>
<th>Property Enhancement</th>
<th>Dispersion Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyd@lanthanide bis-phthalocyanine</td>
<td>Improved corrosion resistance</td>
<td>In-situ polymerisation process</td>
</tr>
<tr>
<td>Polyaniline/zeolite</td>
<td>Significant potential in preventing corrosion</td>
<td>Nanocomposite with commercial Zn-rich epoxy phosphate primer system</td>
</tr>
<tr>
<td>FeCr-slag/polyaniline</td>
<td>Significant improvement in anticorrosion properties</td>
<td>Incorporating with commercial Zn-rich epoxy phosphate primer system</td>
</tr>
</tbody>
</table>

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**Figure 10.** (a) Shows the tortuosity factor \((d'/d)\), and (b) two layer coating approach (adapted from TabkhPaz et al.\(^7^8\)).
Table 1. Comparison of various nanocomposite coatings used for enhancing corrosion resistance.

<table>
<thead>
<tr>
<th>Coating material composition</th>
<th>Coating material synthesis</th>
<th>Properties improved</th>
<th>Comments</th>
<th>Refs.</th>
</tr>
</thead>
</table>
| TiO$_2$ NPs + polyamide adduct cured epoxy | Dispersion | Corrosion resistance improved (OCP $\sim -442$ mV), polarisation resistance 1000 times higher than naval steel, No localised corrosion | • Corrosion studies in Constanta harbour sea water  
• Low cost coating materials. | 30 |
| Silane (SiO$_2$) + polybenzoxazine | Thermal curing method | Surface energy of coating $\sim 15.5$ mJ/m$^2$ lower than that of Teflon ($\sim 20$ mJ/m$^2$), coated mild steel corrosion resistance increased 4 times compared to pristine counterpart. | • Corrosion studies in 3.5 wt% NaCl solution | 98 |
| ZnO + polysiloxane | Ultrasonic dispersion + magnetic stirring | Impedance of nanocomposite $\sim 10^9$ S$^2$cm$^{-2}$. Polysiloxane composite coating preferred as topcoats due to their inherent low surface energy, hydrophobic property. | • Corrosion studies in 3.5 wt% NaCl solution  
• Optimised ZnO: poly-siloxane ratio as 1:1  
• Spin coating on steel | 99 |
| Amino-functionalised silica + epoxy | Sol-gel process | Improved hardness, elastic modulus  
May increase corrosion resistance (experimentally not studied) | Homogeneous coating material with interfacial reaction between organic-inorganic and inorganic-inorganic components | 100 |
| Clay + ZrO$_2$ + epoxy | Slurry method | For optimised clay:ZrO$_2$ (2:1) in epoxy, corrosion resistance is $\sim 5 $Ωcm$^2$. | • Corrosion studies in 3.5 wt% NaCl solution  
• Studied barrier properties and ohmic resistance for various clay to ZrO$_2$ content | 63 |
| GO + ZrO$_2$ + epoxy | Chemical route + ultra-sonication + curing | Enhanced corrosion properties due to sheet like structure, dispersion homogeneity, absence of tiny pores, and exfoliation of GO-ZrO$_2$ hybrid in epoxy matrix. | • Corrosion studies in 3.5 wt% NaCl solution | 71 |
| CNT + Zn-rich epoxy | -Chemical route -Spray coating on steel | Combined effect from Zn and C elements accounts for corrosion protection. | • Corrosion under dynamic conditions in a rotating cylinder electrode  
• 3 wt% NaCl solution as electrolyte  
• Graphene loading optimised (0.4 wt%) for controlled corrosion  
• 3 wt% NaCl solution as electrolyte  
• Graphene loading optimised as $\sim 0.6$ wt% | 101 84 88 |
| Graphene + Zn-rich epoxy | Dispersion in acetone + magnetic stirring -Air spray coating on steel | -Graphene increased percolation structure of coating and hence corrosion resistance  
-Uniformly activated sacrificial Zn particles | • Corrosion studies in 3.5 wt% NaCl solution as electrolyte | 84 |
| Single layer graphene + Zn-rich epoxy | -Magnetic stirring + ultra-sonication -Air spray coating on steel | -Corrosion resistance of Zn-rich epoxy improved due to barrier protection and cathodic protection effects  
-Addition of graphene facilitated ZnO settling at the interface between steel and coating surface | • Graphene loading optimised as $\sim 0.6$ wt% | 88 |

(continued)
be developed in the initial stages for the internal coatings with corrosion inhibitors without completely replacing the whole pipelines.

(v) Environmental issues: It is required to make sure that the coating material would not contribute to any environmentally hazardous by products as the result of sacrificial corrosion.

Discussion

Selection of appropriate coating material to protect metallic objects from corrosion is challenging especially when numerous coating materials are being explored and reaching to the market. Maximum operational temperature without deteriorating material properties is also an important parameter in addition to room temperature material properties when used for high temperature applications. Table 2 shows an overview of upper limit of temperature for coating technologies from recent literatures. It is clear that for a temperature of for example \(200^\circ C\) there can be several options. In this case other factors such as adhesion to the surface, porosity of coating cost, toxicity, crack free coating, etc. may be primary parameters for selection. In a coated film, presence of non-reactive component

Table 1. Continued

<table>
<thead>
<tr>
<th>Coating material composition</th>
<th>Coating material synthesis</th>
<th>Properties improved</th>
<th>Comments</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene + CeO(_2) + polyurethane</td>
<td>-Dispersion via ultra-sonication and drying method</td>
<td>-Corrosion properties optimum for this hybrid at graphene: CeO(_2) ratio of 2 wt%</td>
<td>• Corrosion studies under natural climatic conditions of Kingdom of Saudi Arabia for 30 days exposure</td>
<td>102</td>
</tr>
<tr>
<td>Graphene + polystyrene</td>
<td>-Magnetic stirring + ultra-sonication -coating of suspension on steel using an automatic coating machine</td>
<td>-Corrosion resistance efficiency increased from 37.9 % to 99.53 % by nano-compositing with 2 wt% graphene oxide -Graphene prevents O(_2) and H(_2)O reaching metal surface by modifying diffusion pathways.</td>
<td>• 3.5 wt% NaCl solution used for corrosion studies</td>
<td>93</td>
</tr>
<tr>
<td>Ni-Zn-TiO(_2)</td>
<td>Electrodeposition under ultrasonic vibration</td>
<td>-Hardness 2.5 times improves for the composites -Corrosion resistance improved</td>
<td>• 3.5 wt% NaCl solution</td>
<td>103</td>
</tr>
</tbody>
</table>

Table 2 Upper limit of the temperature range of some polymer materials used as anticorrosion coatings.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature range (°C)</th>
<th>Comments</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy Novolac</td>
<td>240–280°C (without crack and delamination)</td>
<td>Higher temperature resistance of Novolac due to cross link density and lower content of non-reactive components.</td>
<td>NACE SP0198-2012</td>
</tr>
<tr>
<td>Epoxy Mastic</td>
<td>150–200°C (depends on coating material thickness)</td>
<td></td>
<td>108</td>
</tr>
<tr>
<td>High build silicone</td>
<td>205–600°C</td>
<td>Thin film silicone has poor corrosion resistance.</td>
<td>109</td>
</tr>
<tr>
<td>Epoxide pre-polymers + silicone</td>
<td>400°C</td>
<td>Methyl group in silicone found to promote better adhesion of paint to metal surface</td>
<td>110</td>
</tr>
<tr>
<td>Epoxy phenolic</td>
<td>150°C</td>
<td>-Good adhesion properties -Slow curing time in air and hence heat curing at high temperature required</td>
<td>NACE-SP0198-2010</td>
</tr>
</tbody>
</table>
causes its evaporation leading to shrinkage, internal stress and finally cracking.

From our survey on nanocomposite coatings, when a nanocomposite is selected to coat a stainless steel or other metallic substrate the following points need to be considered. (i) There should not be significant mismatch between CTE of the coating material and substrate. If mismatch exists, then coating material delaminates from the substrate at elevated temperatures which causes the exposure of metallic substrate directly to the environment,111 (ii) coating material should have sufficient gas and moisture permeation resistance. In this way coating can act as a barrier against destructive elements and prevent the formation of corrosion environment. The permeability resistance of polymers on steel can be increased by incorporating a second phase which is miscible with polymer reduces the porosity and produces a zig-zag diffusion path for aggressive ions,112 (iii) upper temperature limit that the material is able to withstand without material degradation is important when the steel is used at high temperature environment, (iv) nanomaterials such as MWCNT, graphene, etc. with high mechanical, thermal, corrosion resistance and gas barrier properties can improve the coating performance, (v) aspect ratio and the optimum concentration of reinforcement materials can influence the overall performance. For example as mentioned before graphene NPs with 0.1–0.5 wt% concentration in clay composites gives better performance than pristine clay composites. It is essential to provide a longer path for the penetrant to reach the coating-metal interface so that the corrosion process can be delayed for a longer time. Hence, tortuosity factor is an important parameter which is defined as the ratio of longer path produced by fillers (d) to the shortest distance (d) (Figure 14(a)). The distance ‘d’ is a function of length, thickness and volume fraction of the nano-fillers used.

(vi) Zn particles can be one of the constituent in the coating composite as it can provide galvanic protection to steel in harsh ambient. Therefore many Zn-rich coating solutions are found to give enhanced corrosion resistance. Normally high weight % of Zn (>70 wt%) is required to generate conductive network of Zn particles as shown in Figure 14(b). However, high Zn loading results in poor mechanical properties of coating. Hence, Zn content has to be optimised without much sacrificing for the mechanical properties. Zn as anticorrosion filler along with MWCNTs found to reduce the Zn wt% down to ~10 wt% without much compromise on strength,113 (vii) a combination of NPs for example CNTs, hBN, graphene, Zn, etc. in their optimum weight % can give rise to enhanced performance to the final nanocomposite coating. Also hybrid composites are preferred to single filler for reducing the filler content, (viii) Two layer coating is a new approach79 wherein the first layer is electrically conductive and the second layer is electrically insulative (Figure 14(b)). The electrical insulation is for isolating the steel in direct contact with corrosive atmosphere. It was observed that a layer with $10^8 \, \Omega \cdot \text{cm}^2$ give high protection than that of $10^6 \, \Omega \cdot \text{cm}^2$ resistance.114

Mechanical property enhancement in addition to improving corrosion is the need of the hour for tools used in high pressure environment. In this context metal nanocomposites are gaining more attention and an evolving area of research. For example, CNT-metal nanocomposites, found to increase the mechanical properties of the metals/metal alloys as well as preventing corrosion as CNTs fill the nanopores present in the metal matrices and hence preventing the approach of aggressive ions.115,116 However, for getting maximum performance CNT concentration, CNT dispersion and their aspect ratio, etc. need to be optimised.

After selecting a suitable coating material, the next question is what kind of coating methodology gives the superior performance as substrate-coating property is determined by the deposition process. There are various processes such as chemical vapour deposition (CVD), physical vapour deposition (PVD), thermal spraying, electroless process, brush coating, dip coating, electrophoretic deposition, and electrochemical deposition (ED). Table 3 compares different deposition processes along with their salient features. A few specific examples were selected based on nanocomposite coating on metal substrate via various deposition processes.

The aforementioned processes were developed and implemented with the aim of achieving high adhesion, enhanced uniformity, better reproducibility, high deposition rate, low roughness and low cost. Coating thickness in each processes need to be optimised as it determines the long term performance. For example, to ensure pore free coating of Cu-Ni-Cr in magnesium substrate in open air a minimum coating thickness of ~50 µm is suggested.1

As depicted in Table 3, there are various deposition processes for nano-composite coatings and among them ED gained more attention for the past two decades. ED is a simple and cost-effective technique for surface coating. Electro-deposition technique serves the present need of innovation as it is very suitable for depositing nanocomposites. There are many parameters which affect the deposition of NPs into metal matrix such as particle concentration in solution, particle size in the suspension, current density, stirring speed, solution temperature, composition of the electrolyte bath, electrical nature of the particles.128 Optimisation of various parameters can give rise to a coating with good adhesive properties. However ED is not yet accepted as an industrially viable method.
<table>
<thead>
<tr>
<th>Deposition process</th>
<th>Process description</th>
<th>Coating material</th>
<th>Protected metal</th>
<th>Salient features</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PVD</strong></td>
<td>- Material goes from a condensed phase to a vapor phase and then back to a thin film condensed phase under vacuum. Examples: sputtering, pulsed laser deposition</td>
<td>Cu/Diamond like carbon (DLC)</td>
<td>Mild steel</td>
<td>- Film thickness ~900 nm (controlled by sputtering time) gave super-anticorrosion performance</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td></td>
<td>nc-TiC/a-C</td>
<td>440 C Stainless steel</td>
<td>- Magnetron sputtering from graphite and Ti target at ~150°C, Extremely low coefficient of friction of 0.046 was obtained with oil lubrication, Maximum hardness ~31 GPa</td>
<td>118</td>
</tr>
<tr>
<td><strong>CVD</strong></td>
<td>- Depositing solid material from a gaseous phase under vacuum. - Possible to coat almost any metallic or ceramic compound, including metals, alloys and intermetallics. - Excellent throwing power, uniform coating thickness, low porosity even on substrates of complicated shape. - Capability of selective deposition, on patterned substrates</td>
<td>Polymer-graphene hybrid</td>
<td>Al-alloy</td>
<td>- Long term protection ~4 months based on CVD graphene, Application of CVD graphene in the field of corrosion protection</td>
<td>119,120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silicon powders</td>
<td>AISI 316L stainless steel</td>
<td>- Silicon CVD effective in extending the corrosion resistance of steel in marine conditions, can reduce the overall maintenance costs by extending equipment life time.</td>
<td>121</td>
</tr>
<tr>
<td><strong>Thermal spraying</strong></td>
<td>Plasma spraying is an important thermal spraying technique on boiler tube steels - Homogeneous deposition of metals, ceramics and a combination of metals and ceramics on a wide range of substrate materials - Subject to phase transformation of the components in the composite.</td>
<td>CNT reinforced Al₂O₃</td>
<td>ASME-SA213-T11 boiler tube steel</td>
<td>- Better oxidation resistance and thermal stability than uncoated ones, Nanotubes fill the pores of the coating and hence preventing oxygen in reaching the substrate</td>
<td>122</td>
</tr>
<tr>
<td><strong>Cold spraying</strong></td>
<td>- Coating method wherein solid powders are accelerated to supersonic speed ~500 m/s - Retains the original properties of the feedstock to produce oxide-free deposits - Do not adversely influence underlying substrate materials during manufacture</td>
<td>SiC/AZ91D</td>
<td>Magnesium substrate</td>
<td>- No phase transformation/oxidation occurred, SiC particles reduces the porosity and increases the microhardness of cold-sprayed AZ91D coatings</td>
<td>123</td>
</tr>
<tr>
<td><strong>Electroless process</strong></td>
<td>- Known as chemical or autocatalytic coating without the use of electric current - Process involves several chemical reactions</td>
<td>Ni-P-Ti</td>
<td>API X100 steel</td>
<td>- Microhardness improved, Incorporation of Ti particles increased toughness, Annealing (~350°C) of as deposited film was found improving wear resistance</td>
<td>124</td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>Deposition process</th>
<th>Process description</th>
<th>Coating material</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Dip coating</td>
<td>-Dip the substrate to be coated on the composite solution for the required time and dry it in an oven -Can be repeated for several cycles for the required coating thickness -Cost effective</td>
<td>Copper stearate@Fe₃O₄</td>
<td>Stainless steel mesh</td>
<td>Superhydrophobic surface (contact angle 155°) used for oil/water separation -Excellent chemical stability in 1 M HCl, 1 M NaCl, 1 M NaOH</td>
<td>125</td>
</tr>
<tr>
<td>Electrochemical deposition</td>
<td>-Uses electric current to reduce dissolved metal cations to form a thin metal coating on an electrode -Can incorporate NPs into metals matrix -Many parameters affect quality of coating e.g., solution pH, current density, etc.</td>
<td>Ni(OH)₂ reinforced polyaniline</td>
<td>304 stainless steel</td>
<td>-Improves hydrophobicity and decreases diffusion of aggressive species -Prolonged corrosion protection (~15 days in 3.5 wt% NaCl solution without any degradation</td>
<td>126</td>
</tr>
<tr>
<td>Brush plating</td>
<td>-Portable process used to apply localised electroplated deposits -Quick plating, can correct dimensional errors, useful for large machine part coating without disassembling, controlled thickness, wide application, etc. are some of the pros.</td>
<td>Fe/MWCNT</td>
<td>AISI 1045 steel</td>
<td>-Addition of WMCNT increased the coating hardness -Friction coefficient and weight loss of composite coating is superior compared to pure Fe coating.</td>
<td>127</td>
</tr>
</tbody>
</table>
Cold-spray deposition is most suitable one for large scale industrial coating applications. Cold spray (CS) is low temperature process and induces limited thermal effect on spray materials unlike thermal spraying or other high temperature processes.\(^\text{129}\) Conventional thermal spraying method causes grain growth, oxidation, and decomposition of the metal and reinforcement particles.\(^\text{130}\) Cold spray can avoid all the deficiencies of thermal spray and results in better material performance of the coating. High temperature methods are not advisable for nanomaterials, due to their high surface area and reactivity, CS is hence well suited not only for composites or metal alloys but also for nanocomposite coating.

**Conclusions**

Steel degradation in extreme corrosive environments is a serious issue in many industries. To tackle this issue, fundamental understanding on the corrosion process at the interface between corrosive electrolyte and steel surface is essential. Also corrosion process will be different depending on the nature and the properties of steel surfaces viz. 304 SS, 316 SS, and carbon steels. Functional coating made of nanocomposite materials is one of the best methods to prevent corrosion. Our literature review shows that anticorrosive coating materials are capable of retaining the integrity of metallic surfaces. However, the extent to which protection can be favoured in extreme oilfield environment is a big challenge. Techniques such as in-situ corrosion monitoring need to be carried out for understanding the corrosion mechanism in detail. Most importantly, research on novel nanocomposite materials requires more attention. Composite coating material with low CTE and high gas permeation resistance can resist delamination and corrosion. Optimum concentration of filler material with good dispersion on the metal matrix can lengthen the penetration path of the aggressive ions (high tortuosity factor) and prolongs the life time of steel. Various coating techniques to enhance the corrosion resistance were discussed and compared. We also propose hybrid composite with more than single filler as coating material because combination of NPs can give rise to enhanced performance.

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