A REVIEW ON COATING OF ZINC NANOPARTICLES ON LOW CARBON STEELS TO IMPROVE THE TRIBOCORROSION PROPERTIES

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Abstract : ***Recent technological advancements in surfacing engineering for the development of materials by incorporating coatings comprising nanomaterials to enhance mechanical, environmental and tribological properties of low carbon steel is inevitable. In present paper, an attempt is made to study the feasibility of coating Zinc nanoparticles on low carbon steels using various methods and techniques. Zinc nanoparticles is coated on low carbon steels to improve mechanical, environmental and morphological properties. The studies are investigated on the basis of penetration & adhesion of the nanomaterial over low carbon steel and coating techniques & characterization method has also been investigated. By looking into various coating and synthesis methods Laser ablation method, spin coating, electrodeposition and sol - gel processes were studied.***

Keywords - Zinc nano particles, coating, Low carbon steels, sol-gel process, Laser ablation method, electrodeposition.

I. INTRODUCTION

Nano processing technology is gaining momentum in recent years by providing innovative solutions in the field of biomedical, materials science, optics, electronics etc. The market research indicates nanomaterial coatings (Anti-Fingerprint, Anti-Microbial, Anti-Fouling & Easy-To-Clean, Self-Cleaning and Others) Market for Medical & Healthcare, Water Treatment, Electronics, Building & Construction, Automotive, Energy and other Applications. According to the report (Fig:1), global demand for nanomaterial coatings market was valued at USD 1.50 billion in 2014 and is expected to reach USD 6.85 billion in 2020, growing at a CAGR of 24.9% between 2015 and 2020. In terms of volume, the global nanomaterial coatings market stood at 266.0 Kilo tonnes in 2014.

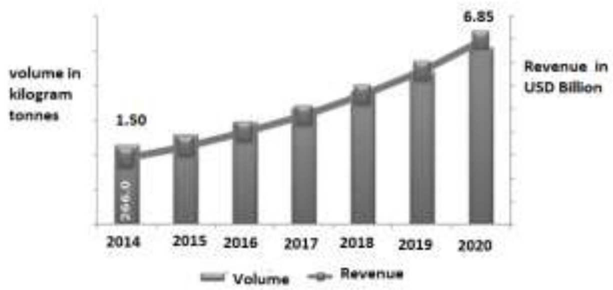


Figure 1. Increases in Nanomaterials coating Demand
Source: "www.marketresearch.com"

Modern application of engineering materials and the evaluation of nano-coating in the field of mechanical engineering unrelished the functional properties in terms of improved corrosion resistance and wear resistance with minimum material usage, minimum distortion and reduced cost compared to the conventional coating processes. This survey aims to find the best possible methods for coating of Zinc nanoparticles over the low carbon steel substrate. An attempt was made to study the improvements that can be provided by coating of nano materials to the commercially available material such as low carbon steel with the improved corrosion properties. Nanomaterial coating techniques such as Chemical Vapor Deposition(CVD) , Physical Vapor Deposition (PVD) , Spin coating, dip coating, electrodeposition, DC sputtering, epitaxial deposition could be used to coat steel substrate [1]. Sa-nguanmoo et al reported steel undergoes corrosion when exposed to different environments. Zinc coatings is extensively used for the protection of steel. The more active zinc metal corrodes preferentially than the steel substrate by a cathode reaction that prevents steel from undergoing anodic corrosion reaction. The life of the coating is likely to be improved by Zinc nanomaterials coating [2]. Almeida E et al concluded without sacrificing the natural, physical and mechanical properties of the material, the corrosion resistance is improved [3]. The survey is conducted in the following criteria to optimise the methods available for nanomaterials synthesis, coating & characterization are

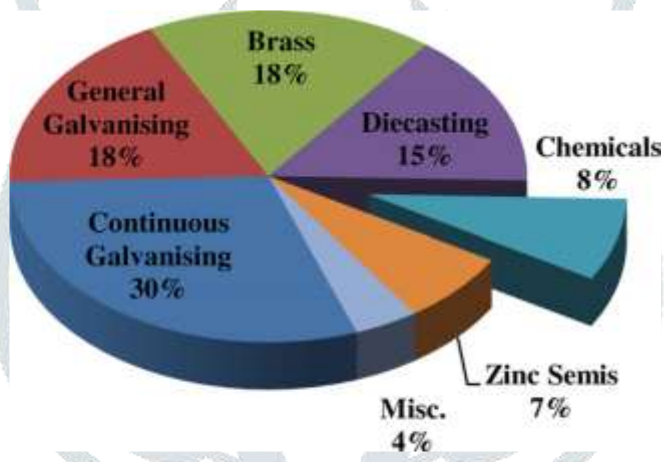
(1) Coating materials
(2) Synthesiszing methods for nanomaterials

(3) Coating methodology for nanomaterials
(4) Characterization techniques for evaluation (Mechanical, Environmental and Morphological properties)

II. SURVEY ON MATERIALS FOR COATING

The study on coating materials is done to identify the materials available across the globe and its behaviour after coating on a metal substrate. In addition, an attempt is made to identify coating material suitable for industrial applications and commercial applications as well. It is likely to create a new market for the coating materials in the upcoming decades. Frankel, G.S et al is reported the corrosion resistance of Aluminium alloys and steel alloys coatings arises from its ability to form a natural oxide film on its surface that greatly reduces the corrosion rate. The electrodeposition of this metal from aqueous solution is impossible due to the hydrogen discharge and high vacuum techniques such as chemical vapour deposition (CVD) and physical vapour deposition (PVD) are slow and very expensive. Electrodeposition from molten salts is widely used for Aluminium production but the high temperature required, higher than the Aluminium melting point, makes this process useless for plating [4]. Petrova, L.G *et al researched Zinc* metal has a number of characteristics that make it a well-suited corrosion protective *coating* for iron and *steel* products. It also used for improve the hardness and wear resistances. Zinc coating is the possibility for the formation of dense strengthened layers which smoothness the sharp hardness decrease through depth and thus, avoids the embrittlement of a zinc filled coating [5]. Estrada-Martinez J et al, according to their research Titanium-based materials, such as Titanium dioxide (TiO_2), Titanium oxide (TiO_x) and Titanium nitride (TiN), are good candidates as coatings because of their anti-corrosive and the inhibitory properties against steel in an environment [6]. Gerdemann. S.J et al reported the Titanium extraction technique is not easy because it forms Titanium carbide by using carbon while reducing from ore which makes the metal very brittle [7]. Tiwari, S.K et al described the Zirconium is preferred choice for pre-treatment over traditional iron phosphates. It used to ensure the long lasting protection and self-healing properties. It also enhances the mechanical strength, thermal stability, and wear and corrosion resistances. ZrO2 shows good chemical stability and high hardness [8]. Xinke Deng et al reported that the coatings of Molybdenum significantly improves the wear resistant property of the metal substrate. From this research, it is evident that it can be used as a nanomaterial coating to withstand high wear resistant [9]

Figure 2 – Pie chart shows the significant amount of Zinc based materials has been used in coating of semiconductors [11]



The following tabular column indicates that various coating nanomaterial used for variety of applications in diverse fields are shown

Table 1 – Different nanomaterial for coating and its applications

References	Base material for coating	Coating material	Application
L. Cordero-Arias et al [10]	Stainless Steel	TiO_2	Biomedical applications such as implants, surgical knives etc…
Amir Moezzi et al[11]	Semiconductors such as silicone, germanium, antimony etc.,	ZnO	Grabbing interest in the area of optoelectronic devices and electronic devices and textiles as well. Zinc has also been used to withstand corrosion.

Tiwari, S.K et al[8]	Mild steel	ZrO_2	Automotive, household appliances, business machines and heavy construct.
M. Surender et al[12]	Mild steel	Ni–WC composite coatings	Gear drives, brake discs, cylinder liner, pistons, clutch plates etc.,
Xinke Deng et al [9]	Steel	Mo	Gear drives, bearings, valves etc.,

Amongst all, Zinc coatings are often used to provide sacrificial cathodic protection for steel against corrosion even they are scratched or damaged. The lower cost and larger reserves of zinc, compared to other metals, as well as nontoxic and recyclable properties make it to be the most widely employed surface Protective coating.

III. SURVEY ON SYNTHESIS METHODS OF NANOMATERIALS

The precipitation method involves a reaction between a zinc precursor and a precipitating reagent. The solution of precipitating agent (e.g., sodium hydroxide, ammonium hydroxide, urea, etc.) is added in drop wise to the aqueous solution of a zinc precursor (e.g., zinc nitrate, zinc sulfate, etc.). On Mixing of these solutions, the results formed as intermediate product, which ultimately converts to ZnO after calcination at high temperature. Sabir S et al reported that the ZnO nano particles have tremendous physical, antimicrobial, antifungal and optical properties [13]. Kumar S S et al synthesized ZnO nanoparticles using the precipitation method by the reaction of zinc sulfate and sodium hydroxide in a molar ratio of 1:2. The nanoparticles obtained were very pure, as revealed by the method of X-ray diffraction analysis; in addition, the crystallinity of the nanoparticles increased as the calcination temperature increased [14]. Srivastava V et al studied the synthesis of n-ZnO particles, solution of zinc chloride was prepared by dissolving zinc chloride in distilled water. After preparation of ZnCl2 solution, ammonium hydroxide was drop wise added to it from burette. There action mixture was continuously stirred in a magnetic stirrer at room temperature till complete precipitation. The precipitate was washed with distilled water and then dried in a hot air oven for complete drying and concluded that dried precipitate was crushed, milled and then sieved to get uniform sized particles [15]. The sol was prepared using zinc acetate dihydrate, ethylene glycol, n-propyl alcohol, and glycerol. Ethylene glycol was added to zinc acetate dehydrate and kept at for some time over a hot plate to obtain a uniform transparent solution. On cooling to room temperature the content of the flask solidified to a transparent brittle solid which could be dissolved in n propanol. The solution thus obtained was highly water sensitive and readily gels on addition of a few drops of water. Trimethylamine was also added to help hydrolysis of zinc acetate. The resulting solution was colourless and transparent. The solution was then slowly heated to remove all organics. The pure ZnO powders were then obtained [16]. Mohan A C et al reported the precursors used for Zinc oxide nanoparticle synthesis is zinc sulphate heptahydrate (M=287.49g/mol, Sigma Aldrich), and zinc acetate (M=219.5g/mol, Merk), Poly Vinyl Alcohol (PVA) (Sigma Aldrich) was used as the surface modificant, distilled water was used as the solvent [17]. Mohan, A.C et al reported that the synthesis involves mixing zinc acetate and sodium bicarbonate. The mixture is then pyrolyzed. Zinc acetate converts to ZnO nanoparticles, while sodium bicarbonate converts to sodium acetate, which is then washed away with deionized water. The particle size of the nanoparticles can be controlled by adjusting the pyrolytic temperature. The by-products also have an important role in controlling particle growth and agglomeration. Sodium acetate can become distributed on the surface of the nanoparticles, preventing them from agglomerating. These nanocomposites can then be converted into nanoparticles via the dissolution of sodium acetate. Wang Z et al reported that the synthesized ZnO nanoparticles of different sizes, ranging from 8 nm to 35 nm, by varying the pyrolysis temperature of the reactant mixture [18]. The wet chemical synthesis of ZnO nanoparticles is a modification of the precipitation method. In this method, an additive is used for stabilize the nanoparticles formed. The method utilizes the precipitation reaction between zinc nitrate and sodium hydroxide. Briefly, an aqueous solution of starch is mixed with a zinc nitrate solution, whereby sodium hydroxide solution is added drop wise until the solution attains a pH of 12. The precipitate obtained by this reaction (zinc hydroxide) is then converted into ZnO by calcining. Addition of excess hydroxyl ions should be avoided because these solubilize zinc hydroxide and convert it to zincate ions, which are soluble in aqueous medium. Starch is used as a stabilizing agent, is adsorbed at the surface of nanoparticles, providing stability. The mechanism of stabilization involves either increasing the viscosity of the solution or forming a complex with metal ions via the hydroxyl groups. Thus the ZnO nanoparticles is obtained by using the wet chemical method P.K Mishra et al synthesised Zn nanoparticles and obtained particle size in the range of 400nm [19]. In filtered cathodic vacuum arc (FCVA) technique, Zinc films were deposited on silicon substrates at room temperature. ZnO films can also be prepared by this technique. Zinc ions are produced in a vacuum arc discharge between the cathode and the grounded anode. The cathode act as the zinc target mounted on a water-cooled copper plate. A turbo-molecular pump evacuates the chamber to a base pressure before deposition. The zinc films were annealed in a thermal tube furnace in open air. The films were transferred into the furnace when the temperature reached the set point. The annealing time was fixed for some time. After thermal oxidation, the sample was removed from the furnace and cooled quickly in air. XU XL et al reported that the thickness of films obtained in the process where approximately 200-400nm when deposited at a rate of 20nm/min. [20-22]. Singh et al studied that the zinc nanoparticles were produced from the piece of zinc metal in an aqueous solution of sodium dodecyl sulfate (SDS) as a solvent. Zinc rod was placed at the bottom of glass vessel containing the SDS aqueous solution. A piece of metal was irradiated by the focused output of the second harmonics of pulsed nanosecond Nd: YAG laser. Larger particles and free SDS appearing as residue were separated from colloidal solution by centrifugation. Vacuum evaporation of colloidal solution was used to raise the concentration of particles in the solution [23]. According to the survey done, sol-gel process is suitable to synthesis when cost factor is considered but when the quality is taken into account Laser ablation method is the most suitable method.

IV. SURVEY ON COATING METHODOLOGY

The studies are done to protect metals from corrosion, the base material must be protected from the vigorous environment otherwise it should be coated with protective films or coatings, which protect the base material from corrosion [24, 25]. Several techniques are available for deposition of nano coatings on metals such as physical vapor deposition (PVD), chemical vapour deposition (CVD), electrochemical deposition, plasma spraying and sol–gel process. In general, a sol-gel process can be applied to a metal substrate through various common techniques like spin coating, dip coating, thermal spraying [26, 27] and electrodeposition [28-30,38]. According to Duhua Wang et al, corrosion protection sol-gel coatings are classified broadly into four, such as coatings on steel substrate, Aluminium substrate, copper and magnesium substrate. These substrates may also be coated with metal oxides, Organic–inorganic hybrid sol–gel, Inhibitor doped sol–gel coatings and Inorganic zinc-rich coatings [31]. Besides corrosion inhibitors, sacrificial metal pigments such as zinc, Aluminium, magnesium and their alloy particles can be included into the sol–gel coating. Generally, steel substrate is often a suitable target under this cathodic protection. Zinc alloys electro deposition with required properties is one of the latest trends in plating industry. Zinc alloys are attractive because it offers cathodic protection for the base metal to be coated. The coatings of Zinc protects steel better than other element under the conditions of high humidity and corrosive environment. It serves better to the marine & industrial atmosphere [32]. In the recent times, thermal spray coating method attracting many researchers that produces anti-corrosion layer on the surface of steel materials by melting Zn, which has a relation to the sacrificial anode, using gas or electricity instead of the conventional corrosion resistance method[33]. Thus, from the above studies electrodeposition have been selected as the best suitable method to coat Zinc nanoparticles since the stickiness of the coating is well and good and nature of particles deposited is uniform.

V. SURVEY ON CHARACTERIZATION TECHNIQUES

Nanoparticles coating can be characterized using different techniques such as Ultraviolet spectroscopy (UV-VIS), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-Ray Diffractometer (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). Sekar Vijayakumar et al reported that the optical properties of the coating were studied using UV-vis spectroscopy, crystalline phase and size were studied by X-Ray Diffraction, possible functional groups are identified using FTIR, finally morphology, topology, size and distribution of the nanoparticle were determined using SEM & TEM [34]. O.S.I Fayomi et al studied about the deposition of Zinc on the surface of the substrate and observed the uniformity and better homogenous with crack free & fewer pores of the coating is observed. In addition, their research revealed that the micro-hardness of the mild steel significantly improved for the deposited surface of the Zinc [35]. Y. Castro et al studied the stability of the suspensions in terms of viscosity, using a rheometer (Haake, RS50, Germany) under controlled rate conditions [36]. S C Singh et al reported that the angle of the particle is small and had a good average size as well [23]. V S Vasantha et al reported that the electrochemical behaviour of the Zinc alloy deposited increase of thickness to be shifted in the direction of noble metals. Also reported that Zinc content significantly increased the corrosion current density. Also added that the salt spray tests showed that after coating of Zinc alloy significant delayed the time for corrosion [32]. A. Ricoa et al carried out the Wear tests in a wear testing machine (WAZAU 14000) with a pin on disc tester apparatus under dry sliding conditions without eliminating the debris formed. Specimen and counter body were cleaned using methanol to avoid the presence of humidity and other non-desirable films such as grease before the test also recommended. Also, reported that the disc was made of the same coatings, regarding the industrial application in which this material is involved and it rotates horizontally at sliding speed of 0.1 m/s [37]. The above studies indicate various methodologies available to characterize the coated steel substrate with Zinc nanoparticles, all the tests are done according to the American Standards for Testing Materials (ASTM) standards, and the various tests are being studied.

Table 2 - Characterization techniques to identify various parameters of material coating.

References	Instrument used for Characterization	Parameters identified
Sekar Vijayakumar et al[34]	1. UV-VIS 2. XRD 3. FTIR 4. SEM 5. TEM	1. Optical properties of material 2. Crystalline phase and size 3. Functional group present. 4. Crystalline structure 5. Topology & distribution of particle.
O.S.I Fayomi et al[35]	Vickers hardness tester	Micro-hardness of the particle is determined.
Castro et al[36]	Rheometer	Stability of the suspension in terms of viscosity.
V S Vasantha et al[32]	Salt spray tester	Corrosion rate is examined.
A. Ricoa et al [37]	Pin on disc tester	Wear rate is evaluated.

VI. CONCLUSION

The study shows that there are numerous methods available for the synthesis of Zinc nanoparticles and it's understood from the survey, the best method for the synthesis of Zn nanoparticles is laser ablation method due to uniformity and same size particles are reported. Sol gel method is most preferable in terms of coating cost, but in electrodeposition process the coating is preferred is good in terms of quality since particle size distribution and uniformity of the coating is excellent with good mechanical and morphological properties. In addition, it is evident from the study that coating of Zinc nanoparticles has wide applications in various fields and the technique under study can be utilised in the industry where there is a need for tribo-logical property improvements.

To the conclude from the survey conducted on coating materials, it is evident from the study, the Zinc nanoparticles has

- Wide application in the industry such as Marine, Fluid transportation etc.,
- Excellent corrosion resistant property
- Biocompatibility of nanoparticles makes it suitable for biomedical applications.
- Combined with specific additives elements of Mo, Ti & Co, wear resistant property of the material is improved.

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