

EXPLORING THE CORROSION INHIBITION OF MAGNESIUM BY COATINGS FORMULATED WITH NANO CeO and ZrO PARTICLES

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ABSTRACT. In this study, zirconium oxide (ZrO)-cerium oxide (CeO) based composite coatings were fabricated using doctor blade method to protect pure magnesium from corrosion. The effects of ZrO and CeO on corrosion resistance of magnesium coatings were investigated using Tafel polarization method. Uniform deposition of composite coating without micro-voids was observed from scanning electron microscopy (SEM) analysis. The results exhibit that the addition of CeO show a higher corrosion resistance in comparison with the specimen coated without CeO in the electrolyte and bare Mg, and also it reduces the corrosion rate of Mg up to 3.67×10^{-5} mpy. Surface morphology of the so developed composite coating result a minimum corrosion on the surface. The usage of ZrO/CeO as coating material is a promising anticorrosive measure for Mg and its alloys due to its elevated corrosion resistance and durability.

KEY WORDS: Magnesium, Cerium oxide synthesis, composite coating, Tafel polarization, Surface morphology

INTRODUCTION

The rapid technological growth leads to an upsurge in necessity of materials having better mechanical and corrosion resistance. Magnesium (Mg) and its alloys holds various outstanding properties, such as low density, high thermal conductivity, high damping resistance and better shielding characteristics [1], these properties make Mg as a prime material in various fields of application such as automobile, workstation parts, aerospace components and mobile phones [2–3]. However, Mg and its alloys are highly chemical reactive and likely to agonize severe corrosion in almost all industrial environments during service, that extremely limits their possible application in industrial practice [4–8].

To overcome this restriction, many researchers adopted traditional techniques such as new alloy design, surface alteration and protective coatings to increase corrosion resistance. In this, the surface alterations are applied over metal surface by implementing technologies like chemical conversion, micro-arc oxidation, ion implantation and electro plating to improve the corrosion resistance [9–11]. Among them, the chemical conversion method is usually preferred for its simplicity in operation, low cost and widely applied as a pretreatment for Mg and its alloys. Chromium-based conversion coating was considered as an effective treatment technique. Nevertheless, the toxicity of the hexavalent chromium in the chromate has been strictly restricted in industry [12]. In order to replace the chromium-based treatment, some environmentally-friendly chemical treatment method such as cerium conversion coatings, polymer duplex coatings etc. has to be developed to improve the corrosion resistance of Mg and its alloy. Such coatings are effective and they are used on metal surfaces such as steel, aluminum alloy and Mg alloys, showcasing excellent corrosion resistance [13–15].

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In recent years hybrid composite coatings comprises metal matrix embedded with second phase particles of ceramics or rare earth metals have become an object of great interest in science and industry. The ceramic particles such as SiC, TiC, B₄C, BN, Zr, etc are used to improve the hardness and corrosion resistance of coating materials. Likewise, the rare earth metals like CeO, Yr, La, etc. possess unique properties like chemical stability, thermal resistance etc. Such composite coatings have desirable properties of the metal matrix viz. electrical conductivity and high hardness [16–18]. Different preparation techniques such as plasma spraying, chemical vapor deposition, sol-gel have been adopted by researchers in order to produce composite coating materials. Among the available rare earth metal cerium exhibits self-healing properties and have better efficiency to resist the ion flow from metal to electrolyte [19]. Few researchers made an attempt to develop surface coatings over Mg to enhance the corrosion resistance property.

Zr doped graphite composite coating was fabricated by Bia *et al.* [20], magnetron sputtering method was used to improve the tribological and corrosion behaviors of Ti₆Al₄V alloy. Potentiodynamic polarization method was adopted by them over the developed coating in hanks solution. The results reveal that Zr doped graphite coating exhibits excellent wear and corrosion resistance due to the solid lubricant tendency of graphite and chemical stability of Zr. Etienne *et al.* [21] developed Zr-based thin film coating over metallic glasses using magnetron sputtering method and found that the fabricated coating display high hardness, good young's modulus, excellent corrosion resistance and appropriate bacterial protection.

Cathodic arc deposition method was adopted by Yunchang *et al.* [22] to fabricate Zr based coating over Mg alloy. Potentio-dynamic polarization test and EIS method under simulated body fluid solution were performed. The observation results that the corrosion potential of the coated alloy is more positive and the corrosion current density of coated alloy is about two orders of magnitude lower. Dongfang *et al.* [23] developed Al, Ti, Zr and Hf-based metallic coatings over AZ91D magnesium alloys using magnetron sputtering technique. Salt spray tests and electrochemical polarization test were performed under 3.5 wt.% NaCl solution and observed results reveals that Zr and Hf exhibits low difference in potentials, the excellent corrosion resistance and the good adhesion to the substrate are considered probable causes for the anti-corrosion performance of the fabricated coating. Hossein *et al.* [24] developed cerium-chitosan based conversion coating over aluminium alloy. Polarization technique and electrochemical impedance spectroscopy were performed under 3.5 wt.% NaCl solution and observed that addition of chitosan in cerium solution noticeably reduce the cracking. An extremely high corrosion resistance coating was obtained when the value of chitosan was 0.01 wt.%. In contrast, when the chitosan value was greater than 0.01 wt.%, the cerium oxide coating was obtained with high porosity, the developed coating exhibits better corrosion resistance compared to base Al alloy. Plasma electrolytic deposition method was adopted by Ruonan *et al.* [25] to develop CeO coating over Mg alloy. Electrochemical impedance spectroscopy technique was adopted and the result indicates that the coatings had adhered excellently to the substrates. Therefore, the CeO coating is a promising anticorrosive measure for magnesium alloys due to its great corrosion resistance and durability. Phuon *et al.* [26] developed cerium and phosphate conversion coating over Mg alloy. Potentio-dynamic polarization and immersion tests were performed in 0.5 M NaCl solution. Results reveal that double sealing treatments of cerium followed by phosphate solutions exhibited the best corrosion resistance without pitting corrosion formation.

From the literature survey, it was observed that Zr and CeO exhibit better corrosion and mechanical properties. However, CeO and ZrO based hybrid composite coating over Mg was not yet reported. Hence the objective of this research is to enhance the corrosion resistance of magnesium by hybrid composite coating of CeO and ZrO using doctorblade method. Further Tafel polarization method is proposed to measure the corrosion rate of developed coating.

EXPERIMENTAL

In this research pure magnesium metal strip with 2 mm thickness is used as substrate material. Cerium oxide and zirconium oxide particles are used as coating material. In this ZrO particles and CeO particles are synthesized by chemical reduction method.

Synthesis of cerium oxide nanoparticles

Cerium oxide nanoparticles are synthesized by chemical reaction method. Herein cerium nitrate solution is used as precursor for CeO nanoparticle synthesis. In this methodical procedure, 0.3 M of NaOH solution is added drop wise into 0.1 M cerium nitrate solution, further continuously stirred for 3 h at room temperature. Subsequently, a pinkish white precipitate was formed as a reaction product. The achieved solution was centrifuged at 10000 rpm for 10 min, then the collected product is repeatedly washed with solution contain deionized water and ethanol to remove impurities. Finally, the obtained product is dried at 60 °C for 3 h in hot air oven and annealed in box furnace at 270 °C for 4 h.

Sample preparation

Before coating, the Mg strips are mirror polished with SiC abrasive sheet with different grit size, subsequently organic solvent is used for cleaning and deionized water is used to remove metal debris formed during polishing. Further the polished Mg strip is dried at 60°C in hot oven for 12 h. Herein the composite coating is developed over Mg surface by adopting doctor blades method. In this calculated amount of synthesized CeO nanoparticles is grinded with PVDF (polyvinylidene fluoride) at ratio of 9.8:0.2, then the mixture is dispersed in acetone solution and sonicated for 4 h to obtain slurry. The slurry is further coated over Mg surface, the process is repeated for four times to obtain uniform composite coating of ~17 µm thickness. Same procedure was adopted to developed ZrO/Mg, ZrO/Ce/Mg composite coating.

Material characterization

Crystalline nature of synthesized nanoparticles is characterized by X-ray diffractometer (Bruker D8), scanned at 2θ range of 20 to 80°. Surface morphology and cross-sectional analysis of developed coating is done by Scanning Electron Microscopy (SEM) and the elementary confirmation is done using energy dispersive X-ray analysis (EDAX).

Electrochemical corrosion study

Corrosion resistance of the developed composite coating is evaluated by CHI604C electrochemical workstation with 3.5 wt.% NaCl solution. It consists of three electrode setups, in this setup the coated strips are used as working electrode, platinum wire and saturated calomel electrode is respective to reference and counter electrodes. The Tafel polarization method is adopted to obtain corrosion parameters and the scanning is done at the range of -1.4 to -2.0 V at the scanning rate of 0.001 V.

RESULTS AND DISCUSSION

XRD of synthesized CeO particles

Figure 1 show the attained XRD pattern of synthesis CeO nanoparticles. The peaks obtained near 28.5, 33.0, 47.5 and 56.2 are the corresponding planes of 111, 200, 220 and 311.

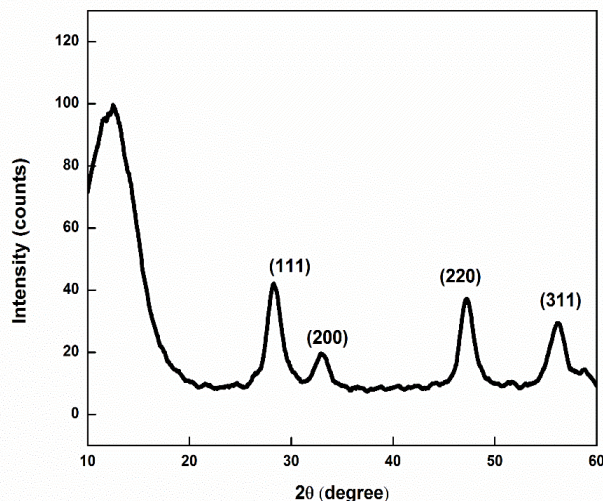


Figure 1. XRD of synthesis CeO particles.

The obtained peaks are matches with standard JCPDS (Joint Committee on Powder Diffraction Standards) No.34-0394 of CeO nanoparticle with the purity level of 98.4%. The crystalline size was measured by using Debye-Scherrer equation and the crystal structure of CeO particle is identified as cubic fluorite structure measured with ~ 34 nm.

SEM of developed coating

Surface morphology of CeO/ZrO composite coated Mg strip is shown in Figure 2a. The uniform dispersion of nanoparticles is clearly visible in the Figure 2a this is due to the coating made by doctor blade method. This is an efficient method to investigate the influence of nano particles in the surface properties of the developed coating. Likewise, surface damage normally occurs due to curing is not evident this doctor blade method. Thickness of the developed coating is measured to be $\sim 17 \mu\text{m}$ as depicted in Figure 2b. The elementary analysis is done over the coated strip after formation in order to trace the presence of element formation.

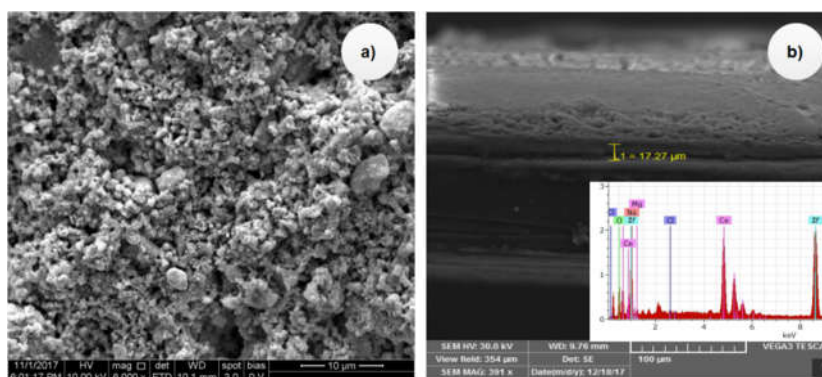


Figure 2. (a) Scanning electron microscopic image of CeO/Zr composite coating and (b) cross-section and EDS of CeO/Zr composite coating.

Corrosion behavior

Tafel polarization method is adapted to measure the corrosion rate of the developed composite coating. Corrosion parameters like Cathodic Tafel constant (β_c), Anodic Tafel constant (β_a), corrosion current density (i_{corr}) are extrapolated from the Tafel plot Figure 3. Corrosion rate (CR) and polarization resistance (R_p) are calculated using the equations employed by Kavimani *et al.* [4, 27] and the calculated values are shown in Table 1.

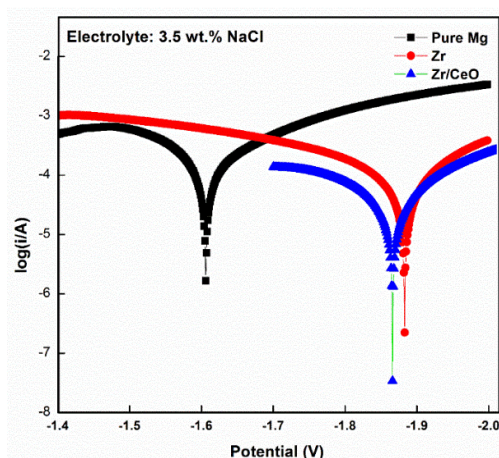


Figure 3. Tafel plot of developed samples.

During corrosion, magnesium undergoes anodic and cathodic reaction, due to these reactions' magnesium ions are formed as a corrosion product of anodic reaction and magnesium hydroxide layer are developed during cathodic reaction which acts as a barrier to resist the metal to electrolyte conduct area, thus reducing the chance of corrosion. However, these layers begin to peel off after a certain time interval due to the corrosion action of saline electrolyte. In general corrosion rate is proportional to corrosion current density. Polarization resistance denoted the resistance offer by the material against dissolution [28].

Table 1. Corrosion parameter of developed composite coating.

Coating	Cathode Tafel constant (β_c), 1/V	Anode Tafel constant (β_a), 1/V	Corrosion density (i_{corr}), $\times 10^{-5}$ $\mu\text{A cm}^{-2}$	Resistance polarization, (R_p) $\Omega \text{ cm}^2$	Corrosion rate (CR), $\times 10^{-5}$ mpy
Bare Mg	5.548	3.708	2.950	239	1.78×10^{-4}
Zr	6.116	4.472	1.031	597	6.22×10^{-5}
Zr/CeO	5.929	3.758	0.607	1107	3.67×10^{-5}

When uncoated Mg strip is dipped in 3.5 wt.% its corrosion potential shifts toward the cathodic region, the i_{corr} value is noted as $2.95 \times 10^{-5} \mu\text{A cm}^{-2}$ and corrosion rate is noted as 1.7×10^{-4} mpy. During corrosion reaction chlorine ion present in the aqueous electrolyte reacts over the surface of Mg surface. The result is the formation of Mg^{2+} ions that reacts with ions present in the electrolyte viz. Cl, O, H and forms magnesium chloride and magnesium hydroxide as the corrosion products. Among these, magnesium chloride is the reaction product of anodic reaction and magnesium hydroxide is the reaction product of cathodic reaction. In this formed magnesium hydroxide act as the passive layer to inhibit the corrosion active of electrolyte in the saline

environment [29]. When ZrO coated strip is hosted in corrosive electrolyte its CR value reduced drastically to 6.22×10^{-5} mpy. These ZrO particles act as a passive layer on the Mg surface when exposed to the saline environment. Current flow under anodic polarization is avoided due to the continuous growth of non-conducting oxide layer on top of the naturally existing one. The growth of the oxide is allowed because of the migration of defects viz. oxygen vacancies in passive layer between the substrate and coating interface [30]. When ZrO/CeO composite coating is dipped in corrosive electrolyte, the CR rate decreases to 3.67×10^{-5} mpy. This might be the combined effect of oxide-based particles that enables the molecular oxygen reduction reaction, resulting the development of apparent oxide/hydroxide. The combined particles are driven by the potential differences between the Mg and inter-metallic inclusions that lowers the local pH. In this condition hydrogen evolves and oxygen reduce to form OH^- that induces the precipitation of more stable compounds as hydrated cerium oxide [31, 32].

Surface morphology of developed coating after corrosion test

Figure 4a shows the SEM micrograph of bare Mg strip after corrosion reaction. The formation of pits and several cracks with surface damages is observed in the Figure 4a indicating the corrosive action of electrolyte.

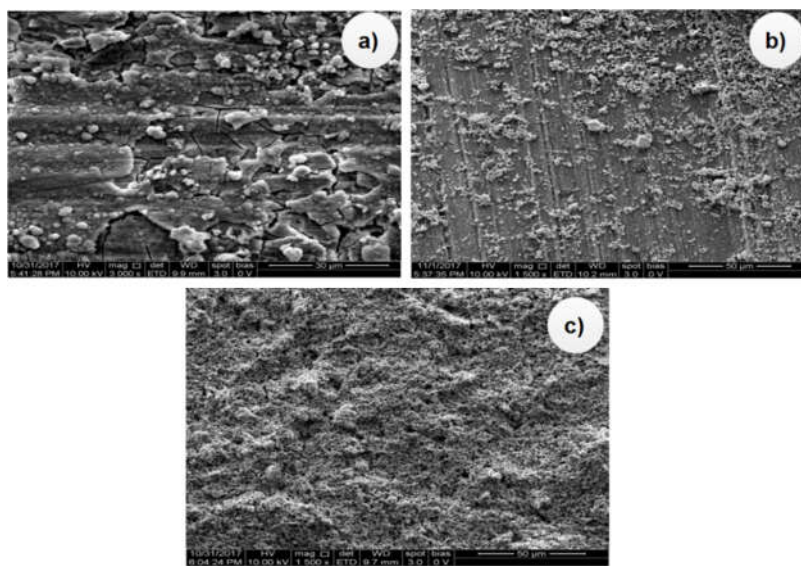


Figure 4. (a) Scanning electron microscopic image of bare Mg strip, (b) scanning electron microscopic Zr/Mg strip, and (c) scanning electron microscopic Zr/CeO/Mg strip after corrosion test.

The formation of microvoids is also evidenced over the scanned surface that shows the presence of metal dissolution caused by anodic reaction. A clear surface with lesser damages is noted for CeO coated strip as depicted in Figure 4b. The passive layer formed by cerium hydroxide avoids the chance of metal substrate contact over corrosive solution. Therefore a minimum surface damage is observed. A clear surface of composite coating is depicted from Figure 4c this is due to the formation of passive inhibiting oxide layer formed by CeO.

CONCLUSION

In this research, a hybrid composite coating over Mg was developed using CeO/ZrO to enhance the corrosion resistance property of the magnesium. CeO particles were synthesized by chemical reduction and sol-gel method. CeO/ZrO composite coating was developed using doctor blade method. Corrosion behaviour developed coating was analyzed by Tafel polarization under 3.5 wt.% NaCl solution. The following observation has been made: (1) Polarization resistance of Mg increases upto $1107\Omega\text{ cm}^2$. (2) Corrosion rate of Mg decrease from 1.78×10^{-4} to 3.67×10^{-5} mpy. (3) SEM micrograph demonstrates that the developed composite exhibit clear surface with minimal surface damages compared to bare Mg. The outstanding corrosion resistance of developed composite coating in corrosive electrolyte suggested that this composite coating might be employed in a saline environment and biomedical implant applications.

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