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ORIGINAL ARTICLE

Multifaceted incorporation of Zn-Al_2O_3/Cr_2O_3/SiO_2 nanocomposite coatings: anti-corrosion, tribological, and thermal stability

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Abstract Nano-sized particle incorporation into metal matrix has gained worldwide acceptance. Al_2O_3, Cr_2O_3, and SiO_2 nanoparticles have been co-deposited with Zn using electrodeposition process to produce advanced alloy. The coatings were characterized using SEM/EDX and XRD. The mechanical properties of the coatings were studied using microhardness indenter and dry abrasive wear tester. Zn-10 g/L Cr_2O_3 nanocomposite exhibited the highest microhardness of 228 HVN; Zn-5 g/L Al_2O_3 nanocomposite possessed the highest corrosion resistance and lowest wear loss. Zn-5 g/L SiO_2 nanocomposite showed good stability against other composite coatings. The incorporation of the Al_2O_3, Cr_2O_3, and SiO_2 shows grain refinement and modify orientation on Zn matrix.

Keywords Corrosion behavior · Nanocomposite coatings · Microhardness · Thermal stability · Wear

1 Introduction

Zinc coatings have been employed to protect steel from corrosion for several decades. The wide use of these coatings is due to their good corrosion resistance properties, cost-effectiveness, and ease of fabrication. Despite the good ability to protect steel from corrosion degradation, continuous improvement of Zn deposits is required for the ever increasing performance. Novel Zn alloy and composite coatings have been developed to meet the demand and better perform under demanding environments at a reduced thickness than the traditional Zn coatings [1–3].

Zn nanocomposite coatings exhibit enhanced Zn self-healing properties, good thermal stability, and wear resistance. The excellent surface properties exhibited by Zn composite coatings are ascribed to the strengthening effect of the reinforcement materials incorporated. Materials such as Al_2O_3, SiO_2, CeO_2, ZrO_2, TiO_2, etc. have been used to reinforce Zn matrix for improved performance [2–12].

The incorporation of SiO_2 particles into Zn matrix have been studied by several authors. Kundo et al. studied the electrodeposition of Zn-SiO_2 composite on mild steel. The results showed that the particles precipitate on the hexagonal plane crystals [2]. Micron/Sub-micron sized particles of SiO_2 were reported to be easily co-deposited into Zn matrix better than their nano-sized counterparts [16, 17]. Hammami et al. studied the inclusion of SiO_2 nanoparticles into Zn-Ni matrix and the produced composite alloy exhibited high microhardness, improved corrosion resistance, and better thermal stability [6].

Al_2O_3 particles have also been used by many researchers to enhance the surface properties of Zn coatings. These particles possess excellent corrosion resistance, low friction, and thermal expansion coefficient. The incorporation of Al_2O_3 nanoparticles were reported to improve the microstructural characteristics and electrochemical properties of Zn-Ni matrix [5]. Blejan et al. reported substantial improvement in corrosion resistance due to the inclusion of Al_2O_3 particles into Zn-Ni matrix [4].

The incorporation of Cr_2O_3 into Zn matrix is scanty in literature, and the only available work is on Ni matrix. These particles were reported to positively influence the thermal stability, hardness, and wear properties of Ni matrix. However, their inclusion yielded no significant effect on the corrosion

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resistance of Ni coatings [13]. Ni matrix embedded Cr_2O_3 particles was found to possess corrosion inhibitory effect, the lowest effect on Ni coated samples [14]. The electrodeposits prepared by Hamid et al. contained 29 % Vf Cr_2O_3 as compared to 1.5 and 1.8 wt.% obtained by Srivastava et al. [13, 14].

No work has been published on the fabrication of Zn-Cr_2O_3 nanocomposite coatings according the best of our knowledge. The investigation of thermal stability and wear resistance of Zn-Al_2O_3 and Zn-SiO_2 nanocomposite coatings is also scarce. Therefore, this work reports on the development and fabrication of novel Zn nanocomposite coatings reinforced with nano-sized Al_2O_3, Cr_2O_3, and SiO_2 particles. The electrochemical behavior, microhardness, wears, and thermo-mechanical performance of the fabricated coatings were also evaluated.

2 Experimental

2.1 Sample preparation

Table 1 shows the electroplating bath composition and operating conditions for the experiments. Sectioned mild steel (25×40×1 mm) cathodes were polished using 180 and 400 grit SiC emery papers to remove the unwanted material on the substrate. The samples were then stored in a desiccator to prevent formation of rust prior to electrodeposition. They were then suspended into ethanol to degrease them, dipped into 1 M HCl to activate the surface, and then rinsed in water before plating. Two zinc (99.9 %) plates were used as anodes. The solutions for plating were prepared a day prior to the tests. Al_2O_3 (50 nm), Cr_2O_3 (100 nm), and SiO_2 (20 nm) nanoparticles added into the bath were kept in suspension for 18 h using a magnetic stirrer to prevent agglomeration of particles in the solution. The pH of the bath solution was kept constant at 3.8 and adjusted by addition of HCl or NaOH. All the experiments were conducted under ambient conditions, and the plating time was 20 min at a speed of 300 rpm. After electrodeposition, the plated samples were rinsed in water for 5 s and then left to air dry. The coating description are shown in Table 2.

Table 1 Bath composition and operating condition

Composition	g/L	Parameters	
$ZnCl_2$	150	Cathode	Mild steel
KCl	50	Anode	Zn
Boric acid	30	Temperature	25 °C
Glycine	30	pH	3.8
Thiorea	10	Current	1.5 A
Al_2O_3	5–10		
Cr_2O_3	10–20		
SiO_2	5–10		

Table 2 Sample codes and description

Sample code	Sample description
ZA1	Zn—5 g/L Al_2O_3
ZA2	Zn—10 g/L Al_2O_3
ZC1	Zn—10 g/L Cr_2O_3
ZC2	Zn—20 g/L Cr_2O_3
ZS1	Zn—5 g/L SiO_2
ZS2	Zn—10 g/L SiO_2

2.2 Surface characterization

JEOL–JSM–7600 F Field Emission and Vega Tescan scanning electron microscope affixed with energy dispersive spectrometry was used to investigate the surface morphology and content of the inert particles in the coatings. The structural analysis of the coatings was done using PANalytical X'Pert Pro diffractometer.

2.3 Corrosion behavior

AUTOLAB Pontentio/Galvanostat was used to study the corrosion behavior of as-received sample and the coatings in 3.65 wt% NaCl environment. The polarization measurements were carried from a start potential of −1.5 to an end potential of 1.5 V at a scanning rate of 0.01 V/s. Ag/AgCl was used as a reference electrode and graphite served as a counter electrode. The sample was used as working electrode, and only 1 cm^2 of the specimen was exposed to the corrosion environment.

2.4 Microhardness test

Microhardness of the electrodeposits was evaluated by using a diamond base microhardness tester and the values recorded are an average of three measurements obtained in different locations at a load of 10 g.

2.5 Thermal stability

The thermal stability tests were conducted in an air-circulated laboratory tube furnace at a constant temperature of 250 °C. The samples were exposed to heat treatment conditions for a time range of 0.5, 2, and 16 h. After each time of exposure, the samples were tested for microhardness using diamond base microhardness indenter. Microhardness indentations were taken in different areas of the sample and only an average of three values were used for plotting microhardness evolution graph.

2.6 Wear

The wear resistance of the samples was evaluated by Dry Abrasion Rig tester. The tests were conducted under dry sliding conditions at normal load of 5 N and wheel speed of 200 rev/min. Silica sand was used as the wearing medium.

3 Results and discussion

3.1 Characterization of the starting materials

Figure 1 shows the SEM micrographs of as-received sample and nano-oxide powders that have been used for incorporation into Zn matrix to fabricate a quaternary composite alloy coatings. As-received sample as depicted by Fig. 1a has surface defects such as pores and microholes which serves a weak sites that can be easily attacked by corrosive media. Al_2O_3 powder exhibit regular shaped and uniformly dispersed particles as depicted by Fig. 1b. This arrangement and nature of particles implies uniform dispersion when added in the plating bath and hence promotes uniform incorporation of the particles onto the surface of the cathode. These particles can easily be dispersed in solution without intense agitation. Figure 1c, d reveal fine and agglomerated particles of SiO_2 and Cr_2O_3 which poses difficulty in uniform dispersion in solution and requires intense stirring to counteract the problem. Nano-sized particles can easily fill microholes and pores on the surface of mild steel and hence improve the surface properties of this metal.

3.2 Effect of particle loading on microhardness

The effect of bath particle loading on the microhardness of Zn matrix is shown in Fig. 2. All the composites coatings show significant increase in microhardness as compared to as-received sample and pure Zn coating. The increase can be attributed to the inclusion of the reinforcement nanoparticulates in the coating.

Ceramic oxide particles have been reported to hinder grain growth which promote greater number of grain boundaries due to the small crystallite size [6, 11]. An increased number of grain boundaries will impede dislocation movements and results in formation of harder films. Addition of 5 g/L Al_2O_3 and SiO_2 into the bath increased the microhardness of pure Zn coating from 132 to about 192 HV (ZA1 and ZS1). ZC2 shows the highest improvement of 228 HV, and this is ascribed to excellent mechanical properties exhibited by Cr_2O_3 particles. Increasing the bath particle loading of Cr_2O_3 from 10 to 20 g/L creates an elevated microhardness from 161 to 228 HV. The quantity of embedded particles in the coating affects the hardness of the material. This result can be explained by Guglielmi's two-step adsorption model which implies that increasing concentration of particles in the bath promotes the availability of particles to be adsorbed at the cathode [3]. High and optimum content particles incorporated into the matrix improve the microhardness properties of the coating [9]. This denotes that the degree of presence of the particles in the plating bath and in the coating is responsible for the improvement. The increment of Al_2O_3 and SiO_2 from 5 to

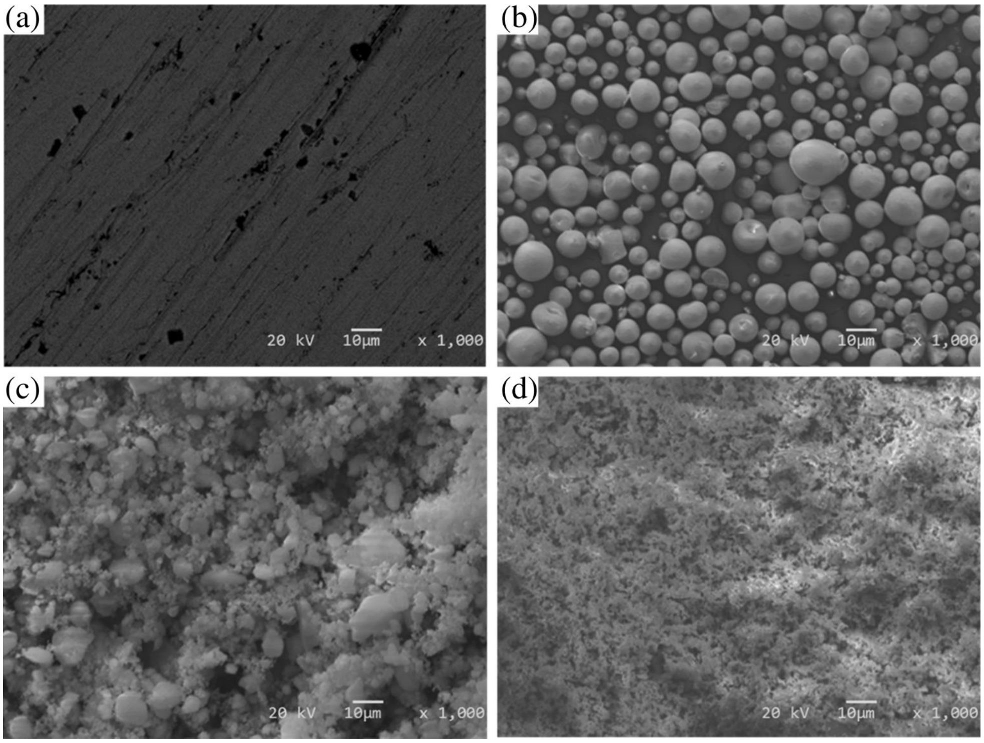

Fig. 1 SEM micrographs of starting materials **a** as-received sample, **b** Al_2O_3 powder, **c** Cr_2O_3 powder, and **d** SiO_2 powder

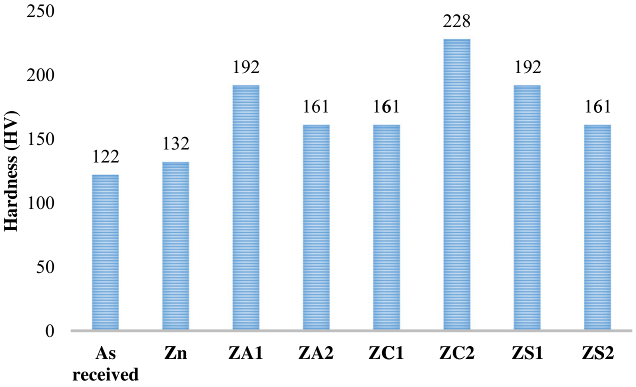

Fig. 2 Microhardness values of as received, Zn coating and Zn composite coatings

10 g/L yielded no positive results. The optimum particle concentration of these nanoparticles for improved microhardness is 5 g/L and deviation from this can cause agglomeration of particles in the bath or rapid deposition which can lead to formation of coatings with defects. It should also be known that hardness of a material depends on various factors except the amount of the embedded particles present in the coating but surface morphology, homogeneity, and local particle densities also affect the mechanical behavior.

3.3 Effect of particle loading on corrosion resistance

The employment of Zn coatings in industry owes mainly to its good corrosion resistance properties. Therefore, it is mandatory for the developed composites to improve the conventional Zn coatings to be tested for their anti-corrosive characteristics. Figure 3 shows the polarization curves of as-received Zn and Zn composite coatings obtained in 3.65 wt% of NaCl environment. A notable positive shift in polarization potential was observed for pure Zn coating as compared to as-received sample. This result shows that coating the as-received sample with Zn increases its corrosion resistance. All the composites coatings except ZC1 and ZA2 exhibited more positive potential in reference to pure Zn.

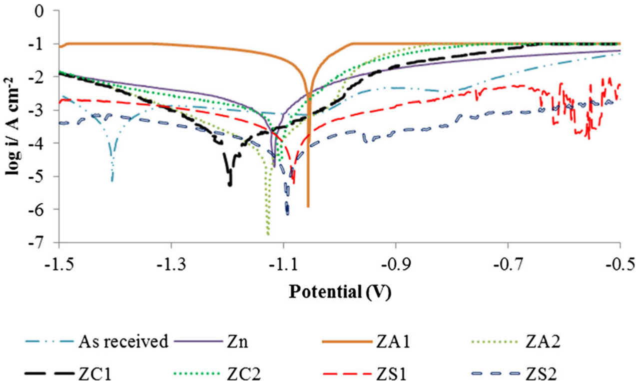

Fig. 3 Polarization curves for as received, Zn coating, ZA, ZC, and ZS nanocomposite coatings

The inclusion of Al_2O_3 nanoparticles into Zn matrix increased the potential by 0.072 V from −1.1282 V of Zn. The increment of these particles in the bath from 5 to 10 g/L yielded no significant results. ZS nanocomposites shows a similar trend as that of ZA but particle of 10 g/L of SiO_2 resulted in positive shift of 0.036 V. The optimum particle loading for best corrosion resistance for ZA and ZS nanocomposite coatings is 5 g/L of Al_2O_3 and SiO_2, respectively. Nanoparticles incorporated in a metal matrix form inert physical barriers that protect the metal matrix from corrosion attack of the corrosive medium. Therefore, improvement in corrosion resistance of the Zn matrix is owed to the presence of the inert particulates in the coating. However, the reduction in potential showed by ZA and ZS composites due to increasing the particle concentration in the bath can be attributed to agglomeration of particles when they exceed optimum levels. Agglomeration of particles in the bath reduces the availability of particles at the cathode for incorporation. Poor quality coatings result as a consequence of inefficient co-deposition [4]. Incorporation of Cr_2O_3 particles showed a different behavior as compared to ZA and ZC composites. The increment in particle concentration yielded positive results. Increasing particle loading of Cr_2O_3 from 10 to 20 g/L resulted in shifting the potential from −1.1972 to −1.1075 V. Therefore, the better corrosion potential exhibited by ZC2 can be ascribed to the increasing of particle concentration in the bath. Cr_2O_3 have been reported to act as corrosion inhibitor when incorporated into a metal matrix and hinder corrosion degradation of the coatings [14].

3.4 Thermal stability

The thermal stability of the Zn coating, ZA1, ZC2, and ZS1 nanocomposite electrodeposits have been evaluated by following microhardness evolution of the deposits as revealed by Fig. 4. The deposits were exposed to heat treatment conditions at annealing temperature of 250 °C in air circulation tube furnace for a duration of 0.5, 2, and 16 h. Reduction in microhardness for both pure Zn and composite coatings is evident

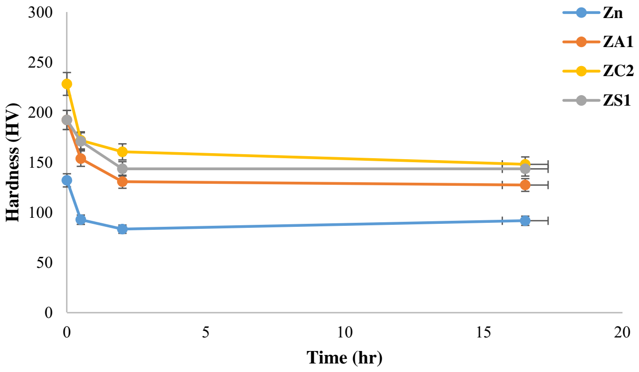

Fig. 4 Microhardness evolution values (average of three measurements) of heat-treated Zn coating, ZA1, ZC2, and ZS1 nanocomposite coatings

from the figure. The rate of reduction also proves to be a function of time of exposure to heat treatment conditions. In the first 2 h of exposure, drastic reduction in microhardness is observed for all the samples. Heat treatment induces grain growth, and the presence of oxygen in the furnace promotes surface oxidation at elevated temperatures resulting in lowering of microhardness [13]. Furthermore, 32, 29, and 25 % decrease in microhardness was noted for ZA1, ZC2, and ZS1, respectively, compared to 37 % of pure Zn coating. These results can be attributed to the pinning effect induced by reinforcement particles on the Zn matrix grain boundaries. The presence of these particles inhibits excessive Zn grain growth hence better thermal stability. Longer exposure of the samples up to 16 h led to stability in microhardness. This suggests that grain growth can reach equilibrium after 2 h of exposure to the annealing temperature. Driving out of oxygen in the furnace by hot air can lead to low concentrations of oxygen in the furnace causing mild surface oxidation. The microhardness values of the composites were retained higher than that of the pure Zn coating throughout the tests. This shows that the composites exhibit better thermal stability than Zn. ZS1 proved to be the best thermally stable sample but ZC2 retained higher values in microhardness in throughout the time of exposure.

3.5 Wear

The percentage wear mass loss of the as-received Zn coating and nanocomposite coatings are shown in Fig. 5. The tests were conducted under dry sliding conditions at normal load of 5 N and a wheel speed of 200 rev/min. The composite coatings revealed an appreciable reduction in percentage wear loss as compared to as-received and pure Zn coating. The inclusion of the nanoparticles into Zn matrix is believed to be responsible for the reduction. Ceramic reinforcement particles retard dislocation movements of a metal matrix and thus increasing the plastic deformation resistance of the coating [15]. The microstructure and grain size are some major factors that affect wear behavior of the produced coatings [9]. The

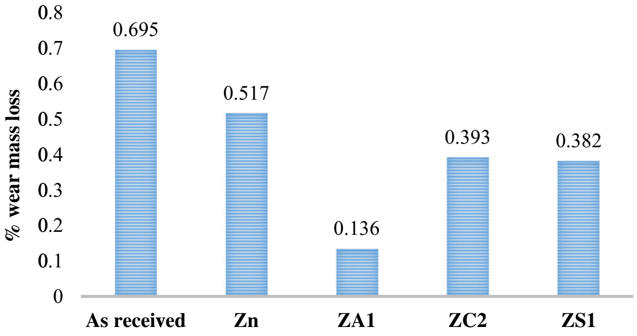

Fig. 5 Percent wear mass loss obtained of as received, Zn coating, ZA1, ZC2, and ZS1 nanocomposite coatings

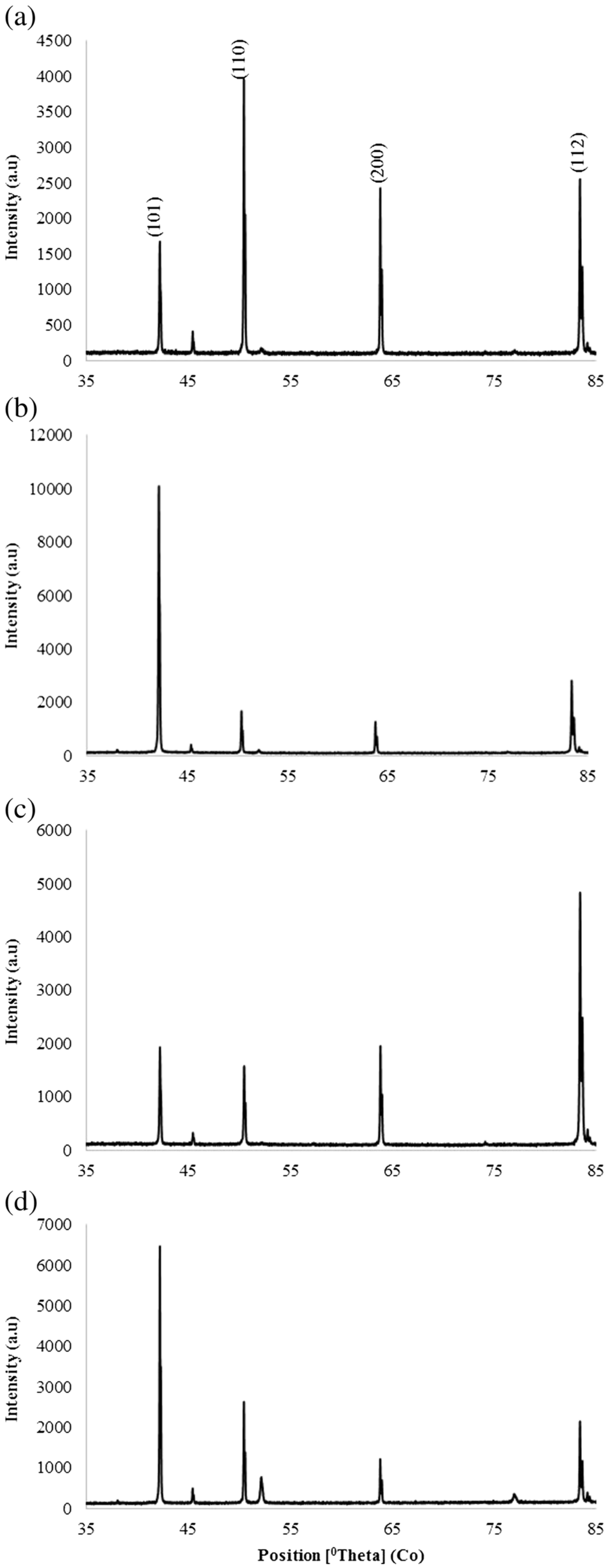

Fig. 6 XRD diffractograms of **a** Zn coating, **b** ZA1 nanocomposite, **c** ZC2 nanocomposite, and **d** ZS1 nanocomposite coatings

composite coatings exhibited refined and improved microstructure as compared to Zn matrix.

ZA1 nanocomposite coating possesses the lowest wear loss than all the composites deposits. The presence of Al_2O_3 nanoparticles reduced the wear loss from 0.517 to 0.136 %. Al_2O_3 particles have been reported to exhibit low coefficient of friction and excellent self-lubricating properties and when incorporated into a metal matrix reduces the friction that is caused by the wearing medium on the matrix [9]. Therefore, the reduction in wear loss can be attributed to the incorporation of Al_2O_3 nanoparticles into Zn matrix.

3.6 Structural analysis

The XRD patterns of Zn coating, ZA1, ZC2, and ZS1 nanocomposite coatings are shown in Fig. 6. The major diffraction lines have been obtained at (101), (110), (200), and (112) crystallographic planes. Most of the diffraction lines in the diffractograms can be ascribed to Zn hexagonal structure. Substantial modification in preferential crystallographic orientation can be observed for the nanocomposite coatings in reference with pure Zn deposit. This result can be ascribed to the inclusion of nanoparticles into the metal matrix. Fe peak (200) of all the composites is when the nanoparticulates were introduced. This reduction suggests the formation of a uniform deposit which provides better surface coverage of mild steel than pure Zn coating. The incorporation of particles into a metal matrix promotes homogeneity and reduces porosity [8]. ZA1 nanocomposite alloy show more reduced Fe peak than all the composite alloys. Al_2O_3 particles have been reported to influence the microstructure of Zn matrix [8].

3.7 Morphological studies

The morphology of Zn coating, ZA1, ZC2, and ZS1 nanocomposite coatings are shown in Fig. 7. The coatings were fabricated under the same experimental conditions, and the presence of the nanoparticulates was confirmed by EDS analysis. Pure Zn-plated sample displays a flake-like crystalline structure, and the composite follows the same pattern. However, the composite coatings exhibit compact microstructure and smaller grain size as compared to pure Zn coating. The refined microstructure exhibited by the composites can be attributed to the inclusion and uniform dispersion of the nanoparticles in the Zn matrix. Incorporation of nanoparticles in a metal matrix promotes increase in number of nucleation sites and impedes crystal growth resulting in small-sized grains [11]. Zn-5 g/L Al_2O_3 (ZA1) and Zn-20 g/L Cr_2O_3 (ZC2) showed better microstructures as compared to Zn-5 g/L SiO_2 (ZS1). This might have been caused by the nature of SiO_2 particles which are very fine and tend to agglomerate when dispersed in solution. SiO_2 particles are hydrophilic and their co-deposition onto the surface of a cathode is difficult [6]. On the other hand, Al_2O_3 particles can easily disperse in the plating bath promoting their incorporation into Zn matrix as shown in Fig. 7. EDS results showed an incorporation of Al_2O_3 (2.45 wt%), Cr_2O_3 (3.8 wt%), and SiO_2 (0.85 wt%) in the composite deposits.

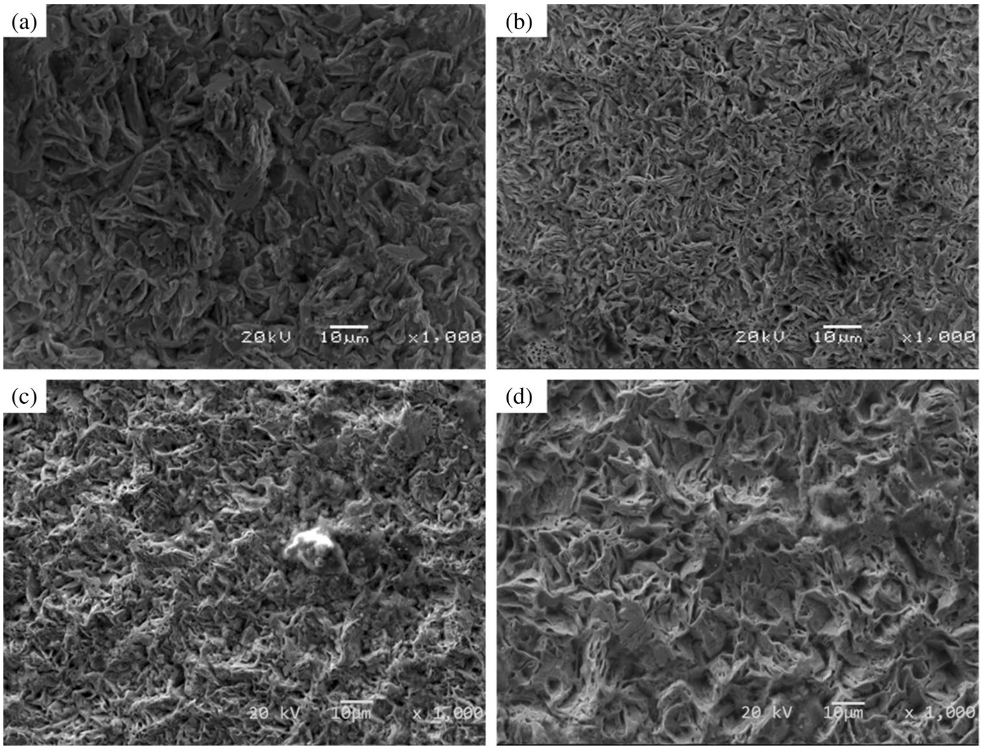

Fig. 7 SEM images of **a** Zn coating, **b** ZA1 nanocomposite coating, **c** ZC2 nanocomposite coating, and **d** ZS1 nanocomposite coating

4 Conclusion

- Zn-Al_2O_3, Zn-Cr_2O_3, and Zn-SiO_2 nanocomposite coatings have been successfully produced by electrodeposition technique. 5 g/L of Al_2O_3 and 10 g/L Cr_2O_3 and 5 g/L SiO_2 proved to be the optimum bath loading for improved hardness and corrosion resistance of Zn matrix.
- SEM and XRD analysis showed that the presence of the nanoparticles in the coating inhibits grain growth and modify crystollographic orientation of Zn matrix.
- Optimum particle concentration improved the hardness, thermal stability, corrosion, and wear resistance properties of Zn matrix. ZA1 and ZS1 exhibited better anti-corrosive properties while ZC2 possessed high hardness.
- With the produced coating showing good uniform growth, perfect crystal, and bright metal matrix composite deposit, the anti-corrosion resistance performance increase geometrical against the as-received sample.
- The wear characteristics also show excellent plastic resistance propagation as a result of interfacial mechanism and good solid precipitation of the thin films.

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