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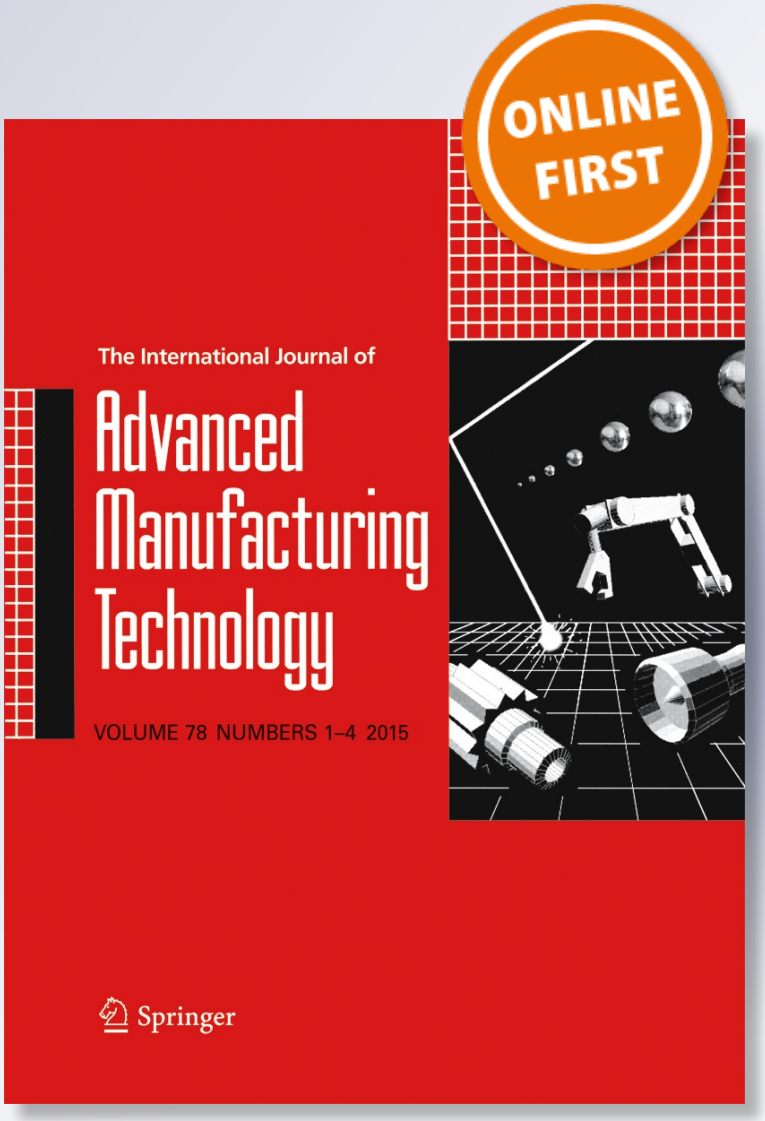

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ORIGINAL ARTICLE

Microstructure, tribological and mechanical strengthening effect of multiphase Zn/ZrO_2-SiC electrodeposited composite coatings

O. S. I. Fayomi [1,2] · A. P. I. Popoola [1] · A. Oheiza [3] · T. Adekeye [2]

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Abstract In an attempt to improve the mechanical and thermal resilient properties of mild steel, Zn-ZrO_2-SiC composite coating was fabricated from zinc-based sulphate electrolyte with incorporated composite particles of ZrO_2/SiC at 2.0 A/cm^2 for 10 min. The effects of particle on the mechanical properties were examined using scanning electron microscope attached with energy dispersion spectroscopy and atomic force microscopy. The micro-hardness and wear resistance behaviour were determined with high diamond micro-hardness tester and three body abrasive MTR-300 testers with dry sand rubber wheel apparatus with 5 N. The fabricated coating was thermally heated at 200 °C for 4 h to evaluate the coating stability. From the results, a modification in the microstructure and topographic orientation as a result of incorporated composite was noticed on the zinc matrix. The mechanical and thermal properties were observed to be considerably improved by the incorporation of the ZrO_2/SiC weight fraction. A significant improvement in wear and hardness properties were also obtained for the multiphase embedded coatings.

Keywords Microstructure · Strengthening effect · Mechanical properties · Co-deposition · Zn-ZrO_2-SiC

✉ O. S. I. Fayomi
ojosundayfayomi3@gmail.com

[1] Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, P.M.B. X680, Pretoria, South Africa

[2] Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria

[3] Department of Metallurgical and Foundry Engineering, Federal Polytechnic Idah, Idah, Kogi State, Nigeria

1 Introduction

In the past decades, mild steel has been receiving tremendous attention of the erudite researchers. This attention has been supported by many engineering applications most especially in industries for the automotive system. However, the vulnerability of this metallic material to corrosion, hardness and poor wear resistance has been a major concern. In an attempt to provide suitable remedy by material experts, coating through electrodeposition route is known to be versatile [1–3]. The use of coating for metal protection against corrosion [1], aesthetic value and mechanical improvement had been widely studied [4–6]. The breakup of coating films at certain environmental conditions could be a huge limitation to thin film industries. Effort to strengthen this atmospheric, high temperature corrosion and mechanical deformation on most fabricated components, moving vessels and equipment is thus a concern of recent [7, 8]. Alloy development with thin film co-deposition for the purpose of combating high temperature corrosion and improved mechanical value is now gaining ground [8–12].

According to [13], microstructural modification is strongly affected by the degree of addition and the kind of particles incorporated. The co-deposition of a sufficient amount of non-agglomerated particles should lead to the production of harder and more resistant coatings [14, 15]. Zirconium particles addition had been reportedly known to enhance structural build-up into Ni^+ and Zn^{2+} ion [6]. Reported work from [7, 8] affirmed that composite or ceramics co-deposited such as SiC, TiC, Al_2O_3, SnO_2 and ZrO_2 alloys had also shown reasonable properties of attention for automotive and aerospace process industries, good mechanical resistance attainment, hardness and thermal stability [16]. Interestingly, binary deposited alloy had been attested to give a more strong coating above single deposits [17]. The choice of the ternary Zn-ZrO_2-SiC alloy

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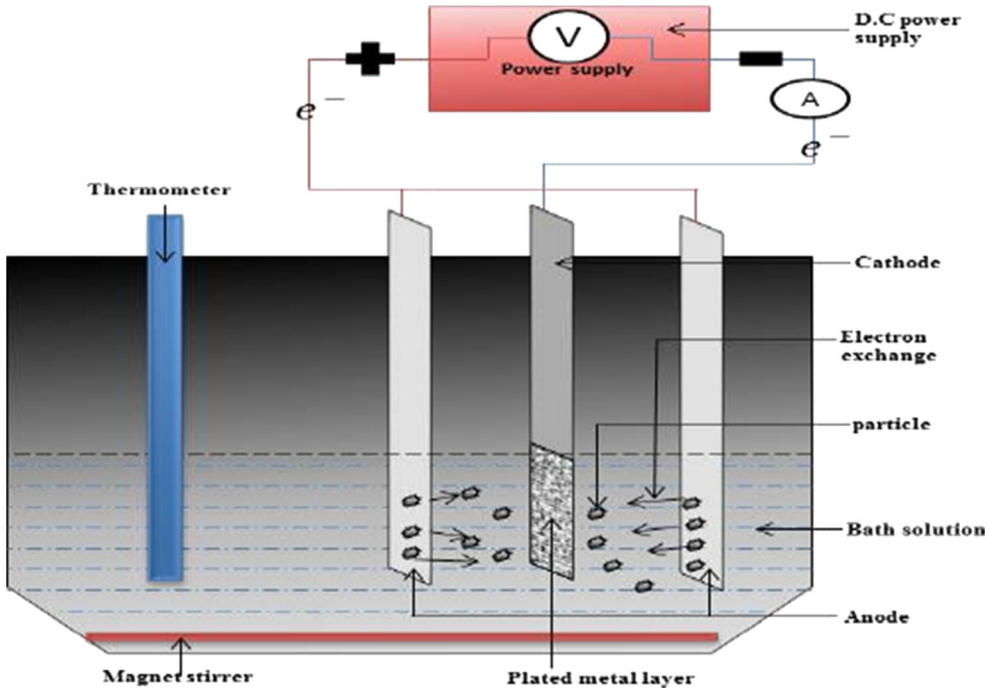

Fig. 1 Schematic diagram of electrodeposited experimental set-up

was based on improving further the tribological and structural properties using binary Zn-SiC and Zn-ZrO_2 system and investigates if both composite would affect the strengthening characteristics of the expected coating towards improved mechanical behaviour.

In view of this, the present work centres on the investigation of structural, mechanical and tribological behaviour of fabricated multiphase Zn–ZrO_2–SiC composite coatings. The tribological properties of surface-coated particles were evaluated using dry abrasive wear machine and their hardness response by diamond-based micro-hardness tester. The overall surface morphology and topography were examined by atomic force microscope (AFM), scanning electron microscope attached with energy dispersive spectrometer (SEM-EDS).

2 Experimental procedure

2.1 Preparation of the substrates

Flat specimens of commercial mild steel of 30 mm×20 mm×1 mm was used as cathode substrate, and zinc sheets of 50 mm×30 mm×2 mm as shown in (Fig. 1) were prepared as anodes. The initial surface preparation was performed with the fine grade of emery paper, properly cleaned with sodium carbonate, descaled/pickled and activated with 10 % HCl at ambient temperature for 10 s then followed by instant rinsing in deionized water. The mild steel specimens' chemical composition is shown in Table 1. The cathode was made of mild steel coupons and the anode used commercially 99.99 % pure zinc obtained from SERC research centre, Pretoria, South Africa.

Table 1 Nominal chemical composition (wt%) of mild steel substrate

Element	C	Mn	Si	P	S	Al	Ni	Fe
% composition	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance

2.2 Composition and formulation of the coating bath

In the electro-deposition processing of mild steel, Zn-ZrO_2-SiC composition alloy was performed in a single cell containing three electrodes (two anodes and one cathode). Zinc plates were used as anodes and the mild steel samples as a cathode. Prior to the plating, all chemical used were analytical grade

Table 2 Zn-ZrO_2-SiC sulphate bath formulation and plating parameters

Composition	Mass concentration/ parameter
$NaSO_4$	30 g/l
Thiourea	10 g/l
Boric acid	10 g/l
ZrO_2	10 g/l
SiC	10 g/l
$ZnSO_4$	75 g/l
pH	5.0 g/l
Current density	2.0 A/cm^2
Time	10 min
Temperature	40 °C
Stirring rate	200 rpm

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Table 3 Formulated designed bath composition of Zn-ZrO_2-SiC deposited at 10 min

Matrix sample	Weight gain (g)	Coating thickness (μm)	Current density (A/cm^2)
Zn-10ZrO_2	0.2111	192	2.0
Zn-10gSiC	0.2200	199	2.0
Zn-10gZrO_2-10gSiC	C 0.4100	250.2	2.0

and de-ionized water for all processes to prepare the plating solutions. The bath composition used for the coating is shown in Table 2; the formulated Zn-ZrO_2-SiC coating produced are presented in Table 3.

The samples were polished using 1200 grit abrasive paper. After the surface preparation, the samples were dipped in HCl for 10 s and cleaned with distilled water. Cathode and anodes were connected to the D.C. power supply through the rectifier. Electrodeposition was carried out with varying current density of 2.0 A/cm^2 for 10 min. The plating bath was continuously stirred at 100 rpm by magnetic stirrer for 2 h as described in (Fig. 1). Thereafter, the samples were rinsed again with distilled water and left to dry out.

2.3 Characterization of the deposited coatings

The microstructural evolution and elemental analysis of the sectioned fabricated coatings samples were verified using VEGA 3 TESCAN scanning electron microscope with an attached energy dispersive spectrometer (SEM/EDS). The adhesion profiles and the topography of the coatings were observed with the help of atomic force microscopy (AFM). High optic diamond-based dura scan microhardness tester was used to evaluate the average microhardness of the deposit in equal interval range with a load of 100 g for a period of 20 s. The average microhardness trend was measured across the coating interface in an interval of 20 μm using screw gauge attached to the dura hardness tester.

2.4 Thermal characterization studies

Isothermal heat treatment (direct fired furnace atmosphere) of Zn-ZrO_2-SiC composite coating was carried out at 200 °C for 4 h to check the mechanical stability of the coated samples.

2.5 MTR 300 dry abrasive wear

MTR 300 three body dry abrasive wear tests with ASTM-G65-04 dry sand rubber wheel apparatus was used to study the wear deformation properties. Figure 2 shows a schematic diagram of the wear test set-up. Silica sand procured from wear tech South Africa with a particle size between 300 and 600 μm was used as the abrasive material and set to a flow rate of 7.89 g/s. An applied load of 5 N and a rotational wheel speed of 150 revs/min were used. All samples were abraded for 5 min to evaluate the wear loss.

3 Result and discussions

3.1 SEM/EDS structural studies

Figures 3, 4 and 5 shows the SEM/EDS micrographs of composite coatings on the low carbon steel samples. For Zn-ZrO_2 alloy, the formation of the film deposit on the substrate is spherical and nodular in nature with cohesive structural grain size as observed in Fig. 3.

Disperse metal grains of Zr were seen to adhere perfectly at the surface interface thereby filling up the Zinc gap. Few solid agglomerate were observed with an interfacial precipitation of Zn-ZrO_2 matrix on steel. Elemental identification of Zr

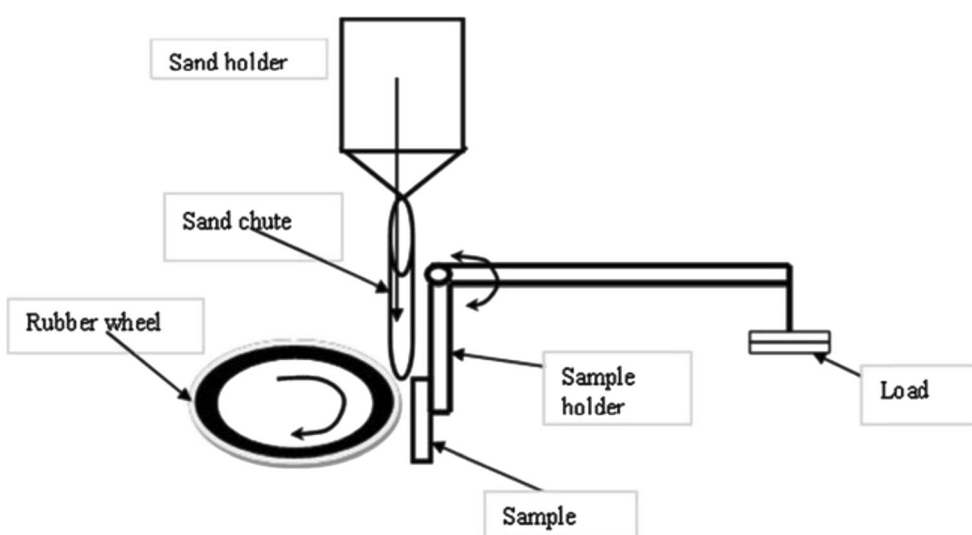

Fig. 2 Schematic representation of MTR 300 dry abrasive wear

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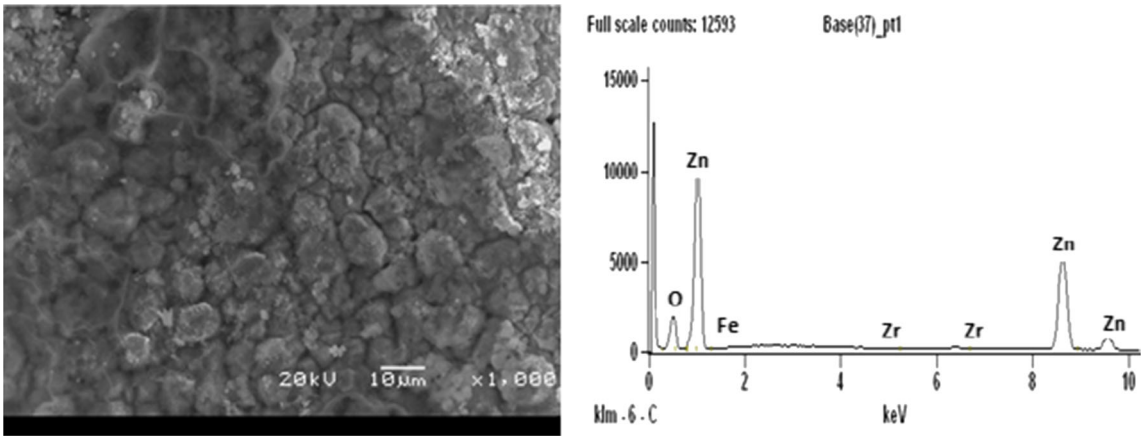

Fig. 3 Micrograph showing the SEM/EDS surface morphology of Zn-ZrO_2 sulphate deposited coating at 2 A for 10 min

particulate content on the zinc matrix is noted on the EDS pattern. The presence of ZrO_2 was observed to provide solid stability, although the results obtained was not far from what [8] noted in his report that cohesiveness of a deposit are dependent on uniform particulate distribution and the dissolving characteristics of the incorporated composite at substantial absorbing rate.

Figure 4 presents the film morphology of Zn-SiC composite electrodeposited substrate sample. From general observation, preferred homogeneous composites blend of SiC in zinc-rich was attained. The film created fine crystals ridges with pronounced equigranular structure was obtained. The SiC is fully blended into electrolyte, and a continuous structure was attained. Report by [8, 15] affirmed that the formation of crystalline particulates of zinc silicate exists higher than 1 μm from ZnO matrix as a result of Si participation in the bath. Therefore, the presence of SiC may contribute to the improved plastic oxidation properties.

In Fig. 5, the deposition of Zn-ZrO_2-SiC microstructural evolution was apparently distinctive at 2 A/cm^2. The crystal grain size was seen to be slightly much in Zn-ZrO_2-SiC phase compared to the formal as indicated in Figs. 3 and 4, respectively. The homogeneous distribution obtained in Zn-ZrO_2 (Fig. 3) and Zn-SiC (Fig. 4) might be absent in Fig. 5, the reason why heterogeneous phase often occur when different individual particulate are mixed to form a single formidable intermediate. Sometimes, agglomeration from the adsorption and precipitate of films of the conjugal grains form separate unique bond.

Nevertheless, it is essential to mention that this separate identity of the metal grain promote strengthening characteristic often than when compare to single alloy matrixes. This characterization is in line with the obtained results by [12, 13] that particle agglomeration occurs when greater attraction than repulsion energy exists between them. Secondly, there is likely oxide growth at the surface of the metal due to the interaction of Zn with O^{2-} or OH^- anions [1, 17]. In view of this, Zr^{4+} and Si cations may migrate from the oxide/metal interface to the electrolyte/oxide interface and are ejected into solution by an electric field. Field-assisted dissolution of the

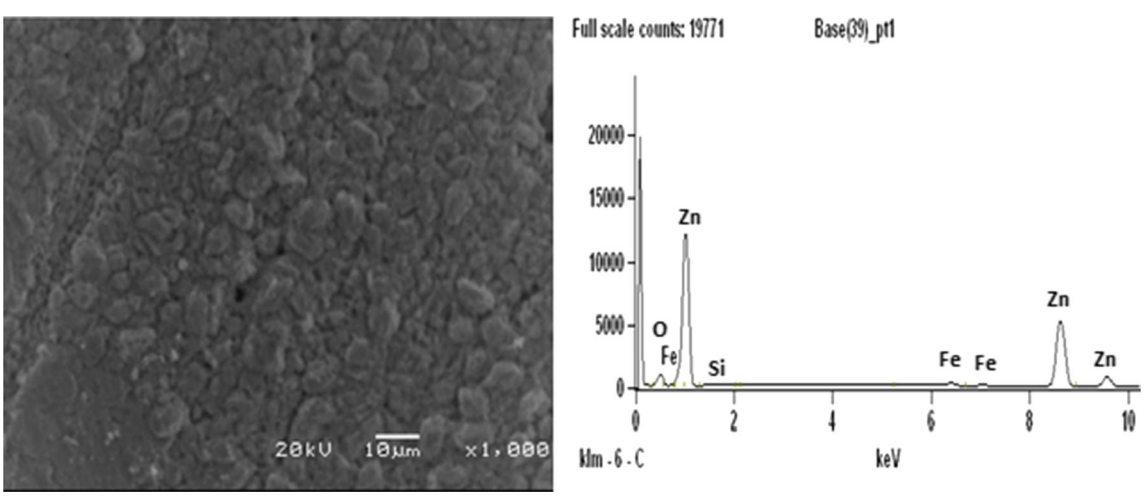

Fig. 4 Micrograph showing the SEM/EDS surface morphology of Zn-SiC sulphate deposited coating at 2 A for 10 min

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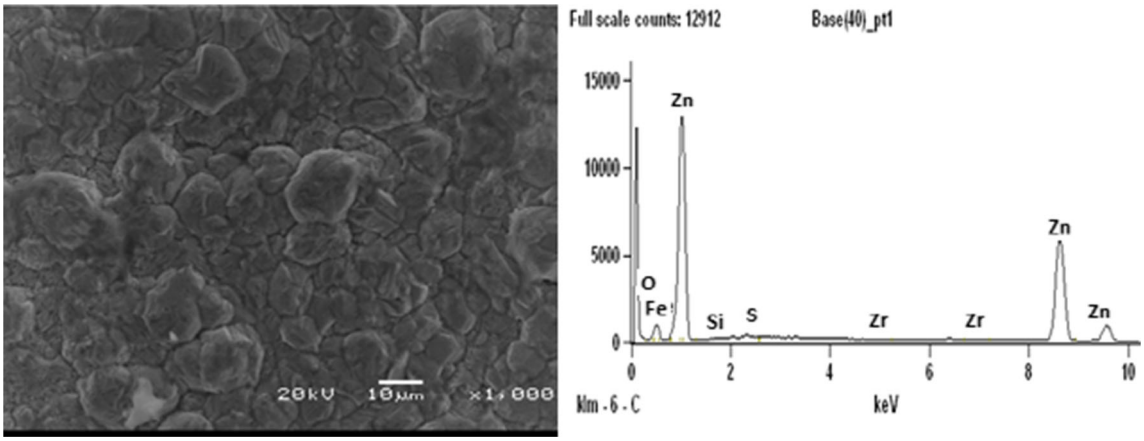

Fig. 5 Micrograph showing the SEM/EDS surface morphology of Zn-ZrO_2-SiC sulphate deposited coating at 2 A for 10 min

oxide according to [8, 17] at the electrolyte/oxide interface must have taken place as well to facilitate the growth characteristics.

In general, the magnitude of the net forces involved in producing an agglomerated structure clearly depends on the conditions and the nature of the deposited system and the induced incorporated particulates [15]. The knowledge of the interfacial region structure is a unique factor for the understanding of the dispersion stability of solid particles within electrolyte [16].

3.2 AFM studies of the composite coatings

The atomic force micrographs of the electrodeposited composite coatings on the mild steel substrate are shown in Fig. 6a–c. Figure 6a explains the structure of the surface topography of the electrodeposited film of Zn-ZrO_2 composite with fine grain surface structure but limited plateau formation. Uneven layer of film morphology is seen in Fig. 6b for Zn-SiC composite coating. The structure shows uniformity and continuity but with little valley in-between distance 10 and 15 µm in the xyz axis.

In Fig. 6c, the obtained film topography for Zn-ZrO_2-SiC deposits may be attributed to the strong diffusion of the ions into the nucleus of the matrix metal. There are good blending and homogenisation of structure but separate topography phase. The introduction of ZrO_2 into Zn-SiC electrolyte possibly improves the coalesce characteristic compared to other deposit in binary phase. In all, it should be noted that deposits surface roughness for Zn-ZrO_2-SiC is affected by the presence of particles suspended. Composite coatings are considered to be rougher than the particle-free coatings due to particles entrapment [5, 6].

3.3 Microhardness behaviour of the fabricated coatings

Figure 7 presents the micro-hardness plot for the deposits at different processes and their comparative micro-hardness of the steel substrate and the electrodeposited coatings with different bath compositions matrix prior thermal treatment. The grain morphology was seen to promote the surface microhardness properties as shown in Fig. 7. The highest hardness value for the deposits is 245 HVN for Zn-ZrO_2-SiC followed by 240 HVN obtained for Zn-ZrO_2 composites electroplated at 2.0 A/cm^2 which is relatively 60 % higher than the micro-hardness value of (143 HVN) obtained for the control steel substrate. It is obvious that the increase in the hardness value may be attributed to the particle inclusion in the Zn matrix which helps in the built-up of adhered thin crystal. This observation is in line with the findings of [7, 8] that network of composite

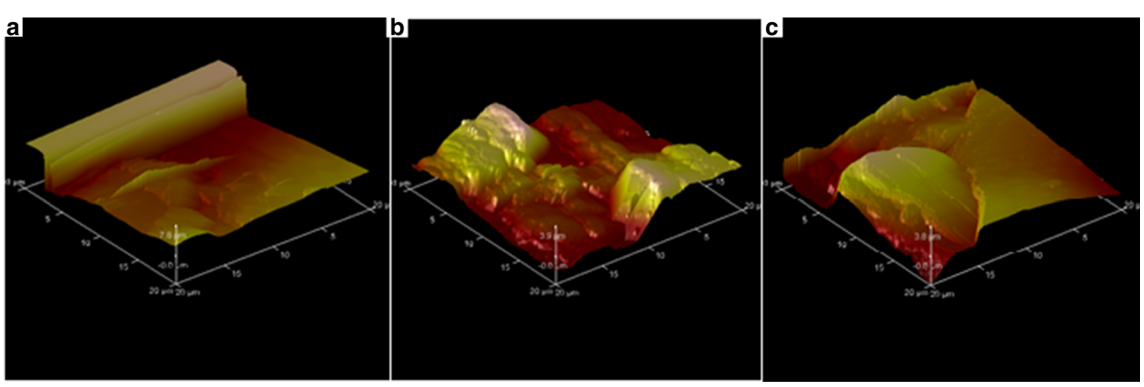

Fig. 6 Atomic force micrograph of **a** Zn-ZrO_2, **b** Zn-SiC and **c** Zn-ZrO_2-SiC sulphate deposited coating at 2 A for 10 min

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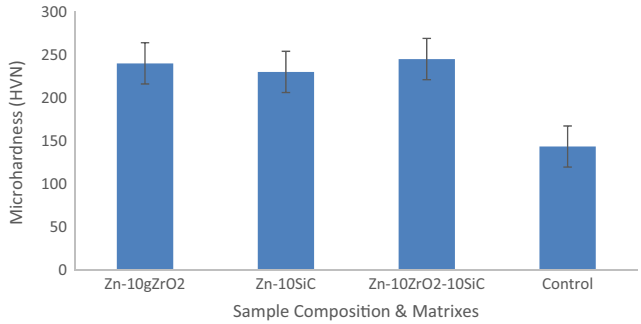

Fig. 7 Micro-hardness/depth profile transition of Zn-ZrO_2-SiO_2 composite coating prior to heat treatment

with SiC influence refinement and proper nucleation of the bath constitute which results in structural change. The new structural orientation thereby affect hardness trend.

On the other hand, weight fraction of ZrO_2 content into the metal lattices resulted into solid structure thereby forming a suitable adhesion and enhancement of hardness properties, although the processed parameters such as degree of agitation, temperature, current density, time, etc. often contribute immensely to change in mechanical properties of a coating. However, at stable processed parameter and variation in composite loading, improved structural built up was attained which significantly provided change in micro-hardness and reduced plastic deformation trend. Reasons for this change in characteristics are dependent on the intermetallic phase assisted by stable process properties which resulted in improved mechanical performance. Comparison of the deposits shows that the irregularities of the particle embedded at the metal/film interface of the binary phase of SiC and ZrO_2 results to a reduction in the hardness value compared to the ternary phase which is in line with the study reported by [8, 17]. More so, it is important to conclude that the bonding properties of SiC/ZrO_2 on Zn rich influence the grain size which is paramount to the multiphase improvement of surface hardness obtained.

3.4 Effect of thermal treatment on the composite coatings

Figure 8 illustrates the micro-hardness of thermal heated deposited coatings treated at 200 °C in 4 h with furnace cooling. From the comparative study of heat-treated and non-heat-treated fabricating coatings from the plots, there is slight decrease in stability of the coatings at various incorporative additives due to thermal treatment of the coated samples, although the behaviour of this deposited alloy at different fabricated coatings still gains significant improvement above the as-received sample with over 60 %. In other words, the little depreciation might be due to little agglomeration which might cause pilled ups of thin films and secondly the unseen voids from the microstructural phase as a results of adhesion. It is expected that the thermal treatment could give a relieve of

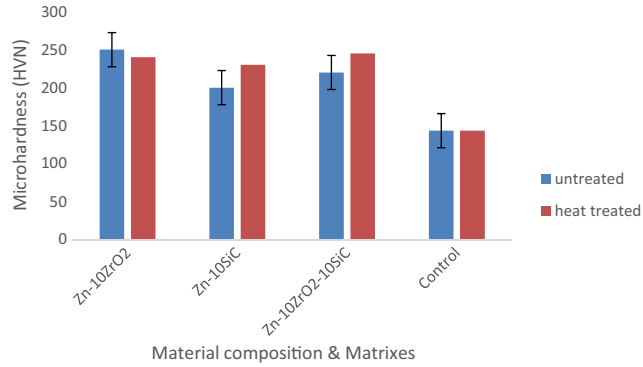

Fig. 8 Comparative micro-hardness trend of deposited composite coatings prior and after heat treatment at 200 °C

stress or grain re-structuring of the electrodeposited film [14, 15] which could either improve or reduce the micro-hardness property as seen in Fig. 8. In view of this, the thermal treatment of the binary composite Zn-SiC and Zn-SiC/ZrO_2 would make it useful for the high temperature application.

3.5 Wear properties of fabricated coatings

The wear loss characteristics of Zn-ZrO_2-SiC and its binary alloys on dry abrasive tester in 5 N force were presented in Fig. 9. The variation of the wear loss is defined as a function of time for all the samples. From all indication, wear loss is very high for the as-received sample (0.08 g/min) as compare to other deposited fabricated alloy. Zn-ZrO_2-SiC possesses good wear resistance performance of 0.01 g/min over the Zn-SiC and Zn-ZrO_2 with 0.03 g/min each. This great influence by the ternary incorporated coatings may be attributed to the high notch of particles travelled from the bath through the influence of the applied voltage as a result of the good throwing power and the conditioning of the bath formulation as attested by [8, 13]; secondly, the microstructural evolution developed by the Zn-ZrO_2-SiC could be seen to strengthen the adhesion properties to retard plastic dislocation to a minimum level as

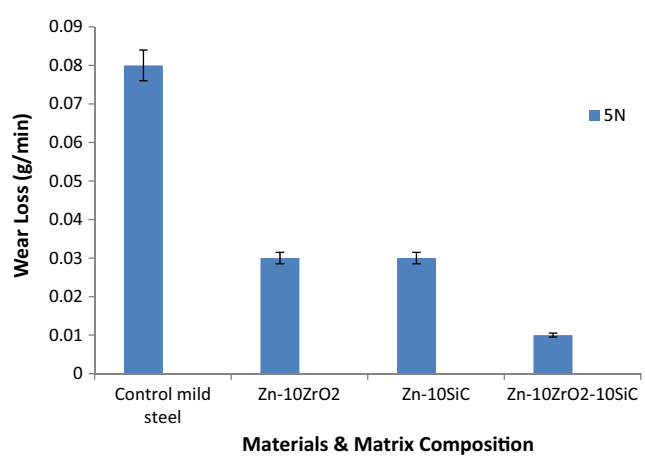

Fig. 9 Comparative wear characteristics of Zn-ZrO_2-SiO_2 composite coating deposited alloy series

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indicated in the variation in Fig. 9, although these results are not far from attested properties that [5, 10] noted that stable adhesion had a better flow than the visible irregular structure from reinforcement in composite grains which could alter positively the compatibility of the coatings by reducing possible scaling and increased the wear resistance.

4 Conclusion

- ZrO_2/SiC have been successfully co-deposited with Zn metal matrix to fabricate Zn/ZrO_2-SiC ceramics composite coating. The presence of ZrO_2/SiC nanoparticles in the deposition bath influences the microstructural properties of the electrodeposited Zn–ZrO_2-SiC coatings.
- The concentration of ZrO_2/SiC nanoparticles in the plating bath leading to developed new composite layer of Zn–ZrO_2-SiC was found to affect the micro-hardness properties with over 60 % improvement against the control sample.
- The response of wear and abrasive deformation was very minimal for the ternary phase Zn–ZrO_2-SiC composite coating under the examined conditions which is in agreement with the results obtained from the hardness performance.
- All coatings show a significant response to thermal stability at 200 °C in 4 h.

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