
NANOSCALE AND NANOSTRUCTURED
MATERIALS AND COATINGS

Evaluation of Composition, Microstructure Characterization and Interfacial Properties of Zn–SnO₂ Metal Matrix Composite Coating¹

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Abstract—In this paper the microstructure and tribological behavior of Zn–SnO₂ (Zn–Sn) alloys produced through chloride and sulphates co-deposition is presented for comparison. 7.0 wt % SnO₂ was added to Zn bath and deposited at 0.3 V. The interfacial effect and microchemistry of the fabricated composite was studied by optical microscope, X-ray diffraction (XRD), scanning electron microscope (SEM) equipped with energy disperse spectrum (EDS). The tribological behavior of the metal composites with SnO₂ particles as reinforcement was studied using reciprocating sliding tester. The scanning electron microscopy (SEM) and atomic force microscope (AFM) of the composite surfaces indicates that there is good interfacial interaction between the alloy formulated matrixes made from the two baths and the substrate. Reasonable uniform distribution of Sn metal phase particulates is shown for both coating alloy. Increases in hardness and wear resistance are attributed to the uniform and coherent precipitation in the metal interface especially for Zn–7Sn–S–0.3V. In general, 7 wt % Sn additions to the bath showed more hastening to improved surface properties and better mechanical characteristics.

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1. INTRODUCTION

Nowadays, metals and their composites are being increasingly engaged globally due to their unique combination and characteristics of good low density, improved corrosion resistance, and excellent mechanical properties [1–10]. However, series of progression of composite and ceramics like TiO₂, Al₂O₃, Fe₂O₃, C₁₂O₃ SiC, and CeO₂, etc., to produce variety of specialize products from automobiles diversity part to beverage can and aerospace structure in their individual or in combination with other metal has proved to give corrosion, wear resistance and unique thermal properties [8–17].

The tribological characteristics and hardening behavior of any coating are mostly modified by the introduction of particulate elements and composite modifier [18–21]. These morphological modifications are due to the coating process, the inter-diffuse reaction between the composite particulate and the base metal, the applied working potential, the volume fraction of the composite materials induced and other process parameter [22–29]. Interestingly, SnO₂ particle which has semiconductor characteristic, tin char-

acteristic are refers to as player in the development of ceramic appearance. It's variegated with other metals to provide a unique character for engineering application in beverage manufacturing processes [11–13, 31].

Present investigations of metal based composite materials affirmed that metal matrix composite informs of carbide, oxide, ceramics and polymers are well known to define the great features in electrolytic processing through direct dispersion on the composite in aqueous sulphates or chloride bath [30–36], and secondly the properties of any produce alloy are basically influence by bath formulation and condition. Hence, since sulphates and chloride bath are two different formulation for surface modification, it become a priority to understand the knowledge of their physical, microstructure and mechanical properties produce in relationship to their process design. Since, It was affirmed that the surface modification provide better surface stability to thermo-mechanical and tribo-oxidation properties [32–36]. Hence, the objective of this present research study is to investigate how the structural, hardness and wear characteristics of the produce composite alloy are affected by different process condition.

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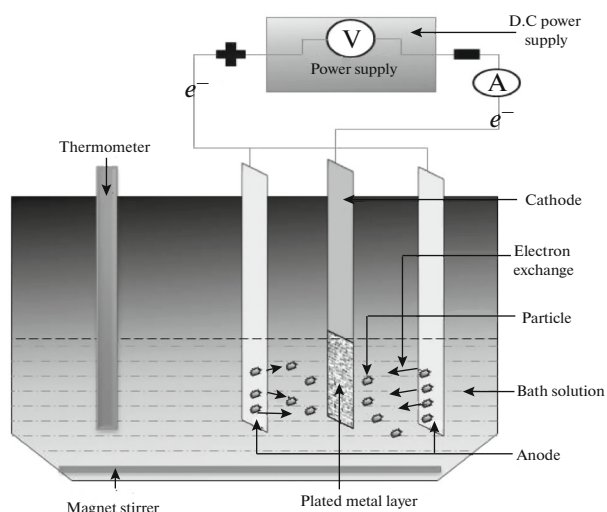


Fig. 1. Schematic diagram of electrodeposited system.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Substrates

Mild steel of (40 mm × 20 mm × 1 mm) sheet was used as cathode substrate, and 99.5% zinc plate of (30 mm × 20 mm × 1 mm) were prepared as anodes. The initial surface preparation was performed with finer grade of emery paper as described in our previous studies [1, 6]. The sample were properly cleaned with sodium carbonate, pickled and activated with 10% HCl at ambient temperature for 10 s then followed by instant rinsing in deionized water. The mild steel specimens were obtained from metal sample site Nigeria. The chemical composition of the sectioned samples is shown in Table 1 as obtained from spectrometer analyzer.

2.2. Processed Composition

The chemical bath of Zn–SnO₂ fabricated alloy was processed in a separate two cell containing two zinc anode and single cathode electrodes as described

schematically in Fig. 1 for both sulphates and chloride formulation. The distance between the anode and the cathode is the two separate cell is 15 mm. Before the plating, All chemical used are analytical analar grade and de-ionized water were used in all solution admixed and preheat at 40°C. The processed parameter and bath composition admixed used for the sulphates and chloride coating is shown in Table 2 and 3. The choice of the deposition parameter is in line with the preliminary study and our previous work [6, 9].

The prepared electrode were connected to the direct current via a rectifier at varying applied potential and current density of 0.3 V at 2 A for 20 min constant time. The distance between the anode and the cathode and the immersion depth was kept constant as described by [10]. The plating was done, rinsed in distilled water and samples were air-dried thereafter sectioned for characterization.

2.3. Characterization of Coating

The structural evolution of the deposited composite coating alloy was characterized with VEGA TESCAN Scanning electron microscope equipped with EDS. The phase change was verified with XRD. Microhardness studies were carried out using a Diamond pyramid indenter EMCO Test Dura-scan 10 microhardness testers at a load of 10 g for a period of 20 s. The average microhardness trend was measured across the plated surface in an interval of 2 cm using screw gauge attached to the Dura hardness tester

2.4. Friction and Wear Tests

The friction and wear properties of the deposited quaternary alloy fabricated were measured using CERT UMT-2 multi-functional tribological tester at ambient temperature of 25°C. The reciprocating sliding tests was carried out with a load of 5 N, constant speed of 5 mm/s, displacement amplitude of 2 mm in 20 min. A Si₃N₄ ball (4 mm in diameter, HV50g1600) was chosen as counter body for the evaluation of tribological behavior of the coated sample. The dimension

Table 1. Chemical composition of mild steel used (wt %)

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

Table 2. Bath composition of Zn–SnO₂ chloride alloy co-deposition

Sample Order	Material sample	<i>t</i> , min	Potential, V	Current, A	Con. of additive, g
Blank	—	—	—	—	—
Sample 1	Zn–7SnO ₂ –0.3V–Sulphate	20	0.3	2A	7
Sample 2	Zn–7SnO ₂ –0.3V–Chloride	20	0.3	2A	7

t—Time of deposition.

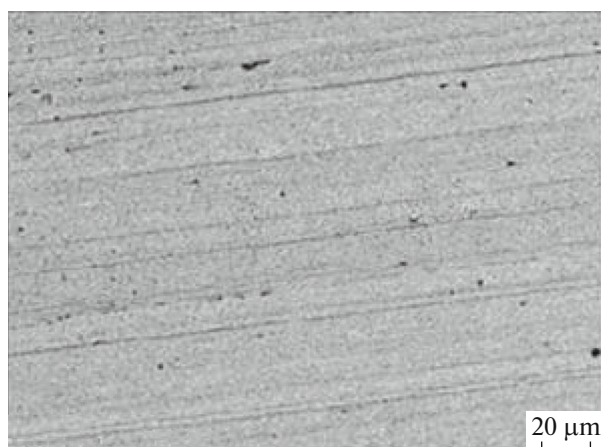


Fig. 2. SEM microstructure of the as-received sample.

of the wear specimen is 2 cm by 1.5 cm as prescribed by the specimen holder. After the wear test, the structure of the wear scar and film worn tracks are further examined with the help of high optic Nikon Optical microscope (OPM) and scanning electron microscope couple with energy dispersive spectroscopy (VEGAS-TESCAN SEM/EDS).

3. RESULTS AND DISCUSSIONS

3.1. Microstructural Studies

Figures 2 show the microscopy examination of the as-received surfaces of the mild steel substrate before deposition. The microstructure of the composite coating deposited through sulphates (Zn-7Sn-S-0.3V) and chloride (Zn-7Sn-Cl-0.3V) bath are presented in Fig. 3a-b respectively. When comparing the deposits from the surface features, formation of the composite coated layers of Zn-7Sn-0.3V gave good account of its adhesion. Although both alloys have good appearance, fine crystal and well disperse flakes was noted for sulphates deposited as seen in Fig. 3b [26, 35] confirm that mass transport might necessitate surface homogeneity deterioration as the thickness of layer gets increased which is in line with the observation from sulphates deposit. For the Zn-7Sn-Cl-0.3V thin films an appreciable film deposit also occurs but not properly dispersed. However, bath composition and parameter, composite particle have strong effect on the deposit surface structure which is caused by the changes in deposition mechanism, the nucleation and the proportion. One vivid observation is that the surface structure of the Zn-7Sn-S-0.3V shows a non-porous characteristic with Sn distributed within the Zn coating interface.

According to [10, 12–14] deposit composition can be influenced by bath control parameter. In all sample, a significant structural chains was witnessed in the morphology as a results of applied potential, current

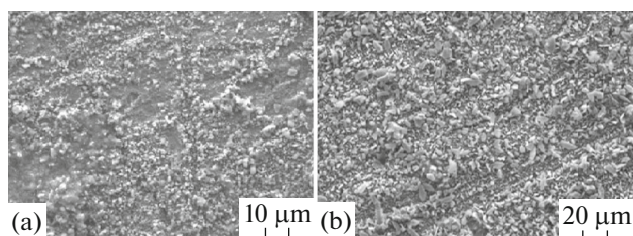


Fig. 3. SEM microstructure of the Zn-SnO_2 sulphates and chloride deposition. (a) SEM images of Zn-7Sn-Cl (b) SEM images of Zn-7Sn-S .

densities and time of deposition. The EDS analyses performed on the deposit of the chloride morphologies obtained revealed that the deposit contains zinc and tin within the interface see Fig. 4. To pair the morphology, atomic force topographic studies of as-deposited thin film Zn-SnO_2 alloy from sulphates and chloride induced were examined as shown in Fig. 5. It is evident from the binary Zn-7Sn-S-0.3V film deposit is more finely grained and had excellent surface appearance triumphed compared to deposit produced in Fig. 5a. With Zn-7Sn-Cl-0.3V alloy damping are much pronounced in the lattices. The topography was not well expressed out as expected form chloride composite coating compare to the sulphates alloy. From all indications, preferred crystal growth uniformity was obtained from Zn-7Sn-S-0.3V (Fig. 5b). This is attributed to the strong diffusion of the sulphates ions creating nucleation there after absorbed atom wanders around the cathode for more homogeneous diffusion.

Table 3. Summarized data of deposited samples for Zn-SnO_2 sulphates/chloride bath formulation

Composition	Sulphates Mass conc, g/L	Chloride Mass conc, g/L
Zn	75	75
KCl	–	50
K_2SO_4	50	–
Boric Acid	10	10
SnO_2	7g–13g	7g–13g
ZnCl	–	75
ZnSO_4	75	–
pH	4.8	4.8
Voltage	0.3–0.5 V	0.3–0.5 V
Time	20	20
Temp	40°C	40°C

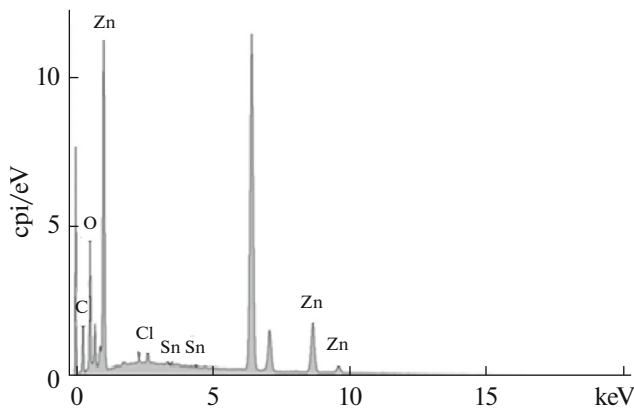


Fig. 4. EDS pattern of Zn-SnO₂-0.3V-Cl Composite alloy.

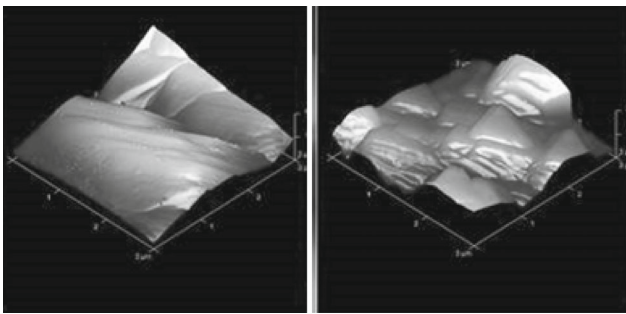


Fig. 5. AFM images of Zn-SnO₂. (a) AFM images of Zn-7Sn-Cl (b) AFM images of Zn-7Sn-S.

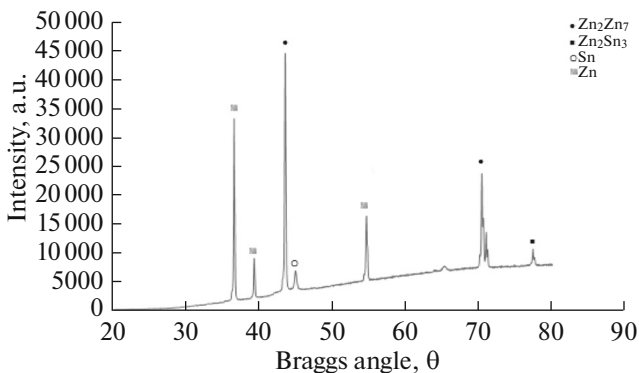


Fig. 6. XRD pattern of Zn-SnO₂-S.

More importantly, Fig. 5a in its zinc rich composite admixed deposit, is of less regular distribution. Meanwhile, a better homogeneous dispersal of Zn-7Sn-S-0.3V on the substrate adhered significantly with fewer pores achieved as a result of the increased additive deposit see Fig. 5b. From observation, most composite coating with coarsely grained can produce a more homogeneous diffusion regardless of the protrusions.

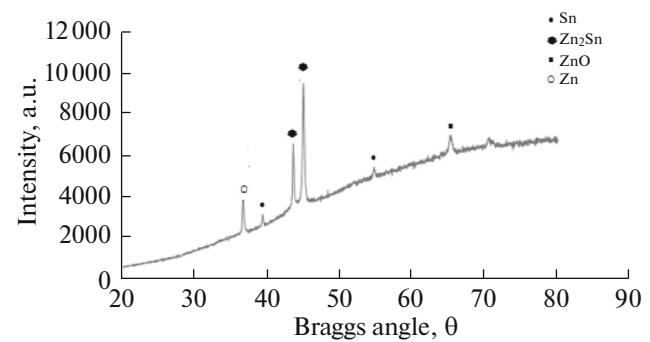


Fig. 7. XRD pattern of Zn-SnO₂-Cl.

3.2. XRD Analysis

The X-ray diffraction pattern of the deposited layers that were coated Zn-7Sn-S-0.3V and Zn-7Sn-Cl-0.3V alloy on mild steel are given in Figs. 6 and 7 respectively. From the phase check for Zn-7Sn-0.3V sulphates pattern Zn, ZnO, Zn₃Sn₇, and Zn₇Sn₃ phases were identified in the coating system (Fig. 6) the major diffractive peak are 38.2°, 24.52°, 55° and 70.12°. The observation for Zn-13Sn-0.3V coating indicate a phase pattern with Zn, ZnO, Sn, Zn₂Sn₂O₂ and Zn₂Sn with major diffractive peak at 38.2°, 43.5° and 45.5° (Fig. 7) as compare to the later. Though, both alloy justify the inclusion of the conditioning SnO₂ composite, however, in correlating the phase change, sulphates alloy maintain its superiority over chloride deposits. It is also a well-known fact that peak intensity resulting from a deposit is a function of the solid crystal and adhesion produced [15, 16]. From the earlier observed structure of Zn-SnO₂, sulphates coating, the predominate intensity of the sulphates coating against the chloride thin film could be as a results of Sn₇Zn phase and other constitutes at the intermediate.

3.3. Microhardness Characterization

The average microhardness results for the compared Zn-SnO₂ composite thin film coating from the various baths were examined and presented in Fig. 8. For critical comparison of the deposited matrix Zn-7Sn-0.3V sulphates show good properties and better improvement above the control samples and the chloride fabricated alloy. The resultant hardness increases from 35 HVN for base mild steel to approximately 116 HVN for the sulphates produced coating.

In general, the hardness profile data for all the samples shows significant average increase with the chloride matrix possessing average of 100 HVN. This further implies that the improvement in hardness double the microhardness of substrate which was attributed to the formation of adhesive mechanism of the composite coating on the working sample. More

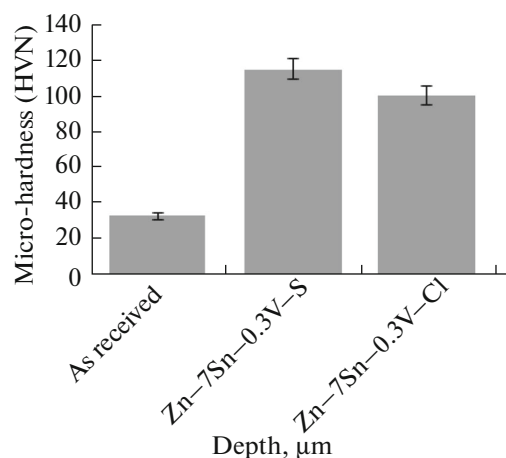


Fig. 8. The microhardness behavior of Zn-7SnO₂-0.3V in sulphates and chloride deposition.

so, it is a well-known fact that the microhardness of the electrodeposited layers can depend on several factors which among essentially include electrolyte or bath formulation [10, 27, 29]. On the other hands, microstructural evolved in coating hinge on the processing parameters which simultaneously emitted into the kind of hardness properties obtained.

3.4. Wear Characterization

Table 4 show the progression of the wear rate as a function of concentration of additives, potential of deposition and bath properties of the successful thin films composite coating. It was observed from the results that wear resistance properties are attained by all co-deposited metal alloy with significant improvement.

The as-received sample have a terrific high rate of wear deformation; in the other hand, all composite induced fabricated alloys have shown a positive level of decrease in plastic deformation with Zn-7Sn-0.3V sulphates indicating an exceptional decrease in surface dislocation. The frictional coefficient was low for Zn-7Sn-0.3V-S as the sliding speed decreases even with coating fabricated with chloride alloy. This behaviour is attributed to the super-potential and activity of SnO₂ influence within the bath formulation. The effort of the thin film helps in the resistance of the damage that could have accelerated the high frictional value. Although, [28, 29] Affirmed that nanoparticle depos-

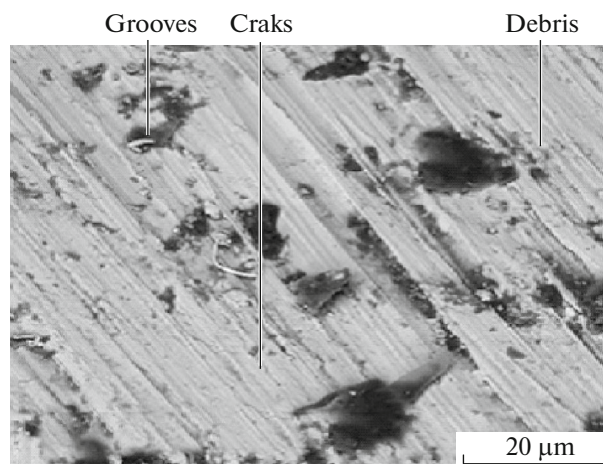


Fig. 9. Morphology of the worn surface of as-received sample.

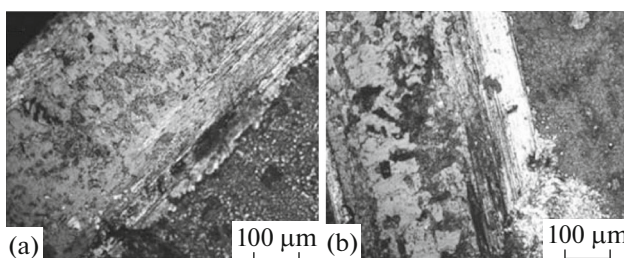


Fig. 10. Morphology of the worn surface of (a) Zn-7Sn sulphates (b) Zn-7Sn chloride composite coating.

ited form a surface protective film which may result to significant anti-wear ability and hence provide a reduce coefficient of friction.

The morphologies of wear scar observe under both condition are presented in Fig. 10 and over all compared with the as-received samples as indicated in Fig. 9. The worn structure revealed debris, groove and crack within as-received surfaces. The damage seems obvious as the voids are massive along the wear track.

This is really expected as it was earlier examined from the degree of the coefficient of friction attain in Table 4. For the both composite coating alloy, there seem a drastic decline in penetration. Although, [14, 17, 26] attested in their study that with thin film within the working samples surfaces, the precipitation and solid intermediate protect against fracture and debris.

Table 4. The value of individual variables with their coded value and wear response

S. no.	Applied load, N	Sliding speed	Coefficient of friction	Wear rate
As-received	5	0.00236	0.655	2.351
Zn-7SnO ₂ -0.3V-S	5	0.00333	0.453	0.005
Zn-7SnO ₂ -0.3V-Cl	5	0.00253	0.455	0.007

In the other hand, the continuous increase in the coefficient of friction during sliding system is attributed to the increase in plastic deformation and fracture seen in the wear morphology in the as-received sample as compare to the few scar noticed with the protected coatings.

4. CONCLUSION

—A bright successful co-deposition were fabricated from bath containing sulphates and chloride induced system with average ratio of $\text{Sn}^{2+}/\text{Zn}^{2+}$ without brighter;

—After successful codeposition, it was observed that adding a small % of SnO_2 particles into the sulphate bath improved the microstructural properties of the Zn–Sn alloy. The Sn ions dissolve homogeneously and further increase the oxidation resistance of the SnO_2 scale over the chloride bath fabricated alloy;

—The hardness value of all deposited alloy increased significantly especially for Zn–Sn–S as against the mild steel substrate. From general observation Zn–7Sn–Cl–0.3V had a better buildup of particulate that enhanced the improvement of hardness from 33 HVN for the as received substrate compared to 116 HVN for best composite coating;

—A good anti-wear behavior was obtained for Zn–7Sn–S–0.3V alloy coating; the friction coefficient is low compared to as-received based metal and chloride alloy. Although both bath performed excellently well.

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REFERENCES

- Popoola, A.P.I., Fayomi, O.S., and Popoola, O.M., *Int. J. Electrochem. Sci.*, 2011, vol. 6, p. 3254.
- Praveen, B.M. and Venkatesha, T.V., *Appl. Surf. Sci.*, 2008, vol. 254, p. 2418.
- Chuen-Chang, L. and Chi-Ming, H., *J. Coat. Technol. Res.*, 2006, vol. 3, p. 99.
- Xu, R., Wang, J., Guo, Z., and Wang, H., *J. Rare Earths*, 2008, vol. 26, p. 579.
- Sancakoglu, O., Culha, O., Toparli, M., et al., *J. Mater. Des.*, 2011, vol. 32, p. 4054.
- Fayomi, O.S.I. and Popoola, A.P.I., *Res. Chem. Intermed.*, 2013, vol. 39, p. 135.
- Mohankumar, C., Praveen, K., Venkatesha, V., et al., *J. Coat. Technol. Res.*, 2012, vol. 9, p. 71.
- Abdel, A., Barakat, M.A., and Mohamed, R.M., *Appl. Surf. Sci.*, 2008, vol. 254, p. 4577.
- Fayomi, O.S.I., Abdulwahab, M., and Popoola, A.P.I., *J. Ovonic Res.*, 2013, vol. 9, p. 123.
- Popoola, A.P.I., Fayomi, O.S.I., and Popoola, O.M., *Int. J. Electrochem. Sci.*, 2012, vol. 7, p. 4860.
- Kazimierzak, H. and Ozga, P., *Surf. Sci.*, 2013, vol. 607, p. 33.
- Hu, C. and Wang, C., *Electrochem. Acta*, 2006, vol. 51, p. 4125.
- Finazzi, G., Oliveira, E., and Carlos, I., *Surf. Coat. Technol.*, 2004, vol. 187, p. 377.
- Yang, G., Chai, S., Xiong, X., et al., *Trans. Non-Ferrous Met. Soc. China*, 2012, vol. 22, no. 2, p. 366.
- Rahman, M., Sen, S., Moniruzzaman, M., and Shorowordi, K., *J. Mech. Eng.*, 2009, vol. 40, p. 9.
- Dong, D., Chen, X.H., Xiao, W.T., et al., *Appl. Surf. Sci.*, 2009, vol. 255, p. 7051.
- Mo, J.L., Zhu, M.H., Lei, B., et al., *Wear*, 2007, vol. 263, p. 1423.
- Dikici, T., Culha, O., and Toparli, M., *J. Coat. Technol. Res.*, 2010, vol. 7, p. 787.
- Volinsky, A.A., Vella, J., Adhietty, I.S., et al., *Mater. Res. Soc.*, 2001, vol. 649, p. 1.
- Rusu, D.E., Ispas, A., Bund, A., et al., *J. Coat. Technol. Resour.*, 2012, vol. 9, p. 87.
- Gençga, P., Temel, S., Tevfik, K., and Samuel, M., *Wear*, 2002, vol. 894, p. 901.
- Abou-Krishna, M.M., Assaf, F.H., and El-Naby, S.A., *J. Coat. Technol. Res.*, 2009, vol. 26, p. 391.
- Subramanian, B., Mohan, S., and Jayakrishnan, S., *Surf. Coat. Technol.*, 2006, vol. 201, p. 1145.
- Zum Gahr, K.H., *Wear*, 1996, vol. 200, p. 215.
- Hammami, O., Dhouibi, L., Bercot, P., et al., *Int. J. Corros. Sci.*, 2012, p. 1.
- Popoola, A.P.I., Fayomi, O.S.I., and Popoola, O.M., *J. Electrochem. Sci.*, 2012, vol. 7, p. 4898.
- Frade, T., Bouzon, Z., Gomes, A., et al., *Surf. Coat. Technol.*, 2010, vol. 204, p. 3592.
- Zhang, W., Liu, W., and Wang, C., *J. Eur. Ceram. Soc.*, 2002, vol. 22, p. 2869.
- Prasad, B.K., *Wear*, 2008, vol. 20, p. 301.
- Mohankumar, C., Praveen, K., Venkatesha, V., et al., *J. Coat. Technol. Res.*, 2012, vol. 9, p. 71.
- Arici, M., Nazir, H., and Aksu, A., *J. Alloys Compd.*, 2011, vol. 509, p. 1534.
- Fustes, J., Gomes, A., and Silva Pereira, D., *J. Solid State Electrochem.*, 2008, vol. 121, p. 1435.
- Wang, T.G., Jeong, D., Liu, Y., et al., *J. Surf. Coat. Technol.*, 2012, vol. 206, p. 2638.
- Chacko, S.M.A., Chacko, F., and Divya, C., *Corros. Sci.*, 2010, vol. 52, p. 518.
- Gomes, A., Frade, T., and Nogueira, I., *Current Microscopy Contributions to Advances in Science and Technology*, Microsc. Book Ser., Badajoz, Spain: *Formatex Res. Center*, 2012, vol. 2, p. 1146.
- Srivastava, M., Balaraju, J., Ravishankar, B., and Rajam, K., *Surf. Coat. Technol.*, 2010, vol. 205, p. 66.