Journal of Alloys and Compounds 637 (2015) 382–392

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Development of smart oxidation and corrosion resistance of multi-doped complex hybrid coatings on mild steel

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ARTICLE INFO

Article history:
Received 22 January 2015
Received in revised form 18 February 2015
Accepted 20 February 2015
Available online 28 February 2015

Keywords:
$Zn–Al–SnO_2–TiO_2$
Composite
Multifunctional deposition
Interfacial interaction

ABSTRACT

The microstructure, mechanical and thermal treatment behavior of $Zn–Al–SnO_2/TiO_2$ (Zn–Al–Sn/Ti) produced through chloride deposition system was studied. 7.0–13.0 wt% TiO_2 and SnO_2 was added to chloride Zn–Al bath. A thermal treatment characteristic was done for 2 h at 200 °C, 400 °C and 600 °C. The ageing behaviors of the co-deposited alloys were evaluated using (SEM/EDS) and XRD. The hardness and wear value of the solid coatings were examined with micro-hardness and UMT-2 sliding tester respectively. The corrosion properties were investigated by linear polarization method in 3.65% NaCl environment. From the obtained results, the deposited alloys revealed excellent stability. The even distribution of the particulate on the produced coating and thermal-treatment were observed to cause the improvement on mechanical, tribological and electrochemical properties. The overall best coating was obtained at Zn–Al–7Sn–Ti–0.3V–Cl for as-coated and Zn–Al–7Sn–Ti–0.3V–Cl at 400 °C for the thermo-mechanical treated samples. The hardness, corrosion and micro-mechanical resistance performance against the working substrate were depended on the development of coherent and regular precipitation from the incorporated strengthening particulate.

1. Introduction

Despite the impact of zinc based coatings as a result of their excellent mechanical and electrochemical resistance properties for steel protection in industrial applications, their less becoming popular are due to poor reaction in atmospheric environment and lesser life-span from thermal and mechanical fallout [1–4]. Consequently, tremendous approaches from literature survey to improve on this limitation are being made on the use of metal–reinforcement composite combination and manufacturing process variables [5–13]. Lately the intention on the choice of composite particulate is due to their significant constituent of solid grains and the novel attention such properties gives in advanced materials [1,14–20].

The suspended co-deposition of metal composite such as SiO_2 [16,22], Cr_2O_3, TiO_2 [19,20], ZrO_2, Al_2O_3 SnO_2 CeO_2 and ZnO [19–25] had been established to offer vital functional individual properties. However [1] attested that for excellent application especially in high temperature performance, high surface modifications are required and incorporation of high temperature composite particle had been proven to provide such safeguard. Regrettably, results on modified-binary composite alloys through this route are prone to possess possible limitation for high temperature performance, wear vulnerability and electrochemical defects.

Furthermore the control of formulated variable for advance materials also has been crucial consideration in metal matrix composite co-deposition. The wear deformation characteristics, corrosion resistance, thermo-mechanical stability and tribo-oxidation behavior of binary alloy composite coating have been reported to give stability only at ambient environment [1,21]. To the best of our knowledge from literature, there were no works done on quaternary particle reinforced using electrolytic route on Al, TiO_2 and SnO_2 especially when subjected to the heat-treatment and wear behavior for multi-facial application in single system. Although, there individual characteristics are known for exceptional properties on zinc blend [18,19,23,26].

In the light of this, since bath formulation and process parameter constitute to the kind of coating properties. We have attempted a successful sulphates produced quaternary alloy in our previous work [1] in a view to improve the tribological and poor thermal stability of the binary-modified composite coating. Our aim in this study is to fabricate a chloride modified structure by quaternary

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http://dx.doi.org/10.1016/j.jallcom.2015.02.154
0925-8388/

metal composite matrix which will offer good thermal stability; improve micro-mechanical properties, and excellent corrosion behavior with stable interfacial characteristics. The wear and structural properties of the co-deposited alloy was evaluated using sliding wear tester, and their morphological crystal structure/topography was characterized by means [AFM, SEM/EDS and OPM]. The phase patterns were examined with the help of X-ray diffractometer (XRD) and Raman.

2. Experimental procedure

2.1. Preparation of substrates

Sectioned flat specimens from commercially sourced 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 [1,9]. 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 in Nigeria. The chemical composition of the sectioned samples is shown in Table 1 as obtained from spectrometer analyzer.

2.2. Processed composition

The electrolytic chemical bath of Zn–Al–Sn–Ti fabricated alloy was performed in a single cell containing two zinc anode and single cathode electrodes as described schematically as reported by [1]. The distance between the anode and the cathode is 15 mm. Before the plating, all chemical used are analar grade and de-ionized water were used in all solution admixed. The bath was preheated at 40 °C. The processed parameter and bath composition admixed used for the different coating matrix is as follows Zn 75 g/L, Al 30 g/L, KCl 50 g/L, ZnCl 75 g/L, Boric acid 10 g/L, SnO_2 7 g–13 g/L, TiO_2 7 g–13 g/L, pH 4.8, time, 20 min and tempt 40 °C. The choice of the deposition parameter is in line with the preliminary study from our previous work [1] (see Table 2).

The prepared zinc electrodes were connected to the rectifier at varying applied potential and current density between 0.3 V and 0.5 V at 2 A/cm^2 for 20 min. The distance between the anode and the cathode with the immersion depth were kept constant as described by Fayomi et al. [18]. The fabricated alloys were rinsed in distilled water and samples air-dried. Portion of the coating were 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. Micro-hardness studies were carried out using a diamond pyramid indenter EMCO Test Dura-scan micro-hardness testers at a load of 10 g for a period of 20 s. The average microhardness trend was measured across the coating interface 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 fabricated alloy were measured using CERT UMT-2 tribological tester at ambient temperature of 25 °C with schematic diagram as reported by [1]. 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 Si_3N_4 ball (4 mm in diameter, HV50g1600) was chosen as counter body for the evaluation of tribological behavior of the coated sample. The dimension 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 Nikon Optical Microscope (OPM) and scanning electron microscope couple with energy dispersive spectroscopy (VEGAS-TESCAN SEM/EDS).

Table 1
Spectrometer 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	99.166

Table 2
Itinerary bath composition of quaternary Zn–Al–Sn–Ti–Cl alloy co-deposition.

Sample order	Material sample	Time of deposition (min)	Potential (V)	Current density (A/cm^2)	Con. of additive (g)
Blank	–	–	–	–	–
Sample 1	Zn–Al–7Sn–Ti–0.3V–Cl	20	0.3	2 A	7
Sample 2	Zn–Al–7Sn–Ti–0.5V–Cl	20	0.5	2 A	7
Sample 3	Zn–Al–13Sn–Ti–0.3V–Cl	20	0.3	2 A	13
Sample 4	Zn–Al–13Sn–Ti–0.5V–Cl	20	0.5	2 A	13

2.5. Thermo/electro-oxidation test

Isothermal heat treatment (direct fired furnace atmosphere) of Zn–Al–Sn–Ti composite coating was carried out between 200 and 600 °C for 1hr to enhance the mechanical stability of the coated samples. The electrochemical studies were performed with Autolab PGSTAT 101 Metrohm potentiostat using a three-electrode cell assembly in a 3.65% NaCl static solution at 40 °C. The developed composite was the working electrode, platinum electrode was used as counter electrode and Ag/AgCl was used as reference electrode. The anodic and cathodic polarization curves were recorded by a constant scan rate of 0.012 V/s which was fixed from ±1.5 mV. From the Tafel corrosion analysis, the corrosion rate, potential and linear polarization resistance was obtained.

3. Results and discussion

3.1. Structural characterization

SEM/EDS of the as-received mild steel substrate are presented in Fig. 1. The microstructure of the electro-fabricated Zn–Al–Sn–Ti alloy composite matrix additions are shown in Fig. 2. The deposits with 7 wt% in 0.3 V revealed a reasonable uniform distribution and a small micro particle inter-link around the major metal lattice. The coating exhibits a new morphology with adorable structural grain. The produced deposits show interference of SnO_2 and TiO_2 evenly conditioned into the Zn–Al–Sn–Ti matrix. The EDS quantification identifies the major embedded particles. A visible coverage by composite micro-crystallites without crack was seen. The structure yield good quality deposit which is attributed to the miscible and excellent control of process parameter of the bath which is in line with the report by Chuen-Chang and Chi-Ming [3]

The activities surrounding the nature of the distributed microstructure can be link to alumina–tin–titanium particles migration assisted by slow/lower potential of deposition. In general solid interfacial precipitation occurs between the integrated particles and the based zinc rich. Secondly, the morphologies obtained which show a well dispersed crystal might also be traced to the influence of additive admixed in the bath and agitation of the bath to disallow agglomeration thereby preventing the initiation of stress propagation [20,21]. Although Rahman et al. [11] said in co-deposition process, crystallization influence the structure and its properties, crystallization exist either by buildup of old crystals or by formation and growth of new one through the deposition rate thereby causing nucleation within the cathode surface and further help to enhance preferential sites.

Comparing these micrographs, with alloy produced at 13 wt% induced at 0.3 V there seems to be de-agglomeration like the formal. However, the movement of particles toward the cathode region could have cause the embedded solid particle within the interface to be stress and in so doing given rise to few crack and pores seen at the interface (see Fig. 2b). According to [19] the nature of composite coating produced can be influenced by the absorption of incorporation and control of process parameter. Hence, increase power or potential, increases further the