J Fail. Anal. and Preven. (2015) 15:54–64
DOI 10.1007/s11668-014-9908-1

TECHNICAL ARTICLE—PEER-REVIEWED

Properties of Tic/Tib Modified Zn–Tic/Tib Ceramic Composite Coating on Mild Steel

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Submitted: 24 May 2014 / Published online: 2 December 2014
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Abstract Researches in the area of zinc coatings on steel are rather unending because of the unique properties and the very low cost that it offers. In this study, an attempt to develop a compact and structurally modified coating that will work against chemical and mechanical deterioration with the help of Zn–Tic/Tib was studied. Scanning electron microscope and atomic force microscope were used to study the surface morphology, the topography, and the surface adherence properties of the coatings. Micro-hardness of the deposited substrate, the electrochemical behavior and the corrosion properties of the deposits were investigated by means of high impact diamond Dura scan micro-hardness tester and gravimetric method. From the results, the deposition of Zn–Tic/Tib composite particles showed good protection against corrosion and also improved the hardness values. Hence, Zn–Tic/Tib alloy coating on mild steel can be used to improve the properties of mild steel.

Keywords Coating · Corrosion · Electron microscopy · Characterization

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Introduction

Coatings are used in both aqueous and high temperature applications. Coal gasification, electric power generation, and waste incineration involve severe environmental conditions, and thick coatings have proved to be an effective solution [1]. Diesel and gas turbine engines are subject to high temperature corrosion, and highly beneficial coatings are required to combat the severe environmental effects [2]. In addition to substrate compatibility, the other factors like adhesion and porosity, the prospects of repair or recoating, inter-diffusion, the effect of thermal cycling, resistance to wear and corrosion, and the cost may also be needed to be taken into consideration [3]. The functional and/or decorative coatings are normally designed as an integrated whole, taking into account all these considerations. The composite coatings usually made up of solid grain and matrix metal have good properties for various applications and have attracted people's attention. At present, many literatures about preparation method, process, and properties of various composite coatings have been published [4, 5] in recent years.

The massive impact of zinc-based coatings for steel protection before the emergence of new materials for engineering enhancement is enormous. They exhibit good electro-oxidation resistance in ambient atmospheric medium but their lifespan decrease in a more aggressive environment due to corrosion product initiation and wear fracture [1–6]. Effort to improve on this limitation has been tremendously attested for from literature by various authors on the use of composite coatings [2]. The primary intention on the choice of composite particulate is due to their significant constituent of solid grains and matrix metal [3].

The stability of these coatings and their surface behavior establishes further development of these coatings for environmental applications. Zinc is widely used as metallic coatings applied to steel surfaces to protect them from deterioration which can be obtained either by hot dipping or electroplating process. Electrolytic deposition of Zn produces thinner coating as compared to hot dipping method, which is suitable for the subsequent forming process in the automotive industries [4].

The impact of corrosion on a system is mostly a surface phenomenon. One of the key factors in any corrosion situation is the medium. This has found a wider influence on material strength and performance behavior [5]. Environment is a variable that can change with time and environments can affect how a metal corresponds to the micro-environmental conditions. However, sulfide solutions are of high application in the industry and most manufacturing areas, fertilizers, and to supply zinc in animal feeds [6]. Due to the distressed strength of sulfide application, electrodeposited metal was made to withstand and reduce this environmental danger. Zinc coating is considered as one of the main methods used for the corrosion protection of steel. The usage in industrial sectors as a protective coating for large quantities of products and other fabricated ferrous metal parts is enormous. Acid zinc plating bath is used where it is desirable to have a high plating rate with maximum current efficiency, and good deposition depends mainly on the nature of the bath constituents [7].

Zinc coatings are obtained either from cyanide or non-cyanide-alkaline or acidic solutions. Because of the pollution and high cost associated with cyanide, deposition from other baths such as sulfate, chloride, and mixed sulfate–chloride baths is gaining importance [1, 2]. Good deposition depends mainly on the nature of bath constituents. Generally, a plating bath contains conducting salts, complexing agents, and metal ions. Among these, the complexing agents influence the deposition process, solution properties, and structure of the deposit. The action of these complexing agents depends on pH, nature of anion, temperature, and other ingredients of the medium [7–9].

Most of the addition agents possess electro-active functional groups. Usually, the electroplating baths are associated with two or more addition agents and are essential to obtain a quality deposit. Too many ingredients cause difficulties in maintaining the operating parameters of the bath solution during the plating process. Some of these agents smoothen the deposit over a wide current density range and the other addition agents influence the production of bright deposits. Therefore, it is essential to develop the bath with a single additive that could produce a quality deposit [8–15]. Therefore, there are lots of R&D works, carried out during the last two decades, regarding the production of zinc alloy coatings used to replace zinc coating. Researches in the area of zinc coatings on steel are rather unending because of the unique properties and the very low cost it offers. In this study, an attempt to develop a compactable and structural modified coating that will work against chemical and mechanical deterioration with the help of Zn–Tic/Tib was studied.

Experimental Procedure

Preparation of Substrates

Flat specimens and sectioned sourced mild steel of (40 mm × 20 mm × 1 mm) sheet were used as cathode substrate and 99.5% zinc plate of (30 mm × 20 mm × 1 mm) was prepared as anode. The initial surface preparation was performed with finer grade of emery paper as described in our previous studies [1–3]. The samples were properly cleaned with sodium carbonate, pickled, and activated with 10% HCl at ambient temperature for 10 s, and then followed by instant rinsing in deionized water. The mild steel specimens were obtained from the metal sample site in Nigeria. The chemical composition of the sectioned samples is shown in Table 1 as obtained from spectrometer analyzer.

Processed Composition

The electrolytic chemical bath of Zn–SnO_2 fabricated alloy was performed in a single cell containing two zinc anodes and single cathode electrode as described schematically in Fig. 1. The distance between the anode and the cathode is 15 mm. Before plating, all chemicals used are of analytical grade and deionized water was used in all the solutions admixed and preheated at 40 °C. The process parameter and bath composition admixed used for the coating is shown in Tables 2 and 3. The choice of the deposition parameter is in line with the preliminary study and our previous work [1, 3].

The prepared electrodes were connected to the direct current source via a rectifier at varying applied potentials and current density between 0.3 and 0.5 V at 2 A for 20 min constant time. The distance between the anode and the cathode and the immersion depth were kept constant as described by [2]. The plating was done, rinsed in distilled water, and samples were air dried thereafter sectioned for characterization.

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

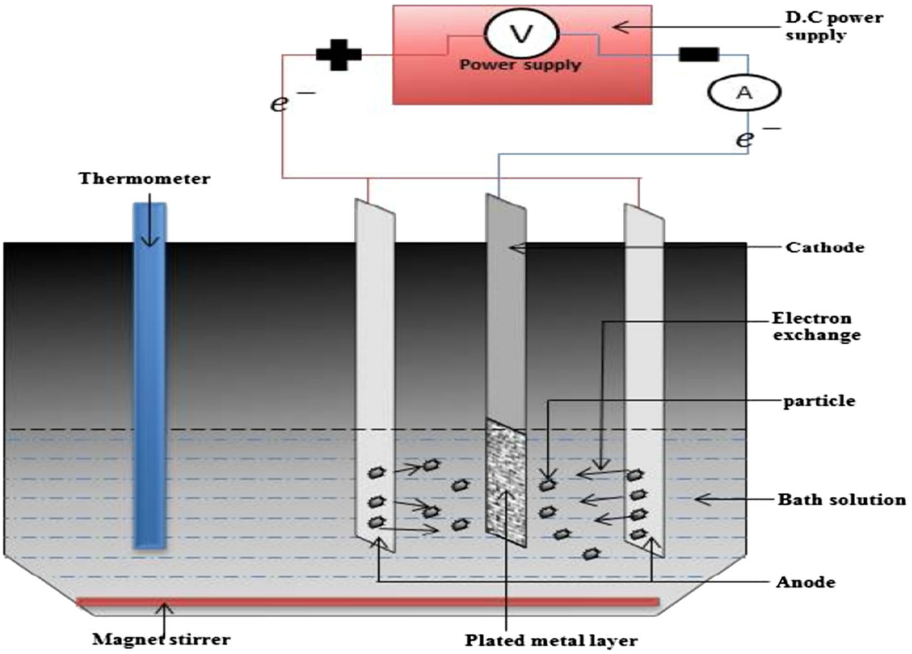

Fig. 1 Schematic diagram of electrodeposited system

Table 2 Itinerary bath composition of Zn–SnO_2 alloy co-deposition

Sample order	Material matrix	Time of deposition (min)	Current (A/cm^2)	Con. of additive (g)
Blank	…	…	…	…
Sample 1	Zn–Tic	10	1.5 A	5
Sample 2	Zn–Tic	10	2 A	5
Sample 3	Zn–Tib	10	1.5 A	5
Sample 4	Zn–Tib	10	2 A	5
Sample 5	Zn–Tic–Tib	10	1.5 A	5
Sample 6	Zn–Tic–Tib	10	2 A	5
Sample 7	Zn–Tic–Tib	10	1.5 A	15
Sample 8	Zn–Tic–Tib	10	2 A	15

Table 3 Process parameter for Zn–Tic/TiB sulphate bath formulation

Composition	Mass concentration (g/L)
$ZnSO_4$	100 g
$NaSO_4$	35 g
Tic/TiB	5–15 g
Boric acid	10 g
Glycerine	10 g
NaOH	1.05 ml
pH	4.5–5
Current	1.5–2.0 A
Time	10 min
Tempt	40 °C

Characterization of Coating

The structural evolution of the deposited composite coating alloy was characterized with VEGA TESCAN Scanning electron microscope (SEM) equipped with EDS and atomic force microscope (AFM). Micro-hardness studies were carried out using a Diamond pyramid indenter EMCO Test Dura scan 10 micro-hardness testers at a load of 10 g for a period of 20 s. The average micro-hardness trend was measured across the plated surface with an interval of 2 cm using a screw gage attached to the Dura hardness tester [1].

Gravimetric Study

Nine clean beakers were prepared as containers for the sample coated sample immersion. Nine Zn–Tic/Tib specimens were wiped with a tissue to remove the excess dirt on the specimens and were weighed. 40 ml of the prepared solution (3.65% Nacl) was poured in the nine clean beakers and the Zn–Tic/Tib-coated samples were then dipped in the solution, respectively. The first beaker was taken as the control where the sample was not coated, and the remaining were the eight coated samples. The weight loss measurement was then conducted with weight loss recording after 2-day interval.

Results and Discussion

The result of the electrodeposition of Zn–Tic/Tib-deposited mild steel is shown in Table 4. From Table 4, electrodeposition conditions affected the composition of Zn alloys in

Table 4 Electrodeposition parameters and results for Zn–Tic/Tib-deposited mild steel

Sample numbers	Time (min)	Coating thickness (µm)	Weight gain (g)	Coating per unit area (mg/mm^2)	Additive conc. (g)
1. Zn–Tic	10	75.1	0.09	0.01071	5
2. Zn–Tic	10	38.6	0.31	0.03689	5
3. Zn–Tib	10	62.2	0.07	0.00833	5
4. Zn–Tib	10	25.5	0.08	0.00952	5
5. Zn–Tic–Tib	10	77.2	0.11	0.01309	5
6. Zn–Tic–Tib	10	74.6	0.05	0.00595	5
7. Zn–Tic–Tib	10	49.0	0.12	0.01428	15
8. Zn–Tic–Tib	10	40.9	0.09	0.01071	15

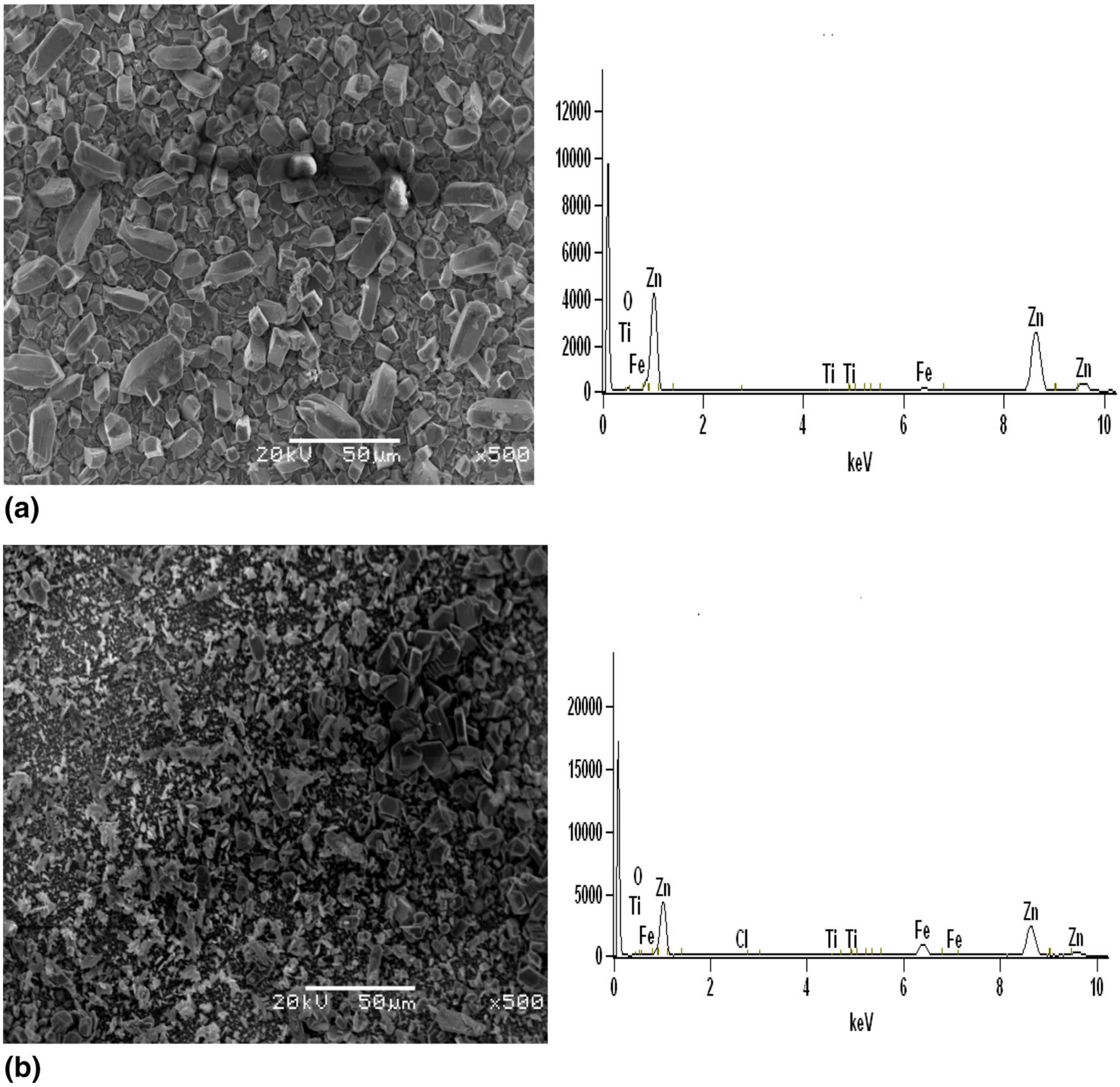

Fig. 2 (**a**) Displays SEM/EDS of Zn–5Tic 10 min at 1.5 A, (**b**) displays SEM/EDS of Zn–5Tib 10 min at 2 A

the following manner: the increase in current caused an increase in the amount of both alloying metals in the deposit. It was observed that as the current of deposition increased from 1.5 to 2.0 A, the coating per unit area also increased. This may be attributed to the increased rate of deposition which leads to increase in the rate of reaction [10].

Figures 2 and 3 show the scanning electron micrographs and attached EDS of the samples. In general, from deposition appearance, the whole plating displays better plating and good adhesion. The nature of the surface morphology and orientation unveiled the homogeneous appearance with good dispatches as expected. One significant reason for this behavior might be as a result of the deposition parameter. Praveen et al. [1] confirmed that the deposition behavior and the adhesion strength of any particular plating often based on the potential, current density, and most especially the time of deposition. In Fig. 2b, the explanation by the author resurfaces in this study in which the time of deposition and the current involved (Zn–5Tib 2A, 10 min) give sufficient plating as compared to that of (Zn–5Tic 1.5A at 10 min as in Fig. 2a).The better adhesion that occurs within the interface is as a result of the presence of boric acid and the conductance. Tib leads to high resistance for mechanical erosion. By observation, Fig. 2b shows smaller grain sizes.

The combined Tic and Tib resolves stress behavior that might occur during the coating due to the relieve agent (see Fig. 3c). The better adhesion that occurs within the interface is as a result of the presence of boric acid and the conductance. No few porosity of coating could be observed in Fig. 3b and c, composite intermediately harnessed properly with zinc interface.

Surface topography studies were based on AFM measurements with the aim of determining the influence of

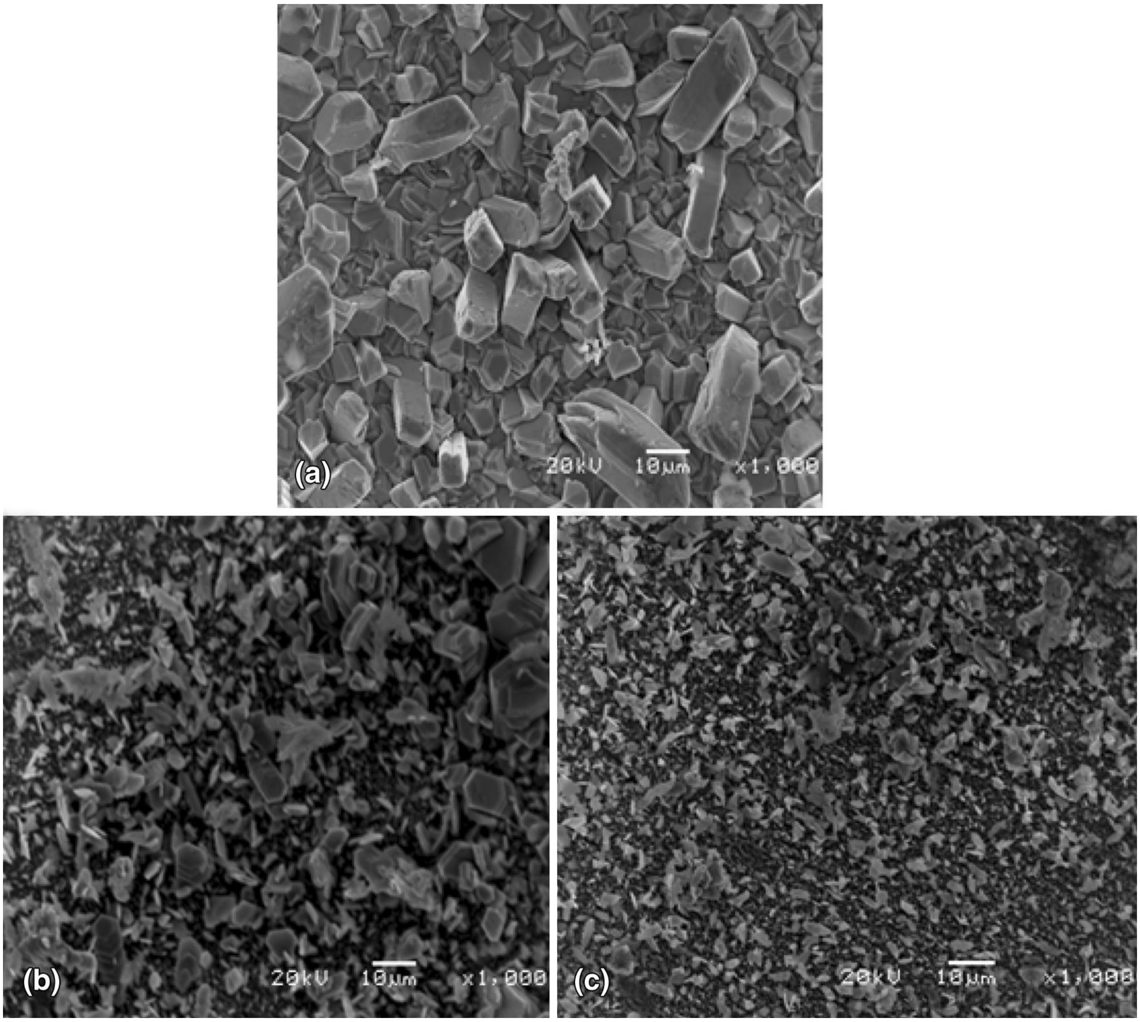

Fig. 3 SEM micrographs of (**a**) Zn–5Tic 10 min at 1.5 A, (**b**) Zn–5Tib 10 min at 2 A, (**c**) Zn–5Tic–5Tib 10 min at 1.5 A at ×1000 magnification

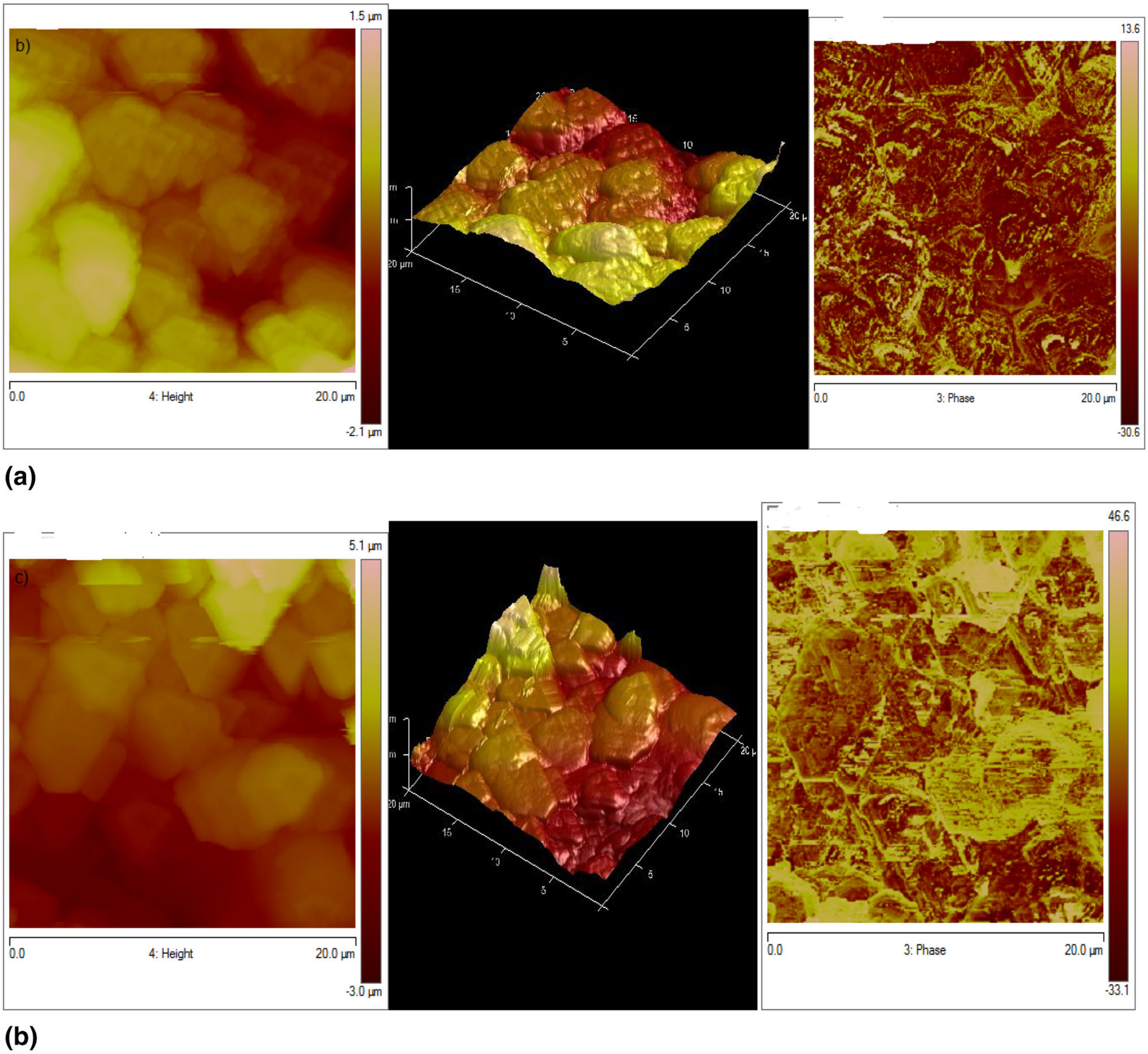

Fig. 4 (**a**) AFM of Zn–Tic 10 min at 1.5 A, (**b**) AFM of Zn–Tib 10 min at 2 A, (**c**) AFM of Zn–5Tic–5Tib 10 min at 1.5 A, (**d**) AFM of Zn–15Tic–15Tib 10 min at 2 A

plating parameters on the grain size dimensions, as well as to find out the deposition conditions, which resulted in the surface macrostructural defect formation. AFM was performed on Zn–Tic/Tib obtained at 1.5 and 2 A deposition in all respect as shown in (Fig. 4).In all alloy deposited, uniform crystallites coalesced with small grain were found affirming the morphological result obtained from scanning electron micrograph; the topography of the Zn–Tic/Tib matrix show better adhesion behavior (see Fig. 4c, d). Figure 4d shows flat, spherical, and hexagonal platelets deposition which indicates Titanium boride dispatches. The growth of spherical crystallites does not cover the entire surface, thereby giving it a non-uniform appearance. But finer grained texture and dendrite-free deposition is obtained and observed in Fig. 4a–d.

Figure 5 presents the effect of Zn–Tic/Tib at different applied currents of 1.5 and 2 A in 10 min on the hardness values. From all indications, the micro-hardness rises with additive dispersed into the bath. The pronounced micro-hardness changes with all sample matrixes at their applied

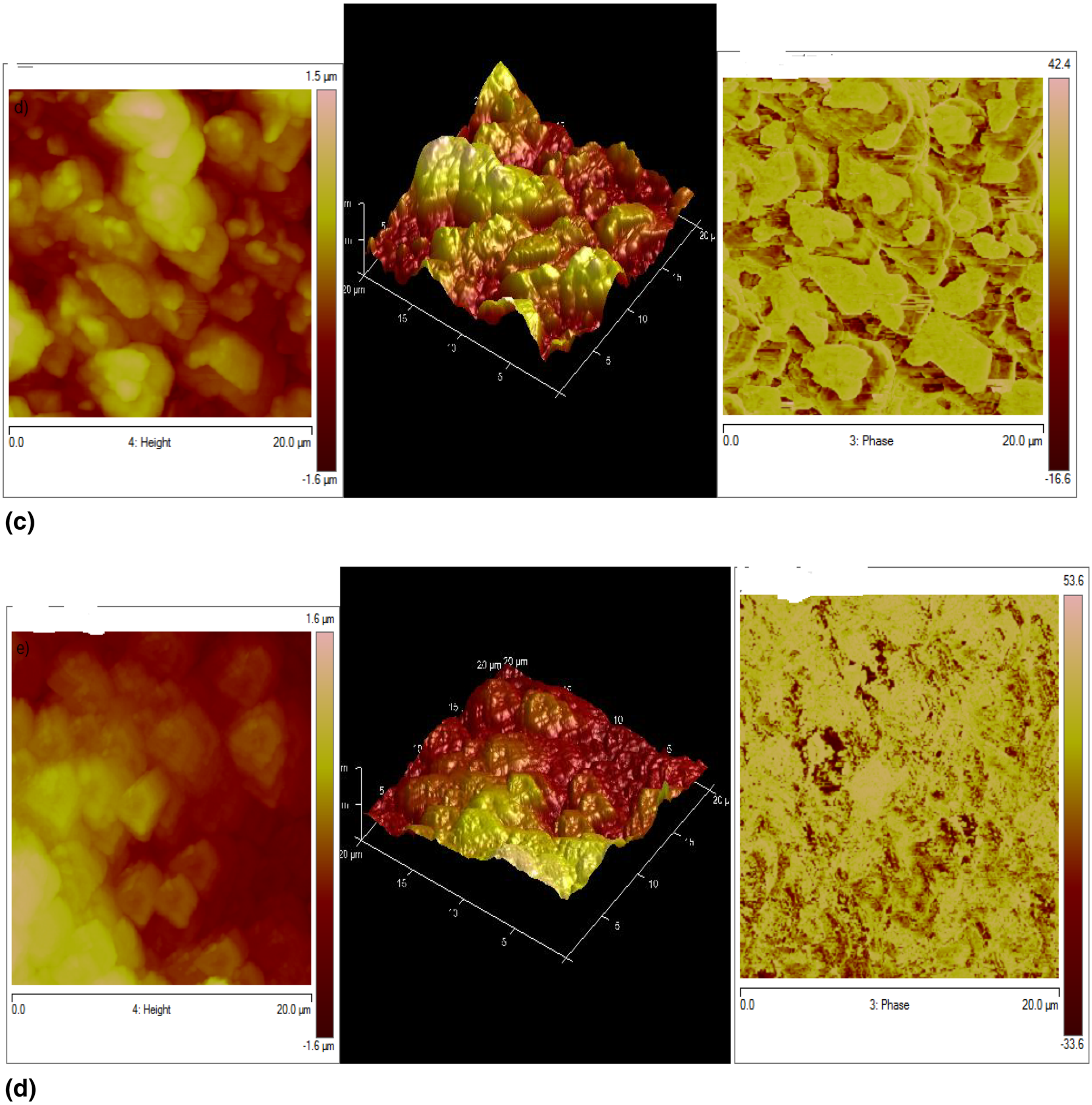

Fig. 4 continued

potentials suggesting Tic/Tib strengthening effect. Report from literature by Fullston [3] and Fayomi et al. [6] shows that ceramic composite particles can lead to refinement in grain structure and improve the micro-hardness of the composite coatings. Composite-Tic/Tib thus changes and cause smaller grain and provides structural modification which could enhance the hardness of the composite coatings [11].

The improvement in hardness was attributed to the formation of adhesive properties on the substrate. The micro-hardness of the Zn alloy-deposited samples under different conditions were carefully observed and studied.

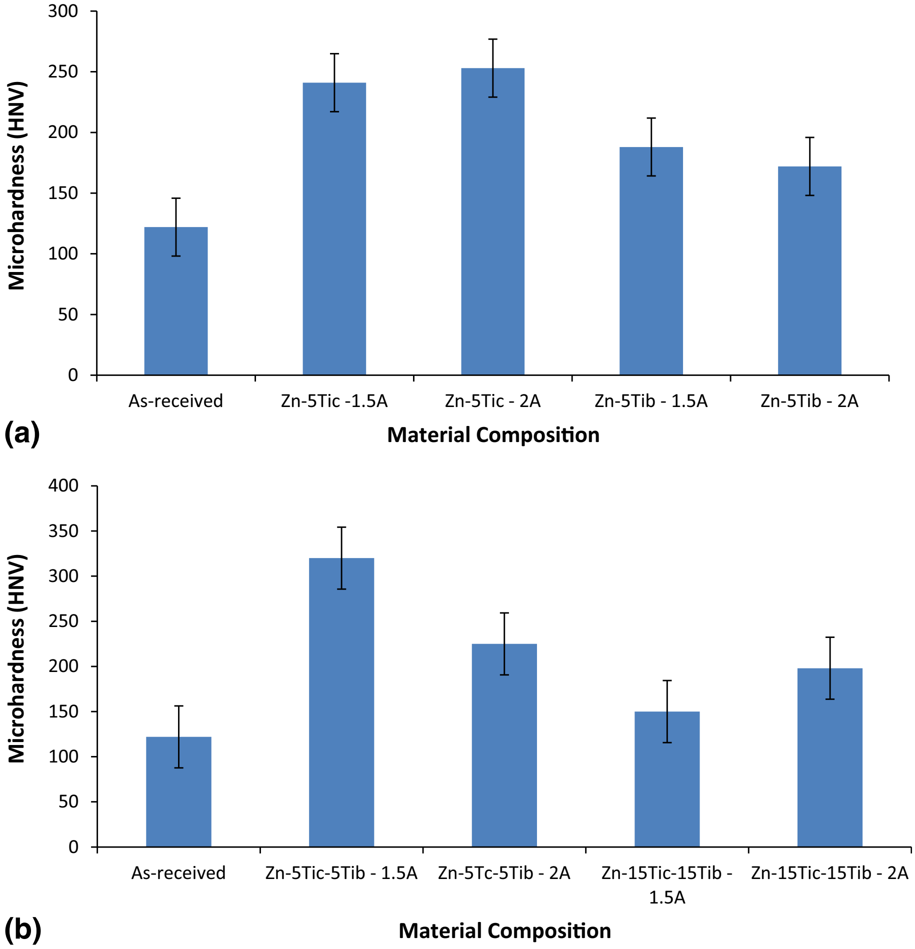

Fig. 5 (**a**) Variation of micro-hardness of Zn–5Tic- and Zn–5Tib-deposited alloys, (**b**) Variation of micro-hardness of as-received sample, Zn–5Tic–5Tib 1.5 A/2 A, Zn–15Tic–15Tib 1.5 A/2 A

Experimental results showed that the micro-hardness property of the zinc-deposited sample depends on the operating current density. Previous work by [12, 13] had affirmed that the microstructure evolved in coating depends on the processing parameters and hence such metallurgical parameters influence the grain size which is paramount to the buildup of surface hardness. It was clearly observed that three regions are distinguished on the curve: a region of initial deposit, a middle region, and a region of high current density.

In general, Tic, Tib, and particulate contribute immensely to the hardness behavior of Zn–Ti coatings and hence the absence of cracks and defect as earlier stated is a requirement to produce a well-adhered coating with good hardness properties. From Fig. 5b, it can be observed that Zn–5Tic–5Tib at 1.5 A has higher hardness values as compared to the rest of the trend.

The vulnerability of the deposited samples to corrode in the 3.65% NaCl environment with time was carried out. Tables 5 and 6 show the corrosion rate and coating efficiency of the Zn–Tic/Tib alloy plated at 1.5 and 2 A, respectively. From the results obtained in Tables 5 and 6, the corrosion rate of the samples generally decreases with time. The corrosion rate data for the uncoated mild steel electrode are typical of a corroding electrode with high anodic currents being observed near the corrosion potential. It is seen that higher corrosion potentials were observed for the coated sample. However, much higher corrosion protection properties can be seen for the Zn–Tic/Tib alloy-coated mild steel system. The corrosion potential is significantly higher than the uncoated sample.

The mild steel sample had a high corrosion rate due to lack of surface protection. This was attributed to the high anodic potential reached by the sample [13–15]. Meanwhile, Zn–Tic/Tib alloy-coated mild steel showed a good decrease in corrosion rate which may be due to the formation of very thin film, which retarded the ingress of chloride ions fully into the plated region and down to the

Table 5 Corrosion rate (CR) and coating efficiency for Zn–Tic/Tib-plated mild steel in 3.6% Nacl solution at 1.5 A

Samples (h)	Samples	Initial weight	Weight loss (wt.)	Corrosion rate (CR)	Coating efficiency (%IE)
96	Control	0.93	0.02	0.0116	0
	Zn–5Tic	1.53	0.01	0.005812	50
	Zn–5Tib	1.50	0.01	0.005812	50
	Zn–5Tic–5Tib	1.60	0	0	100
	Zn–15Tic–15Tib	2.08	0	0	100
144	Control	0.92	0.02	0.007749	0
	Zn–5Tic	1.52	0.01	0.003875	50
	Zn–5Tib	1.50	0.01	0.003875	50
	Zn–5Tic–5Tib	1.60	0	0	100
	Zn–15Tic-15Tib	2.09	0	0	100
192	Control	0.92	0.02	0.005812	0
	Zn–5Tic	1.52	0.01	0.00906	−56
	Zn–5Tib	1.50	0.02	0.005812	0
	Zn–5Tic–5Tib	1.60	0	0	100
	Zn–15Tic–15Tib	2.08	0	0	100
240	Control	0.92	0.02	0.0046497	0
	Zn–5Tic	1.52	0.01	0.002325	40
	Zn–5Tib	1.49	0.02	0.00465	−0.005161
	Zn–5Tic–5Tib	1.60	0	0	100
	Zn–15Tic–15Tib	2.08	0	0	100
288	Control	0.92	0.03	0.005812	0
	Zn–5Tic	1.52	0	0	100
	Zn–5Tib	1.49	0.01	0.0019374	67
	Zn–5Tic–5Tib	1.60	0	0	100
	Zn–15Tic–15Tib	2.09	0	0	100

substrate. But, it is good to know that mild steel displayed the highest corrosion rate than all the deposited samples. Also Tic, Tib, and particulate contribute immensely to the corrosion behavior of Zn–Ti coatings and hence the absence of cracks and defect as earlier stated as a requirement to produce a well-adhered coating decreased the corrosion rate. These data clearly show that the Zn–Tic/Tib alloy-coated mild steel system is considerably more stable and corrosion resistant than the corresponding uncoated mild system. This seems to be associated with the stability of the Zn–Tic/Tib alloy layer that is formed which produced a barrier effect, where any contact between the corrosive medium and the mild steel is prevented.

Conclusions

After vivid study of the deposited zinc–Tic/Tib on the mild steel, the performance evaluation was systematically observed and a homogeneous and coherent surface morphology was maintained; however, at 1.5 A, there is stability in mechanical and physical properties obtained on plated substrates after corrosion investigation. The following conclusions can be made:

1. The Zn–Tic/Tib coatings showed better adhesion strength compared to the one attained from the previous work by other researchers.
2. Improved hardness values were obtained from Zn–Tic/Tib-coated mild steel.
3. In this work, mixed matrix of Zn–15Tic–15Tib showed better corrosion resistance as compared to the rest of the matrices.
4. Uncoated mild steel has been found to be unsuitable for use in chloride-containing water due to its relatively high corrosion rate. The electroplated Zn–Tic/Tib sample was able to protect mild steel in chloride medium to retard corrosion attack.

Table 6 Corrosion rate (CR) and coating efficiency for Zn–Tic/Tib-plated mild steel in 3.6% Nacl solution (2 A)

Samples (h)	Samples	Initial weight	Weight loss (wt.)	Corrosion rate (CR)	Coating efficiency (%IE)
96	Control	0.93	0.02	0.0116	0
	Zn–5Tic	1.64	0.01	0.0058121	50
	Zn–5Tib	1.84	0.01	0.0058121	50
	Zn–5Tic–5Tib	1.78	0.01	0.0058121	50
	Zn–15Tic–15Tib	1.55	0	0	100
144	Control	0.92	0.02	0.007749	0
	Zn–5Tic	1.64	0.02	0.0077495	0
	Zn–5Tib	1.83	0.01	0.0038747	50
	Zn–5Tic–5Tib	1.77	0.01	0.0038747	50
	Zn–15Tic–15Tib	1.55	0.01	0.0038747	50
192	Control	0.92	0.02	0.005812	0
	Zn–5Tic	1.63	0.01	0.0029061	50
	Zn–5Tib	1.83	0.01	0.0029061	50
	Zn–5Tic–5Tib	1.77	0.01	0.0029061	50
	Zn–15Tic–15Tib	1.54	0.01	0.0029061	50
240	Control	0.92	0.02	0.004651	0
	Zn–5Tic	1.645	0	0	100
	Zn–5Tib	1.836	0	0	100
	Zn–5Tic–5Tib	1.777	0	0	100
	Zn–15Tic–15Tib	1.546	0	0	100
288	Control	0.92	0.03	0.005812	0
	Zn–5Tic	1.65	0	0	100
	Zn–5Tib	1.84	0	0	100
	Zn–5Tic–5Tib	1.78	0	0	100
	Zn–15Tic–15Tib	1.55	0	0	100
336	Control	0.91	0.03	0.004982	0
	Zn–5Tic	1.600	0	0	100
	Zn–5Tib	1.843	0	0	100
	Zn–5Tic–5Tib	1.78	0	0	100
	Zn–15Tic–15Tib	1.5514	0	0	100

5. Zn–Tic/Tib alloy coated on mild steel can be used to improve the properties of mild steel.

Acknowledgments This material is based upon the work supported financially by National Research Foundation, South Africa. The analytical input of Surface Engineering Research Centre (SERC) and Technology Innovation Agency (TIA/TSC), Tshwane University of Technology Pretoria, South Africa are appreciated.

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