The Effect of TiO₂ Particulate Reinforcement on the Microstructure and Mechanical Properties of Binary Nano-Composite on Low Carbon Steel

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Abstract- In this Research, the microstructure and mechanical properties of Zn-TiO₂ nanocomposite, co-deposited on low carbon steel substrate were fabricated by electrodeposition route. The structural performance of the composite coating was evaluated by scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). The mechanical property was carried out using a Durascan hardness tester. The result showed that the influence of TiO₂ nano particles greatly enhanced the hardness behaviour. The increase in hardness is ascribed to the uniform homogeneity and dispersion stability of particles in the aqueous solution containing the nano composite.

Keywords: Microstructure, Nano-composite, electrocodeposition, homogeneity and dispersion

1. Introduction

Ever since the invention of galvanic coating technology, electrolytic metal coatings have been used in quite a lot of areas due to their exceptional properties [1–3]. Electrodeposited composite coatings are a surface engineering developed on the basis of electrolytic conducting coating [4-6]. Metallic zinc has been the largely used electrodeposited metal to shield steel against corrosion. Nevertheless, the corrosion resistance rendered by zinc is inadequate. Lately, major efforts to improve the wear, hardness and corrosion resistance of metallic zinc coating, can be traced towards its composites with different materials [11-18]. It is also identified, in particular, that the physical, mechanical and electrochemical properties of materials can be improved with the introduction of nano powders as the second phase particles within the material of interest [13-18]. Due to this improvement, composites and alloys such as Zn-Al₂O₃, Zn-WO₃, Zn-Al and Zn-Ni have tremendously gained a wider range of applications in both marine and manufacturing industries recently as a better alternative for regular zinc plating [19-25]. Even though these coatings offer some benefits over zinc, but usually they cannot cathodically shield steel substrates in different type of corrosive environments [22-25]. Zinc alloy or composite deposited through electrodeposition have greater corrosion stability as compared to thermally obtained Zn alloy [6-8], lately, successful zinc-aluminum electrodeposited coating on low carbon steel were done with the help of aluminium tri-chloride on zinc-aluminium deposited on the rest potential of yellowish and non-chromates zinc-aluminium [9].

In this work comparison of the microstructural and hardness of coated Zn and Zn-TiO₂ coatings on low
carbon steel was studied for the purpose of materials selection.

2. Experimental Procedure

2.1 Preparation of substrate
The measurement of the low carbon steel (substrate) used was (45 x 40 x 20) mm³ piece and zinc pieces of (85 x 45 x 5) mm³ were prepared as anodes. The low carbon steels specimens’ chemical composition is displayed in Table 1. The cathode was the low carbon coupons and anode was the commercially obtained pure zinc (about 99.99%). The low carbon steels specimens were polished mechanically, degreased and rinsed with water as described [6 - 8].

| Element | Composition | Element | Composition | Element | Composition |
|---------|-------------|---------|-------------|---------|-------------|
| C       | 0.330       | Mo      | 0.100       | Ti      | 0.04        |
| Si      | 0.870       | Ni      | 0.030       | V       | 0.01        |
| Mn      | 0.430       | Cu      | 0.110       | W       | 0.01        |
| P       | <0.003      | Al      | 0.030       | B       | <0.002      |
| S       | >0.160      | Co      | 0.030       | Sn      | 0.0014      |
| Cr      | 0.100       | Nb      | 0.010       | Fe      | 99.61       |

2.2 Formation of deposited coating
The low carbon steel substrate previously prepared was actuated by dipping into 10% hydrochloric acid solution for few seconds, then rinsed in deionized water. Analar chemicals grade and deionized water were used to formulate the coating solution at ordinary temperature before the coating process. The preparations of bath were formulated a day earlier and stir constantly at the rate of 400 rpm with continuous heating at 70°C during the course of the coating process, so as achieve standardized solution. The bath configurations used for the diverse coating matrix is as follows KCl 30 g/l, ZnCl₂ 120 g/l, TiO₂ nano particles 20g/l, Cetylpridinium Chloride 0.5g/l, 2- Butyne 1,4 diol 0.5g/l and Thiourea 10g/l.

The select of the coatings variables is in accordance with the study of preceding work of some of our collaborators [9]. The arranged zinc electrodes were coupled to the d.c power supply at varying current ranging from 1.0 and 1.5 A for 1200s (20 min) as shown in Figure 1. The prepared design plan for the coating is displayed in Table 2. The electrodeposited samples were rinsed in water and thereafter air-dried. Then, the plated steels were afterwards sectioned for characterization.
Figure 1: The diagram showing the schematic arrangement of the coating system (Fayomi and Popoola, 2014)

Table 2: Preparation of bath composition for Zn and Zn-TiO₂ nano-composite

| Sample  | Sample Deposition time (min) | Current (A/m²) |
|---------|-----------------------------|----------------|
| 1       | Zn-1.0A 20                  | 560            |
| 2       | Zn-1.5A 20                  | 830            |
| 3       | Zn-TiO₂-1.0A 20             | 560            |
| 4       | Zn-TiO₂-1.5A 20             | 830            |

3. Coating Characterization

The obtained nano-composite coatings were characterized with the aids of JEOL FIELD EMMISSION (JSM – 7600F) Scanning electron microscope coupled with EDS. The structural arrangement was considered with XRD. Micro-hardness characterizations were obtained using a special Diamond pyramid indenter (EMCO) Test Dura-scan micro-hardness testers using a load of 10 g at a period of 20 s. The measured micro-hardness was carried out across the coated surface.

4. Results and Discussion

4.1 SEM/EDS studies of the deposited nanostructure composite

Figures 2 and 3 reveal the SEM/EDS image structure of Zn and Zn-TiO₂ fabricated at 1.5A (current density of 830 A/m²) respectively fabricated on low carbon steel. From the two Figures it is observable that the microstructural nodules of the coats were homogeneously spread on the surface. It is readily clear
that, with the introduction of TiO₂ nanoparticles, a perceptible crystallite of the coating nodules along the edge was observed. Essentially there are two distinguishing phases, the first having a uniform steady deposits and the latter with agglomerate of reinforcements. The introduction of the TiO₂ in the zinc matrix could be traceable to the structure refined morphology coupled with good nodular particles, as can be seen in Figure 4 that presented the nodular Zn-TiO₂ particles (‘Q’ portion), in comparison to flaky (‘P’ portion) Zn particles. This is more pronounced at higher magnification (Figure 4). Figure 5 further revealed the morphology of the samples in nanometer range. The plated outlook and the coating edge of Zn-TiO₂ were quite amusing due to the fortification derived from the nano ceramics particulates of the composite in the metallic zinc matrix. The structural output was as anticipated since the nucleation development initiated from the metallic zinc load bearer, the particulates covering the nucleation points and reinforced the produced nanocomposite [10-11]. Additionally, from Figure 4, it is essential to remark that microstructural variation may be due to the incorporation TiO₂ nanoparticles which led to better deposition and improved orientation. Also, with reference to [11], the preparing factor with respect to the amount of additive can also influence the modification of the crystal route and surface value of a deposited surface. The penchant of electrodeposited materials to adhere and consequently form coatings with unique bright texture is influenced by the nature of the additive and the purity of the foundational particles [12 and 13]. The morphological orientations of the Zn matrix are clue of the strap up capability of the coating formed.

Figure 2: SEM/EDS of Zn-coated low carbon steel showing the surface morphology
Figure 3: SEM/EDS of Zn-TiO$_2$ coated low carbon steel showing the surface morphology of the coatings

Figure 4: SEM/EDS of (a) Zn (b) Zn-TiO$_2$ coated low carbon steel showing the internal morphology of the coatings

Figure 5: SEM/EDS of (a) Zn (b) Zn-TiO$_2$ coated low carbon steel in the nano-range showing the internal morphology of the coatings (P and Q are Zn and Zn-TiO$_2$-rich portions respectively)

4.2 Microhardness study
The microhardness study shown in Figure 6 was done so as to observe the effect of the composite microstructure and TiO$_2$ particle loading on the hardness behaviour of Zn-TiO$_2$ nanocomposite coatings.
In general, all the coatings formed, display excellent and unique improvement compared to the unplated low carbon steel substrate except Zn-1.0 A, which could be traced to the throwing power. However, the sample matrix Zn-TiO$_2$-1.5A showed the highest hardness property with the average value of 130.5 HVN. The outstanding enhancement of this matrix is primarily due to microstructural strengthening of the TiO$_2$ nanoparticles and the increased throwing power via current density (i.e., current density increased from 560 - 830 A/m$^2$). Figure 7 revealed the response of the composite coating to the heat treatment. The thermal deformations were observed in 250°C for 5hrs and mechanical responses of the coated samples
were studied. The mechanical behaviour due to thermal treatment and porosity within the alloy surface could result in hardness distribution. Some literatures also agree to the fact that compression stress could significantly perk up the micro-hardness when it is much less than the ultimate strength of the coating but [14] revealed that the flaws such as porosity, macro-particle at the alloy surface will have unfavourable effect on the mechanical properties. The Figure 7 also compares the hardness properties of the composite coatings before and after thermal treatment. It should be noted that all the samples species increase in hardness after the thermal treatment, which is one of unique property of Nanoparticulate. The average micro hardness values for all the samples calculated indicates that, Zn-TiO$_2$- 1.5A nanocomposite coatings possessed the highest hardness value of 155.5 HVN after the thermal treatment. It can also be deduced from Figure 7 that, the hardness value of Zn after heat treatment increases from 114 to 143 HVN and 121 to 154 HVN when the current increases from 1.0 A to 1.5 A and that of Zn-TiO$_2$ increases from 129 to 145 HVN and 130.5 to 155.5 HVN as the current increased from 1.0A to 1.5 A. The coatings were excellent since the hardness values after heating increase tremendously in their values after thermal treatment [15]. The phenomenon of dispersion strengthening was also observed. The mechanisms of such strengthening are the grain refinement strengthening and the dispersion strengthening of TiO$_2$ deposited on the sample and the deposition current [16]. Hence, the microstructural improvement as a result of buildup of fine particulate and this build up enhances the hardness of the coating.

![Figure 6: Hardness properties of varied current of Zn-TiO$_2$ nano-composite deposited on low carbon steel before heat treatment](image)

Figure 6: Hardness properties of varied current of Zn-TiO$_2$ nano-composite deposited on low carbon steel before heat treatment
5. Conclusion
1. Nano structured TiO$_2$ particulates were used to produce Zn-TiO$_2$ nanocomposite coating from chloride bath.
2. The incorporation of TiO$_2$ in the coating was confirmed by EDX
3. The incorporation of the TiO$_2$ Nanoceramics particles in the zinc matrix as reinforcement enhances the hardness properties of the substrate.
4. The hardness properties increases with increase in deposition current

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Reference
[1] Durodola, B.M. Olugbuyiro, J.A.O. Moshood, S.A. Fayomi, O.S.I. and Popoola. A.P.I.  Int. J. of Electrochem. Sci., 6, (2011) 5605
[2] Amuda, M.O.H. Subair, W.and Obitayo. O.W.  Int. J. of Eng. Research in Africa, 2(2009)31.
[3] Basavanna, S. and Arthoba Naik, Y. J. of Appl. Electrochem., 39 (2009) 1975
[4] Inegbenebor,, O.A.  J. of Mat. and Env. Sci., 3, (2011) 271.
[5] Popoola, A.P.I. Fayomi O.S. and Popoola., O.M.  2011. Proc. of Mat. Sci. & Tech. Conf., Ohio:

Figure 7: Hardness properties of varied current of Zn-TiO$_2$ nano-composite deposited on low carbon steel after heat treatment.
USA. (2011) 393-400.

[6] Rahman, M.J. Sen, S.R. Moniruzzaman, M. and Shorowordi, K.M. J. of Mech. Eng, Tran., 40, (2009) 9.

[7] Deuis, R.L. Subramanian, C. and Yellup, J.M. 1996. Wear, 201, 132-144.

[8] Chen, Y. and Wang. H.M. Surface and Coatings Technology, 168, (2003) 30-36.

[9] Popoola, A.P.I. Pityana, S.L and Popoola. O.M. J. of the South Afri. Inst. of Min and Met., 111 (2011) 345.

[10] Popoola, A.P.I. Pityana, S.L. and Popoola, O.M. Int. J. of Electrochem. Sci., 6, (2011) 5038

[11] Paunovic, M. and Mordechay, S. 2nd Ed, John Wiley and Son Inc. 6 (2006) 388

[12] Paunovic, M. Clevenger, L.A. Gupta, Jr. Cabral, C. and Harper. J.M.E. J. of Electrochem. Sci. 140 (1993) 2690.

[13] Volinsky, A.A. Vella, J. Adhihetty, I.S. Sarihan, V.L. Mercado, L. Yeung, B.H. and Gerberich, W.W. Mat. Res. Soc., 649, (2001)1.

[14] Popoola A.P.I and Fayomi O.S. Int. J. of Electrochem. Sci., 6, (2011)3254

[15] Praveen, B.M and Venkatesha, T.V. Int J. of Electrochem, 261, (2011) 407

[16] Shivakumara, S. Manohar, U. Arthoba Naik, Y. & Venkatesha, T. U.. Bull. Mat. Sci. 30 (2007) 455

[17] Sundararajan, G. and Rama Krishna. L. Surf. and Coat. Tech, 167, (2003) 269.