Estimation the Efficiency of Nano Particles Coating on Carbon Steel by Atomization

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ABSTRACT

In this work, three nanoparticles were applied as coatings on carbon steel using atomization method (cold spraying) by airbrush. The coatings included nano Al_2O_3, nano SiC and nano ZrO_2 materials. The characterization of coated surfaces has been investigated by AFM and SEM. All these inspections indicated that the deposition of nanoparticles on carbon steel surface was uniform and homogeneous. The thickness of coated layers was calculated using gravimetric method, while the particle size and roughness were measured from the analysis of atomic force microscopy. With constant conditions of coating, nano alumina coating gave the highest thickness (6.2216 nm) due to agglomeration of these particles compared with others as illustrated in SEM images. Corrosion test was performed to estimate the corrosion resistance, protection efficiency and porosity percentage which indicated the role of nano particle coating on corrosion control. These data showed that the nano alumina was better than other coatings and gave PE 99.69%.
Cyclic polarization was also estimated to show the probability of pitting corrosion. The coating with alumina gave the best data for decreasing the chance of pitting corrosion.
Keywords: Carbon steel, cold spray, Nanoparticles, Coating.

INTRODUCTION

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Corrosion occurs in the aqueous environment because of protons and oxygen, which are readily available in nature [1,2]. When conferring corrosion control by nano materials, there are two main considerations; the first aspect is the understanding of corrosion behaviors of nanostructured materials, whether or not a nanostructured material possess is better corrosion resistant or not. The second aspect is how nano sized materials can be effectively employed in corrosion prevention strategies. Nano technological advancements are expected to improve corrosion monitoring and inspection sectors [3-6].
Nano coatings can be made by a variety of non-vacuum and vacuum based methods, such as sol–gel, electro-deposition, atomization, magnetron sputtering …etc. [7]. Corrosion resistance of a coating may be inferior with such aggregation due to the accelerated diffusion of aggressive ions along the interfaces between the incorporated particles [8]. Nanoparticles of diamond and other

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chemical compounds used for hard coatings (SiC, ZrO_2 and Al_2O_3) are commercially available, with typical particle sizes in the range 4–300 nm. Co-deposition of ceramic nano scaled particles (ZrO_2 , Al_2O_3 , ZnO, TiO_2, ferrites, etc.) during electroplating and electro less plating can bring improvements in technical properties [8,9]. Nanostructured ceramic (nanostructured diamond, metalloceramics, hydroxyapatite, etc.) and composite coatings increase the general corrosion resistance of bioimplants and enhance the bioactivity and wear resistance [10]. Many researchers highlighted using nano particles to reduce corrosion and other properties as coatings on metallic materials especially by cold spraying method [11-15].

The aim of present work is to apply nano particle coatings using alumina, silicon carbide and zirconia on carbon steel by cold spaying and test the corrosion in seawater in addition to characterize the coated surfaces by AFM and SEM.

Experimental Procedure

Carbon steel (St 44-2-DIN 17100) was used in this work with chemical composition (wt%: 0.115 C, 0.228 Si, 0.54 Mn, 0.008 S, 0.012 P, 0.018 Ni, 0.017 Cr, 0.067 Al, 0.022 Cu, 0.013 Mo, 0.008 V, 0.004 Co and remained Fe) obtained by AMETEK, SPECTRO MAXX in State Company for Inspection and Engineering Rehabilitation (SIER)–Ministry of industry and minerals. Nano powders were used in this work to prepare the emulsion in absolute ethanol with purity 99.9% obtained from Guangzhou Jiechuang Trading Co., Ltd. consist of Alumina (particle size 20-30 nm and density 3.96 g/cm^3), SiC (particle size 20 nm and density 3.216 g/cm^3) and zirconia (particle size 40-50 nm, color is white and density 5.89 g/cm^3).

To prepare emulsion, ultrasonic and magnetic stirring have been used to get homogeneity of coating solution. Ultrasonic cleaner, model: KQ 3200 E, Origin: China used for 20 min. and then magnetic mixing (Brand Name: chtech, Model Number: MS200, Origin: China) for 30 min.

All carbon steel specimens were prepared before coating through cutting, grinding and polishing. Airbrush was used with nitrogen gas to apply cold spray coating on carbon steel surface. The distance between the tip of nozzle and surface was about 5 cm and the surface was heated to 100±5 ^oC using hot plate.

Atomic force microscopy (Veeco dinnova model) was used to observe the coated surfaces in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 µm × 5 µm and the scan rate was 0.6 HZ /second.

The VEGA III TESCAN scanning electron microscope was utilized to document the surface morphology of different specimens.

Corrosion measurements for uncoated and coated carbon steel specimens were tested in 3.5 wt% NaCl (artificial sea water) using potentiostat (WENKING MLab 200/ Germany) which is connected to the computer device with software program. Working electrode holder was used to fix uncoated and coated specimens. Reference and counter electrode were Pt and saturated calomel electrode (SCE) respectively. The results of corrosion were calculated using Tafel extrapolation method.

Result and Discussion

Characterization of Coated Surfaces

Figures (1) to (4) indicate the AFM images (2D, 3D and particle size distribution) of uncoated carbon steel and coated by nanoparticles Al_2O_3, SiC and ZrO_2 respectively. The image of uncoated sample displays the surface topography with no particles may be deposited on the surface. It shows only some scratches due to grinding and polishing process. This figure also displays that the average size of the particle is 172.9nm.

Others AFM images show the uniform distribution of nano particles applied by a cold spraying method. The average size of particles for nano Al_2O_3, SiC and ZrO_2 are 54.44, 51.09 and 89.30 nm, respectively. They are lower than that of uncoated surface. The highest average diameter was for nano zirconia as illustrated in SEM image.

The roughness measurement from AFM analysis was achieved. The roughness of uncoated surface was 0.342 nm, while for coated surfaces were 54, 26 and 5.4 nm respectively. The roughness was increased due to deposit of nano particles on carbon steel and the highest roughness was for nano alumina coating due to agglomeration compared with others materials. This result can also be predicted from SEM inspection.

Figure (5) shows the SEM for uncoated carbon steel which indicates some scratches due to grinding and polishing in addition to atmospheric corrosion. Figures (6) to (8) show clustering of particles on metal surface applied by cold spraying. These images also show the distribution of deposited particles on steel surface.

The thickness of coated layer was 6.2216 µm for Al_2O_3 coating, while it was 0.0781 and 1.5504 µm for SiC and ZrO_2 coating, calculated from the following equations:

$$T = \frac{w}{A \times \rho} \qquad \ldots\ldots(1)$$

Where,
T is the thickness, w is the weight of coating, A is the surface area, and ρ is the density. For the same conditions of spraying, the nano alumina coating had the highest thickness due to agglomeration of particles faster than others.

Electrochemical Behavior

Figure (9) indicates the polarization curves of uncoated and coated carbon steel by nano particle coatings which include alumina, silicon carbide and zirconia. These curves indicate the cathodic region, where the reduction of oxygen can occur as follows:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad \ldots\ldots..(2)$$

At anodic region, dissolution of iron takes place to form ferrous ions according to the following reaction:

$$Fe \rightarrow Fe^{2+} + 2e \qquad \ldots\ldots\ldots..(3)$$

Corrosion parameters were calculated by Tafel extrapolation method. These parameters include corrosion potential (E_{corr}), corrosion current density (i_{corr}) and Tafel slopes (b_c & b_a). The corrosion potential of uncoated specimen is -582.8 mV, and the corrosion currant density is 52.77 $\mu A.cm^{-2}$.

The curves of coated surfaces with alumina and zirconia shifted toward lower current densities and more positive values of potential. The curve of coated carbon steel with nanoparticles SiC gave lower effect than other coatings, but one can observe the protection and breakdown on cathodic and anodic sites. Also cathodic Tafel slope decreased, this means that the polarization decreased after coating process and the rate determining step controlled by concentration polarization due to nanoparticle coatings which reduce the dissolution of metals and then reducing the electrons production needed to reduce reactions at the cathode. This phenomenon leads to accumulation of oxygen molecules at cathode and then concentration polarization will occur.

The rate of corrosion (C_R) in a given environment is directly proportional to its corrosion current density (i_{corr}) in accordance with the relation [16]:

$$C_R = 0.13 \times i_{corr} \times \left(\frac{e}{\rho}\right) \qquad \ldots\ldots\ldots(4)$$

This equation is used to calculate C_R in mil per year (mpy), where e and ρ are equivalent weight and density of carbon steel, respectively. The data of corrosion rate indicate that the nanoparticle coatings led to decrease corrosion rate of carbon steel. The Protection efficiencies (PE%) of applied coatings can be estimated by corrosion current densities for uncoated and coated specimens as follow [17]:

$$PE\% = \left[1 - \frac{i_{corr_{coated\ specimen}}}{i_{corr_{uncoated\ specimen}}}\right] \times 100 \qquad \text{........ (5)}$$

The data of PE% indicate that the nano alumina coating has the highest efficiency followed by nano zirconia and then nano SiC coating as listed in Table (2). Surface porosity fraction was estimated by both potentiodynamic polarization and nano-indentation measurements. In the first case, the porosity percentage (PP%) can be calculated using the following equation [18]:

$$PP\% = \frac{R_{p_{uncoated}}}{R_{p_{coated}}} 10^{\frac{-\Delta E_{corr}}{b_a}} * 100 \qquad \text{........(6)}$$

Where,

$R_{p,uncoated}$ and $R_{p,coated}$ are the polarization resistances of the uncoated and coated samples, respectively, ΔE_{corr} is the corrosion potential difference between them, and b_a is the anodic Tafel slop of the uncoated sample. The nano alumina and zirconia coatings have lower porosity than nano SiC. The lowest porosity can be observed for nano alumina coating. The results of polarization resistance, efficiency and porosity candidate the nano alumina coating as the best.

The most dangerous type of corrosion is the pitting corrosion because always the material body seems in good appearance, but in fact it is suffering from pitting defects, so pitting is defined as "localized accelerated dissolution of metals that occurs as a result of a breakdown of the protective passive film on the metal/alloy surface". The pitting corrosion can be estimated by cyclic polarization measurement. Figure (10) shows the cyclic polarization of uncoated and coated surfaces. The test of uncoated sample shows that the reverse scan appears to the right of forward scan and the potential of reverse scan (-630 mV) was more negative than potential of forward scan (-510 mV). The pitting potential (E_P) and re passivation potential (E_R) are -167.7 mV and -618.2 mV respectively.

This means that the passive zone finished at -167.7 mV. The pitting nucleation and a right loop are obtained; also the return potential at -629 mV (that is characteristic of pitting propagation) and a negative hysteresis due to the reversible damage by pitting are also observed. If the protection potential is more negative than the pitting potential, pitting could occur. The size of the pitting loop is rough indication of pitting tendency; the larger the loop, the greater the tendency to pit.

The cyclic polarization curve for specimen coated with Al_2O_3 shows high pitting potential (+79.7 mV) compared with uncoated specimen, in addition to shift the hysteresis loop to more positive potentials with E_R -622.5 mV. Although the nano SiC coated specimen exhibit more positive pitting potential (+141.5 mV), but this coating don't show re passivation as shown in Fig. (10). This means that the damage which occurs in passive film could not repair it.

In the case of nano zirconia coated specimen, it can be seen that the reverse scan appears at more positive potentials than forward scan with pitting potential -379.0 mV. This result shows that a stable oxide film is formed during the forward scan. It is also observed that the reverse scan curves meet the forward scan curve along the passive range. Finally, it can be said that the coating with alumina and zirconia is better than SiC. This result is in a good agreement with the results of polarization resistance, protection efficiencies and porosity percentages.

CONCLUSIONS

Coating with nano particles has been applied by cold spraying on carbon steel to estimate the corrosion control by nano alumina, silicon carbide and zirconia. The coated surfaces were characterized by AFM and SEM analysis in addition to calculate average diameter, roughness and thickness. The highest roughness was observed for nano alumina coating due to agglomeration of particles as illustrated from SEM image. Corrosion measurements were achieved to measure corrosion parameters, these parameters showed that the nano alumina has the lowest corrosion current density and highest corrosion potential and cathodic Tafel slope. The calculations of polarization resistance, protection efficiency and porosity confirm the role of nano alumina coating to corrosion control. Cyclic polarization also indicated the decreasing in pitting chance in the case of alumina coating compared with other coatings.

Table (1): Measured corrosion data of uncoated and coated specimens with nano particle coatings in seawater.

Specimens	E_{corr} mV	i_{corr} μ A.cm^{-2}	$-b_c$m V.dec^{-1}	$+b_a$m V.dec^{-1}
Uncoated	-582.8	52.77	281.2	56.5
Coated with Al_2O_3	-0.900	0.1637	102.9	107.8
Coated with SiC	-373.3	11.040	40.2	17.5
Coated with ZrO_2	-2.100	0.18212	112.3	131.6

Table (2): Calculated corrosion parameters for uncoated and coated carbon steel.

Specimens	R_px10^3/Ω.cm^2	C_R/mpy	PE%	PP%
Uncoated C.S.	0.387125	24.62618	--	--
Coated with Al_2O_3	139.3901	0.076534	99.690	1.395×10^{-11}
Coated with SiC	0.47954	5.152037	79.079	0.0158
Coated with ZrO_2	144.5635	0.084934	99.655	1.4122×10^{-11}

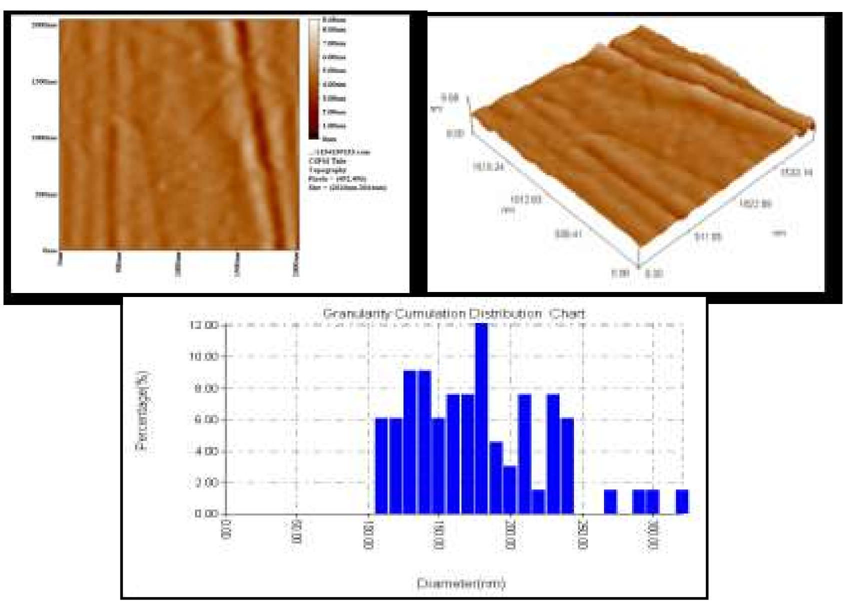


Figure (1): 2D and 3D views of AFM image ofuncoated carbon steel.

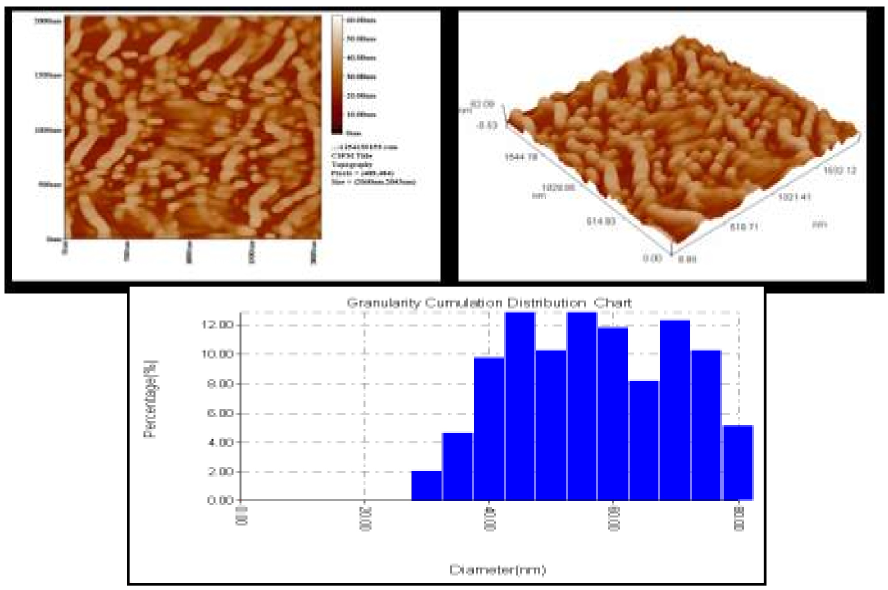
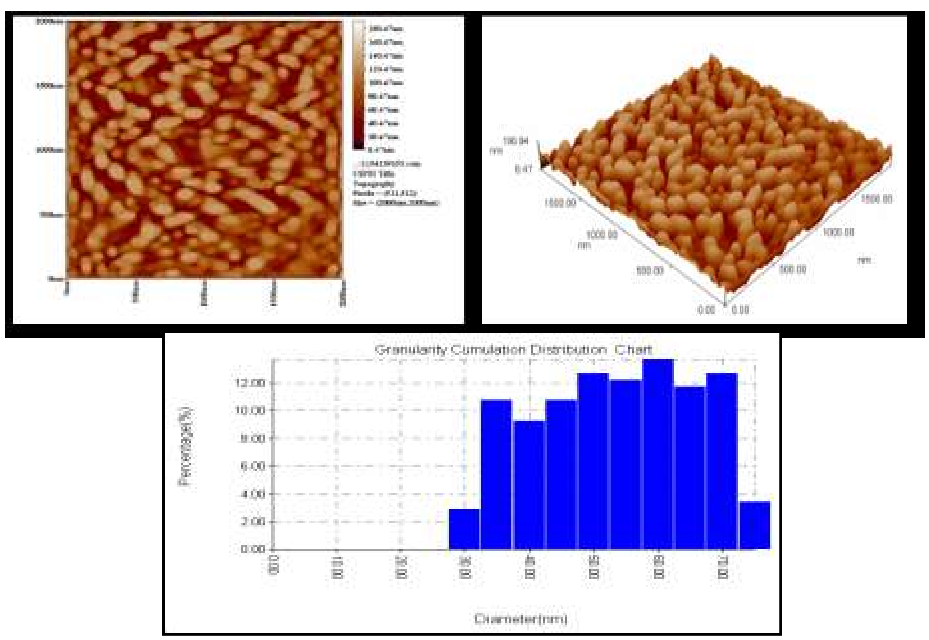


Figure (2): 2D and 3D views of AFM image ofnano Al_2O_3 coated carbon steel.



Figure(3): 2D and 3D views of AFM image of nano SiC coated carbon steel.

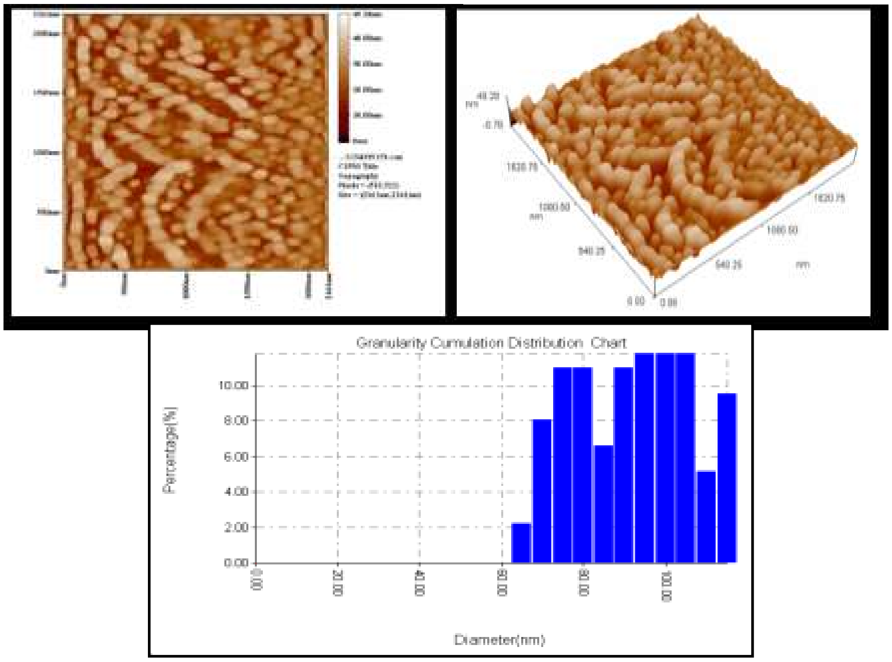


Figure (4): 2D and 3D views of AFM image of nano ZrO_2 coated carbon steel.

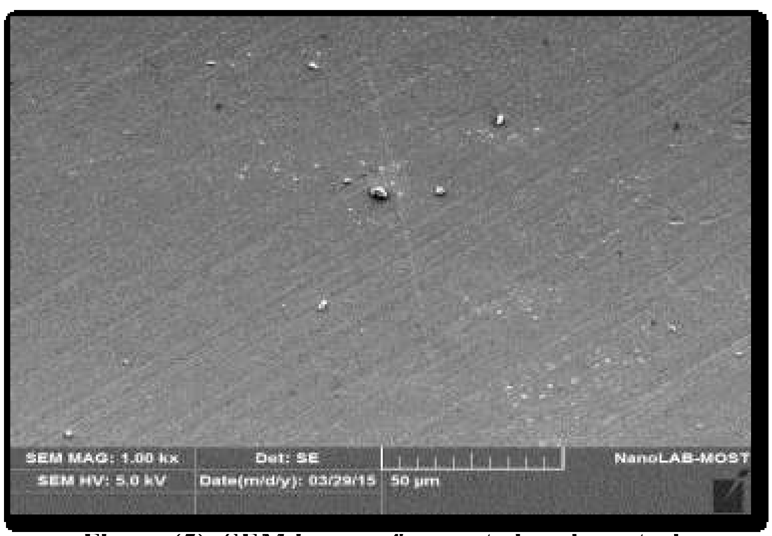


Figure (5): SEM image of uncoated carbon steel.

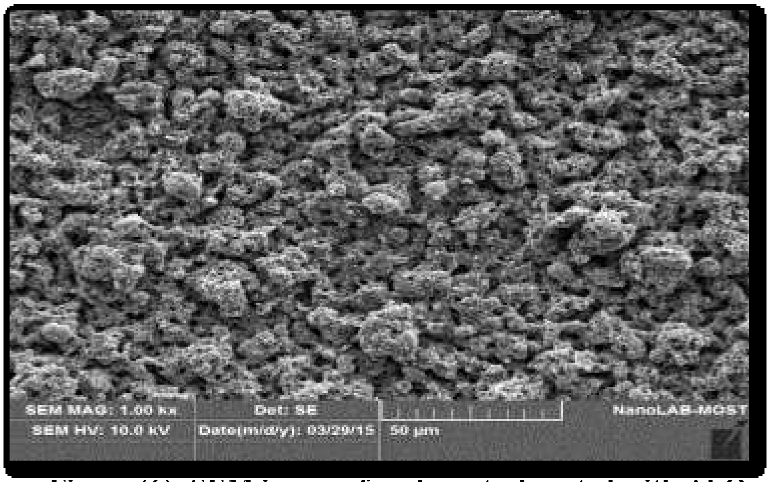


Figure (6): SEM image of carbon steel coated with Al_2O_3.

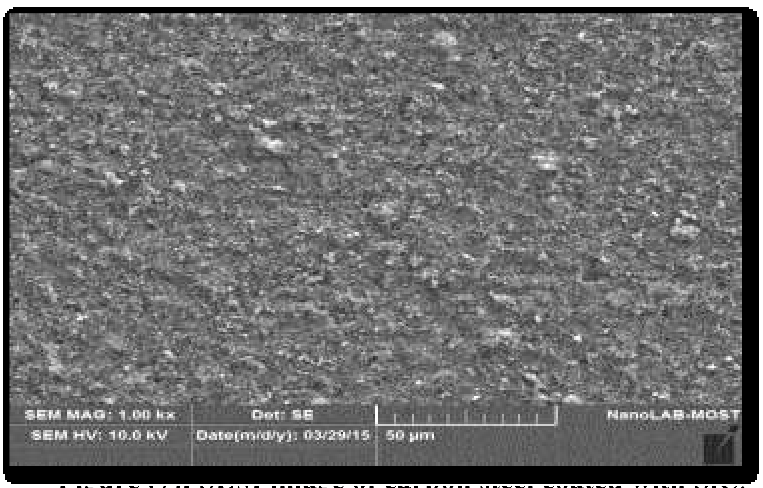
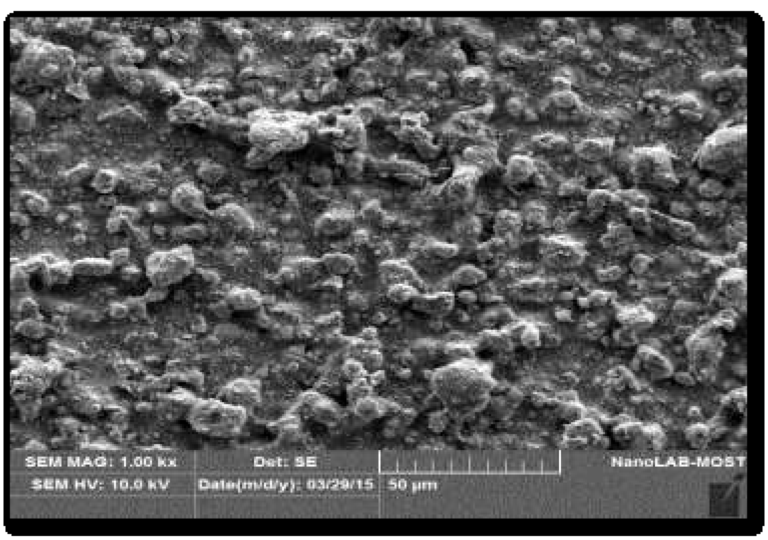
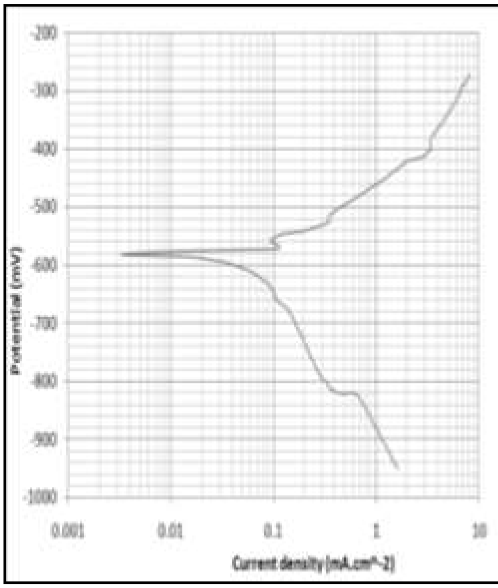
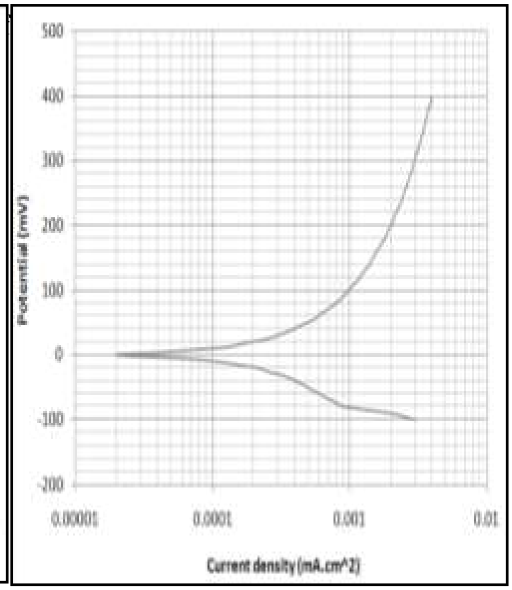


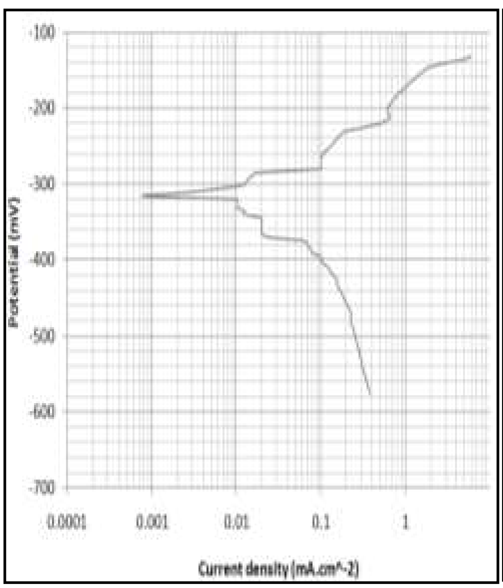
Figure (7): SEM image of carbon steel coated with SiC.

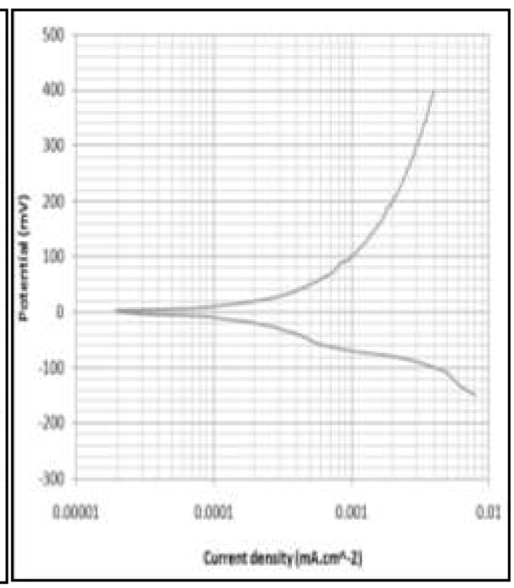






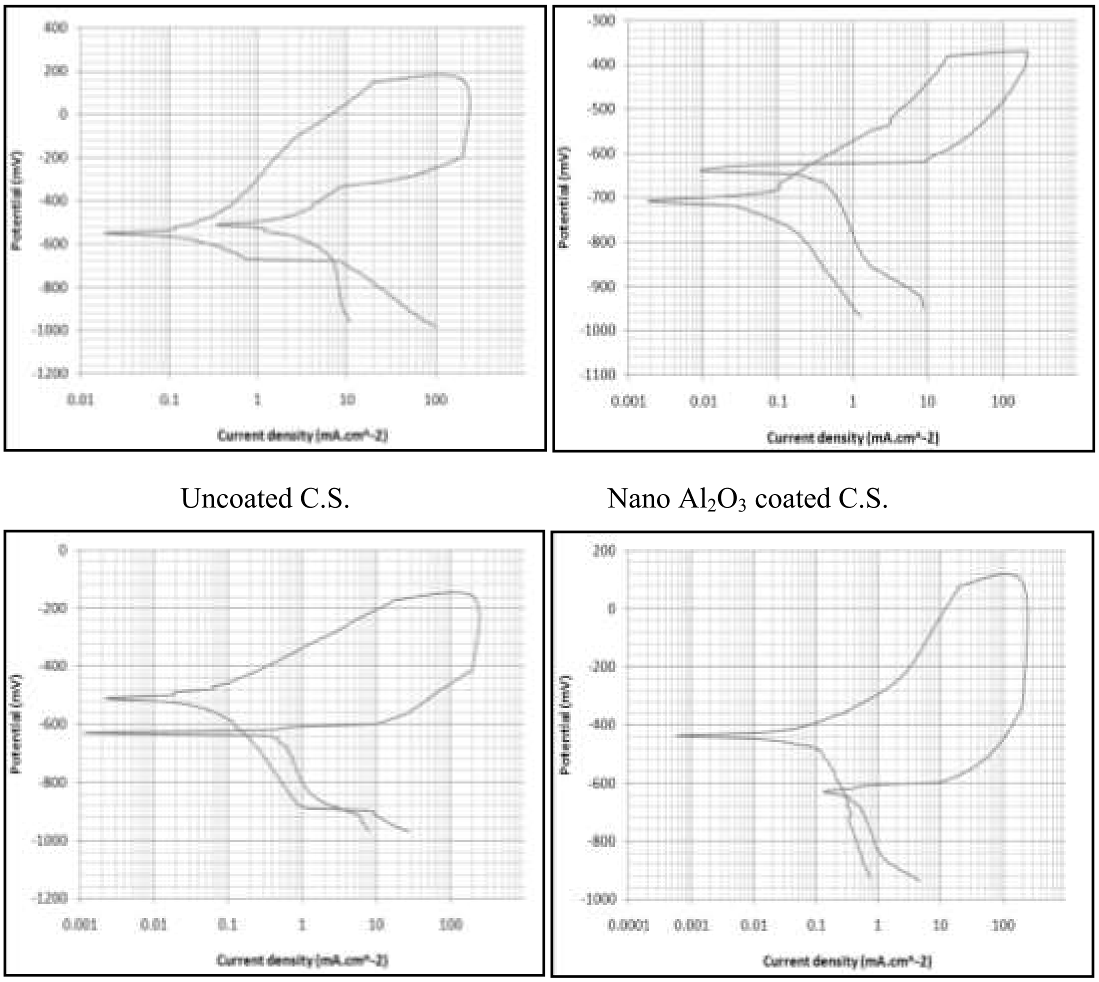
Uncoated C.S. Nano Al_2O_3 coated C.S.





Nano SiC coated C.S. Nano ZrO_2 coated C.S.

Figure(9): Tafel plots of uncoated and coated carbon steel.



Uncoated C.S. Nano Al_2O_3 coated C.S.

Nano SiC coated C.S. Nano ZrO_2 coated C.S.

Figure (10): Cyclic polarization of uncoated and coated carbon steel.

REFERENCES

[1] Smith, P. J., "A Predictive Model for Microbiologically Influenced Corrosion (MIC) in Sub-Sea Production Pipelines" , Ph.D. Thesis, Newcastle University, 2011.

[2] R. Winston Revie and Herbert H. Uhlig "Corrosion and corrosion control: An introduction to corrosion science and engineering" a John Wiley & Sons, INC., publication, 4th edition, Ch. 1, 2008.

[3] Nalwa, H. S., "Handbook of nanostructured materials and nanotechnology", Vol.1, San Diego: Academic Press, 2000.

[4] Saji, V. S., Kim, Y. S., Kim, T. H., Cho, J., and Song, H. K., "One-dimensional (1D) nanostructured and nanocomposited $LiFePO_4$: its perspective advantages for cathode materials of lithium ion batteries", Physical Chemistry Chemical Physics, Vol.13, 19226-237, 2011.
[5] Saji, V. S, Choe, H. C., and Yeung, K. W. K., "Nanotechnolgy in biomedical applications: a review", International Journal of Nano and Biomaterials, Vol.3, 119-39, 2010.
[6] Saji, V. S., Thomas, J., "Nanomaterials for corrosion control", Current Science, Vol.92, 51-55, 2007.
[7] Agarwala, V., Agarwala, R. C., Sunder, B. S., "Development of nanograined metallic Materials by bulk and coating techniques" , Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, Vol.36, 3-16, 2006.
[8] Euler, F., Jakob, C., Romanus, H., Spiess, L., Wielage, B., Lampke, T., Steinhäuser, S., "Interface behavior in nickel composite coatings with nanoparticles of oxide ceramic", Electrochimica Acta, Vol.48, 3063-70, 2003.
[9] Agarwala, R. C., Sharma, R., "Electroless Ni-P nanocoating technology", Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, Vol.38, 229-36, 2008.
[10] Catledge, S. A., Fries, M., and Vohra, Y. K., "Nanostructured surface modifi cations for biomedical implants", Encyclopedia of Nanoscience and Nanotechnology, 741-62, 2004.
[11] Masahiro Fukumoto, Hiroki Terada, Masahiro Mashiko, Kazunori Sato1, Motohiro Yamada and Eiji Yamaguchi, "Deposition of Copper Fine Particle by Cold Spray Process", Materials Transactions, Vol.50, No.6, 1482-1488, 2009.
[12] Harminder Singh, T. S. Sidhu,and S. B. S. Kalsi, "Future of coating deposition processes" , Frattura ed Integrità Strutturale, Vol.22, 69-84, 2012.
[13] Jon Affi, Hiroki Okazaki, Motohiro Yamada and Masahiro Fukumoto , "Fabrication of Aluminum Coating onto CFRP Substrate by Cold Spray", Materials Transactions, Vol.52, No.9, 1759-1763, 2011.
[14] Xinkun Suo , Xueping Guo , Wenya Li , Marie-Pierre Planche , Rodolphe Bolot , Hanlin Liao ,and Christian Coddet , "Preparation and characterization of magnesium coating deposited by cold spraying" Vol.212, No.1, 100-105, 2012.
[15] S. Rech, A. Surpi, S. Vezzu, A. Patelli, A. Trentin, J. Glor, Jenny Frodelius, Lars Hultman and Per Eklund, "Cold-spray deposition of Ti_2AlC coatings" , Vacuum, Vol.94, 69-73, 2013.
[16] Kahtan K.Al-Khazraji, Ali H. Ataiwi, Rana A. Majed and Zina Noori Abdulhameed, "Effect of Some Anti-Inflammatory Drugs on The Corrosion Behavior of Implant Biomaterials in Human Body Fluid", Eng. & Tech. Journal, Vol.30, No.6, 959-973, 2012.
[17] Rana Afif Majed, "Effect of Molybdate Anions On Corrosion Behavior of Stainless Steel 304 In 0.1M Nacl Solution", Eng. & Tech. Journal, Vol.27, No.16, 2931-2945, 2009.
[18] Rana Afif Majed Anaee, "Properties of Functionally Graded Coating of Al_2O_3/ZrO_2/HAP on SS 316L", International Journal of Scientific & Engineering Research, Vol.6, No.5, 953-957, May-2015.