Binary and Ternary Nanoceramic Coatings to Protect Carbon Steel in Artificial Seawater

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ABSTRACT

Binary and Ternary nanoparticles coatings have been applied on carbon steel using atomization method (cold spraying) to corrosion control in seawater. Nanoparticles were included Nano Al₂O₃, SiC and ZrO₂. The characterization of coated surfaces has been investigated by AFM and SEM in addition to calculate the coating thickness. The binary coatings deal with 50%Al₂O₃-50%SiC, 50%Al₂O₃-ZrO₂ and 50%SiC-50%ZrO₂, while the ternary coating was 60%Al₂O₃-20%SiC-20%ZrO₂.

The results showed that 50%Al₂O₃-50%SiC had the lowest thickness and most uniform distribution in AFM and SEM due to closing in particle sizes. Corrosion test achieved to estimate the corrosion resistance, protection efficiency and porosity percentage which indicated the role of Nano particle coating to corrosion control. These data showed that the Nano 50%Al₂O₃-50%SiC coating had the most noble corrosion potential, lowest corrosion current density (lowest corrosion rate), highest corrosion resistance, highest efficiency 99.651 % and lowest porosity percent 1.438×10⁻¹¹. Cyclic polarization also estimated to show the probability for pitting corrosion. The coating with 50%Al₂O₃-50%SiC gave the highest breakdown potential equal to +69mV. Keywords: Cold spray, Nanoparticles, Binary coating, Ternary coating.

INTRODUCTION

When conferring corrosion control by nanomaterial, there are two main considerations. The first aspect is the understanding of corrosion behaviors of nanostructured materials; whether or not a nanostructured material possesses better corrosion resistance (e.g., corrosion/oxidation/cracking resistance of a nanostructured steel substrate/coating) when compared with the microstructure counterpart [1]. The second aspect is how Nano sized materials can be effectively employed in corrosion prevention strategies (e.g., in an automobile or aerospace coating), an area where nanotechnology corrosion control benefits are considerable. Nano technological advancements are expected to improve corrosion monitoring and inspection sectors [1].

Nanoparticle.nanostructured carriers have become a major area of interest in developing smart coatings with ‘on-demand releasable’ corrosion inhibitors and biocides [1]. Nanostructured ceramic (nanostructured diamond, metal-ceramics, hydroxyapatite, etc.) and composite coatings increase...
the general corrosion resistance of bio implants in addition to the expected property enhancement of bioactivity and wear resistance [2].

Nano coating was achieved by different technique [3]. Corrosion resistance of coating may be inferior with such aggregation due to the accelerated diffusion of aggressive ions along the interfaces between the incorporated particles [4]. Different nanoparticles such as SiC, ZrO₂, Al₂O₃, ZnO and TiO₂ were used for applying coatings [4, 5]. Many researches focus using Nano particles to control corrosion by cold spraying method (atomization) [6-10].

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

### Experimental Procedure

#### Materials and Chemicals

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/cm³), SiC (particle size 20 nm and density 3.216 g/cm³) and zirconia (particle size 40-50 nm, color is white and density 5.89 g/cm³).

#### Specimens Preparation and Coating

All carbon steel specimens were prepared before coating through cutting, grinding and polishing. 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.

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 °C using hot plate. Four types of coatings were applied with different weight percent as follow: (50%Alumina-50%SiC), (50%Alumina-50%Zirconia), (50%SiC-50%Zirconia) and (60%Alumina-20%SiC-20%Zirconia).

#### Characterization of Coating

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 study the surface morphology of different specimens.

#### Corrosion Measurement

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 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.

### Results and Discussion

#### Characterization of Coated Surfaces
The thickness of coated layer was calculated by gravimetric method as follow:

\[ T = \frac{w}{A \times \rho} \] ……(1)

Where, \( T \) is the thickness, \( w \) is the weight of coating, \( A \) is the surface area, and \( \rho \) is the density. The data of thickness are listed in Table (1) which indicates that the highest thickness was for Al\(_2\)O\(_3\)-ZrO\(_2\) coating due to the difference in particle sizes between the components of coating, while the lowest thickness was for Al\(_2\)O\(_3\)-SiC coating.

The differences in particle size can be estimated also through AFM images in Figures (1) to (5) that indicate the 2D and 3D of uncoated carbon steel and coated by nanoparticles coatings. The image of uncoated sample displays the surface topography with no particles may be deposited on the surface. It can be seen only some scratches due to grinding and polishing process. The others AFM images show the uniform distribution of Nano particles which applied by cold spraying method.

The roughness measurement from AFM analysis was achieved. The roughness of uncoated surface was 0.342 nm which was lower than for coated surfaces. The highest roughness was obtained for Al\(_2\)O\(_3\)-SiC-ZrO\(_2\) coating (52.2 nm) compared with binary coatings due to the differences in sizes of nanoparticles in addition to agglomeration of these particles. Roughness values are listed in Table (1).

Figure (6 a-e) shows the SEM for uncoated carbon steel which indicates some scratches due to grinding and polishing in addition to atmospheric corrosion. SEM micrographs of coated surfaces show the clustering of particles on metal surface that applied by cold spraying. These images also show the distribution of deposited particles on steel surface as well as the difference in particle sizes.

**Electrochemical Behavior**

Figure (7) indicates the polarization curves of uncoated and coated carbon steel by Nano particle coatings which include binary and ternary coatings. These curves indicate the cathodic region, where the reduction of oxygen can occurs and anodic region, since dissolution of iron takes place to form ferrous ions.

Corrosion parameters were calculated by Tafel extrapolation method (listed in Table (2)). These parameters include corrosion potential (\( E_{corr} \)), corrosion current density (\( i_{corr} \)) and Tafel slopes (\( b_c \) & \( b_a \)). The corrosion potential after coating is shifted to noble direction especially with Alumina-SiC coating, this coating also had the lowest corrosion current density. The rate of corrosion (\( C_R \)) in a given environment is directly proportional with its corrosion current density (\( i_{corr} \)) in accordance with the relation [11]:

\[ C_R = 0.13 \times i_{corr} \times \left( \frac{\bar{e}}{\rho} \right) \] ……(2)

This equation was applied to calculate \( C_R \) in (m/y), where \( \bar{e} \) and \( \rho \) are equivalent weight and density of carbon steel, respectively. The data of corrosion rate indicate that the nanoparticle coatings led to decreasing in corrosion rate of carbon steel and the lowest rate was for Alumina-SiC coating. The Protection efficiencies (PE%) of applied coatings can be estimated by corrosion current densities for uncoated and coated specimens as follow [12]:

\[ PE\% = \left[ 1 - \frac{i_{corr\coated\specimen}}{i_{corr\uncoated\specimen}} \right] \times 100 \] ……..(3)
The best efficiency was for Alumina-SiC coating. 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 [13]:

$$PP\% = \frac{R_{p,\text{coated}}}{R_{p,\text{uncoated}}} \times 10^{\frac{-\Delta E_{\text{corr}}}{b_a}} \times 100 \quad \text{........(4)}$$

Where $R_{p,\text{uncoated}}$ and $R_{p,\text{coated}}$ are the polarization resistances of the uncoated and coated samples, respectively, $\Delta E_{\text{corr}}$ is the corrosion potential difference between them, and $b_a$ is the anodic Tafel slope of the uncoated sample. The lowest porosity can be observed for nano Alumina-SiC coating. The results of polarization resistance, efficiency and porosity candidate the nano Alumina-SiC coating it is the best.

A typical feature of Nano crystalline materials is the defective core structure, which is caused by the incorporation of vacancies, dislocations and grain/interphase boundaries [14]. Grain boundaries are usually more active sites and can be subjected to preferential corrosion. The increased grain boundary fraction can make more anodic sites for nucleation of corrosion in a nanostructured material. Grain boundaries are associated with high diffusivity and higher electrical resistivity. The grain boundaries turn out to be more susceptible to corrosion attack if the inter-granular diffusion of corrosive species. Nano-crystalline materials show promising advantages in preventing high temperature oxide scale formation [15, 16]. On other hand, these nanostructured materials may block the anodic site and prevent it to grow especially in pitting corrosion.

The pitting corrosion can be estimated by cyclic polarization measurement. Figure (8) shows the cyclic polarization of uncoated and coated surfaces. The test of uncoated, if the protection potential is more negative than the pitting potential, pitting could sample shows that the breakdown potential ($E_p$) is -179 mV. The pitting nucleation and a right loop are obtained; also the return potential (that is characteristic of pitting propagation) and a negative hysteresis due to the reversible damage by pitting are also observed occur. The size of the pitting loop is rough indication of pitting tendency; the larger the loop, the greater the tendency to pit. In the above measurements, Alumina-SiC coating was the best. Cyclic polarization confirmed this result and the Alumina-SiC coating recorded the highest breakdown potential equal to +69 mV.

**CONCLUSIONS**

Binary and ternary nanoparticle coatings were applied on carbon steel to estimate the corrosion resistance in artificial seawater. The characterization was performed through AFM and SEM of coated surfaces. Among four nano coatings [(50%Alumina-50%SiC), (50%Alumina-50%Zirconia), (50%SiC-50%Zirconia) and (60%Alumina-20%SiC-20%Zirconia)], 50%Alumina-50%SiC had the lowest thickness due to approaching in particle size. Uniformly distribution was showed in this coating. Also corrosion test gave the best data of corrosion control to reduce the dissolution of carbon steel in artificial seawater.

<table>
<thead>
<tr>
<th>Table (1): Thickness and roughness of the coated layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating material</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>50% Al₂O₃ + 50%SiC</td>
</tr>
<tr>
<td>50%Al₂O₃ + 50%ZrO₂</td>
</tr>
<tr>
<td>50%SiC + 50%ZrO₂</td>
</tr>
</tbody>
</table>
Table (2): Measured corrosion data of uncoated and coated specimens with Nano particle coatings in seawater.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ ($\mu A cm^{-2}$)</th>
<th>$-b_c$ (mV dec$^{-1}$)</th>
<th>$+b_a$ (mV dec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>-582.8</td>
<td>52.77</td>
<td>281.2</td>
<td>56.5</td>
</tr>
<tr>
<td>50%Al$_2$O$_3$+50%SiC</td>
<td>-1.500</td>
<td>0.184</td>
<td>112.9</td>
<td>122.4</td>
</tr>
<tr>
<td>50%Al$_2$O$_3$+50%ZrO$_2$</td>
<td>-558.5</td>
<td>22.38</td>
<td>52.7</td>
<td>10.7</td>
</tr>
<tr>
<td>50%SiC+50%ZrO$_2$</td>
<td>-521.5</td>
<td>8.870</td>
<td>29.7</td>
<td>22.8</td>
</tr>
<tr>
<td>60%Al$_2$O$_3$+20%SiC+20%ZrO$_2$</td>
<td>-480.4</td>
<td>18.10</td>
<td>17.30</td>
<td>24.1</td>
</tr>
</tbody>
</table>

Table (3): Calculated corrosion parameters for uncoated and coated carbon steel.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$R_p \times 10^3$ ($\Omega$ cm$^2$)</th>
<th>$C_R$ (mpy)</th>
<th>PE%</th>
<th>PP%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>0.387125</td>
<td>24.62618</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50%Al$_2$O$_3$+50%SiC</td>
<td>138.5931</td>
<td>0.085867</td>
<td>99.651</td>
<td>1.438 x 10$^{11}$</td>
</tr>
<tr>
<td>50%Al$_2$O$_3$+50%ZrO$_2$</td>
<td>0.172564</td>
<td>10.44407</td>
<td>57.589</td>
<td>83.3320</td>
</tr>
<tr>
<td>50%SiC+50%ZrO$_2$</td>
<td>0.631414</td>
<td>4.139363</td>
<td>83.191</td>
<td>5.04175</td>
</tr>
<tr>
<td>60%Al$_2$O$_3$+20%SiC+20%ZrO$_2$</td>
<td>0.241596</td>
<td>8.446727</td>
<td>65.700</td>
<td>2.46815</td>
</tr>
</tbody>
</table>

Figure (1): 2D and 3D views of AFM image of uncoated carbon steel.
Figure (2): 2D and 3D views of AFM image of coated carbon steel with (50%Al₂O₃ +50%SiC).

Figure (3): 2D and 3D views of AFM image of coated carbon steel with (50% Al₂O₃ +50%ZrO₂).

Figure (4): 2D and 3D views of AFM image of coated carbon steel with (50%SiC+50%ZrO₂).
Figure (5): 2D and 3D views of AFM image of coated carbon steel with (60% Al₂O₃+20% SiC+20% ZrO₂).
Figure (6): SEM micrographs of (a) uncoated carbon steel, (b) coated surface with Al$_2$O$_3$-SiC, (c) Al$_2$O$_3$-ZrO$_2$, (d) SiC-ZrO$_2$ and (e) Al$_2$O$_3$-SiC-ZrO$_2$. 
Figure (7): Tafel plots of uncoated and coated carbon steel.
REFERENCES