Electrochemical Characterizations of Different Ceramic Composite Coatings on Carbon Steel Piping Using High Velocity Oxy-fuel Spray

M. Akhtari Zavareh, Ahmed .A.D. Sarhan, B. Razak, and W.J. Basirun

***Abstract*—Environmental problems have had much attention for saving energy and cost in petroleum industry. For this reason the specification and the use of materials which combine erosion and corrosion resistances with high mechanical strength is a fundamental requirement in petroleum industry. High velocity oxygen fuel (HVOF) is one of the most commonly thermal spraying processes that can be deposited a wide range of chemical composition of material on the top surface of instrument and equipment to protect them from wear and corrosion phenomena. Usually a corrosion resistance of material is measured by electrochemical techniques. Electrochemical behaviors of coatings were mainly investigated by potentiodynamic polarization in sea water (3%NaCl) as a function of process parameters. The results were expected to facilitate the understanding and improvement of the carbon steel piping behavior in sea water. Potentiodynamic polarization and electrochemical impedance spectroscopy show that the HVOF coating of chromium carbide-nickle chromium has the higher corrosion resistance and protects the substrate from NaCl electrolyte penetration.**

***Index Terms*—Al_2O_3-13%TiO_2, Cr_3C_2-25%NiCr, Corrosion current density, Corrosion potential, Electrochemical impedance spectroscopy, High velocity oxygen fuel sprayed**

I. INTRODUCTION

OFFSHORE oil and gas production environments represent aggressive conditions in terms of erosion and corrosion. Up to 15% of failures in oil and gas production are caused by erosion-corrosion mainly at gravel packs, nozzles and Christmas trees before hydrocarbons reach a first separator [1-3]. This phenomenon is accelerated the rate of deterioration of metal by combined action of mechanical erosion and electrochemical attack [4]. In addition to in petroleum industry a carbon steel is the most common material used in piping in both the upstream and downstream is domain due its high performance and relatively low cost compared with higher alloyed materials. However, a curial problem for the carbon steels is their low corrosion resistance [5, 6]. For example, a corrosion of carbon steels in CO_2 containing, oxygen free aqueous solutions is connected with the formation of layers of more or less protective corrosion products. Various methods such as sacrificial anode technique, corrosion inhibitor technique and covering the steels with coatings or films are used to decrease the corrosion rate of steel in different corrosive conditions [7]. One of the most common routes to prevent steels from corrosion is to deposit a protective coating onto the carbon steel surface [8, 9].

Generally the choose of proper materials is an important factor for resistance of instrument from environmental phenomena but the method and fabrication of these products has a vital rule for increase the long life of products. Beside, improving quality of metallic and non-metallic coating along with thermal spray method is one of the newest corrosion and wears prevention methods. The purpose of coating is to get a blend of unique properties at low cost which is not possible from other manufacturing processes. High velocity oxygen fuel (HVOF) is one of the most commonly used thermal spraying processes to produce wear and corrosion resistant coatings. In HVOF, the process is involved with an internal combustion to rapidly heated and accelerated of powder consumable to high velocities. The high combustion pressure and rapid exposures through a nozzle facilitated the particle velocity to reach supersonic speed before impacting on to a surface. This provides excess impacting force which, in turn, results in mechanical adhesion of powders to the solid surface [10-13].

In this research two different types of ceramic composites was chosen that have specific properties. A first group is titanium oxide with titania (Al_2O_3-13%TiO_2). This powders consisting of alumina and 13% titania (nominal) are used to produce coatings for applications that require moderate hardness and grind ability, but higher fracture toughness compared to coatings produced from pure alumina, alumina 3% titania. Coatings of this material is suitable for applications that require hard bearing surfaces, resistance to abrasive grains, fretting and particle erosion at operating temperatures up to 540 °C (1000 °F) [10-12]. When polished, the coatings have low wettability, which makes

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them proper for applications in the chemical processing industry to resistant weak acidic environments [14, 15].

A second group of ceramic composite is chromium carbide with nickel chromium. The nickel-chromium alloy serves as a matrix that improves overall coating integrity and corrosion resistance, while the chromium carbide constituent serves as a hard phase that assures wear resistance [3, 4]. Coatings of these materials effectively combat solid particle erosion (SPE), high temperature wear (abrasion, erosion, fretting and cavitation) up to 870 °C (1600 °F) and hot corrosion [8, 9].

In this work, the corrosion resistance of carbon steel samples that covered with HVOF sprayed Al_2O_3–13%TiO_2 and Cr_3C_2-25%NiCr coatings was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 3%NaCl solution for 27days.

II. METHODOLOGY

In this study, carbon steel was used as a coating substrate. Prior to deposition, steel specimens of 10mm x 10mm x 4mm was sandblasted .Then two different ceramic powders (Al_2O_3-13%TiO_2 and Cr_3C_2-25%NiCr) were deposited for an average of 5 passes. The particle size of the powders was between 45-60 and 35-50 µm respectively and the average thickness of the coating was about 200 µm. The temperature and spray distance were kept constant throughout the deposition process.

The Al_2O_3-13%TiO_2 and Cr_3C_2-25%NiCr composite powders coating were deposited on carbon steel coupons with a Miller HVOF system. The coupons were sandblasted to remove rust and the surface was cleaned prior to thermal spray deposition. Surface preparation is a very important step in thermal spraying because coating adhesion is directly related to surface roughness and is controlled by the type of grit blasting machine, blasting pressure, angle distance, time and grit blasting nozzle [16] Grit blasting was carried out with a highly efficient sand blaster with Alumina grit size of 10-20 mesh, a sand blaster with a 10mm nozzle and operating at a blasting pressure of >0.5 MPa. The distance between substrate and nozzle was 150 mm with a 30^0 angle. The duration of the grit blasting process depends on the required surface roughness. Upon completing grit blasting, deposition was performed using a Miller HVOF system. The parameters for HVOF spraying the ceramic coatings were adjusted to control the material chemical reactions, and also to control phase stability at high temperature. The parameters adopted in the spraying process are shown in Table I.

TABLE I. THE PARAMETERS OF HVOF COATING

Parameters	Unit
Combustion pressure	70 Mpa/sq.cm
Spray distance	150 mm
Spray angle	90^O
Powder feed rate	40-50 g/min
Fuel flow rate	20-30 liter/hour
Oxygen flow rate	45-70 m^3/hour
Carrier gas flow rate	30 liter/hour
Barrel length	198 mm/150mm

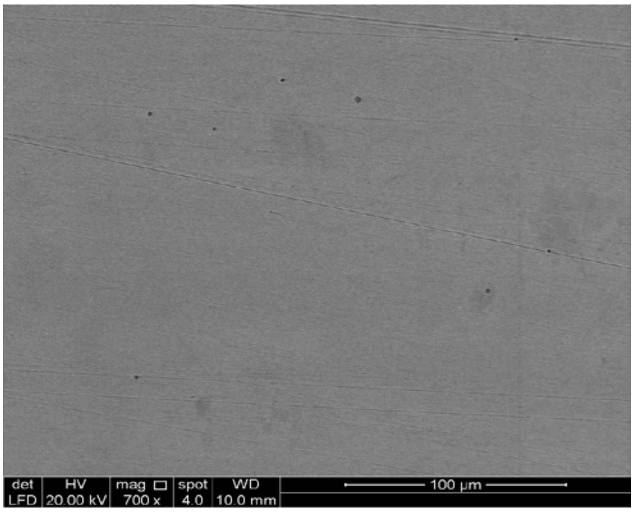
The morphologies of coated surfaces were evaluated using a scanning electron microscope (SEM) with different magnifications before and after corrosion testing.

Electrochemical techniques such as DC (polarization) and AC (impedance) were done using a potentiostat / galvanostat model AutoLab PGSTAT30 from Ecochemie (Netherlands). Polarization experiments were done using a three-electrode cell where the samples were the working electrode (WE), and a platinum wire and saturated calomel electrode (SCE) were the counter and reference electrodes respectively. The electrolyte was 3% NaCl. In this test, the linear scan voltametry, the corrosion current (I_{corr}) and corrosion potential (E_{corr}) were calculated from the Tafel plots.

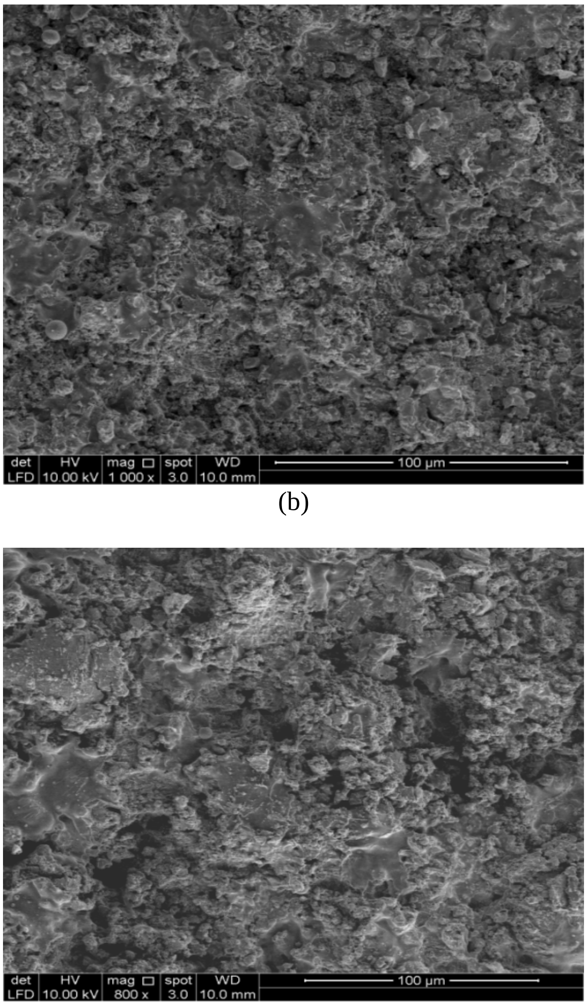
Electrochemical impedance spectroscopy (EIS) was done using a frequency range of 10^5 – 10^{-2} Hz with amplitude potential of Vrms = 5 mV. Simulations with analog circuits were done with the experimental data to obtain values for the charge transfer resistance across the electrode-electrolyte interface, which can be correlated with parameters from the polarization results. A frequency response analyzer (FRA) and general purpose electrochemical software (GPES) were installed in a computer interfaced with a potentiostat and were used to run the DC and AC techniques respectively

III. RESULT AND DISCUSSION

Fig. 1(a) shows a micrograph of pure carbon steel before a corrosion testing. As can be seen the surface is smooth. Fig. 1(b) illustrates a Cr_3C_2-25% NiCr coating that is uniform, homogeneous and free from surface cracking. Applying a homogenous coating without segregation is critical for improving the corrosion resistance of this powder coating. As per Fig. 1(b), some region is fully melted that is belong to NiCr that is completely melted and the grain boundary has increased. The melted regions are attributed to the arrest and deflection of crack propagation through the partially melted regions [10]. Fig. 1(c) shows a micrograph of Al_2O_3-13%TiO_2 that some regions have partially melted because the powder temperature is not high enough during spray coating, so the amount of porosity in this group is higher than a Cr_3C_2-25%NiCr.



(a)



(b)

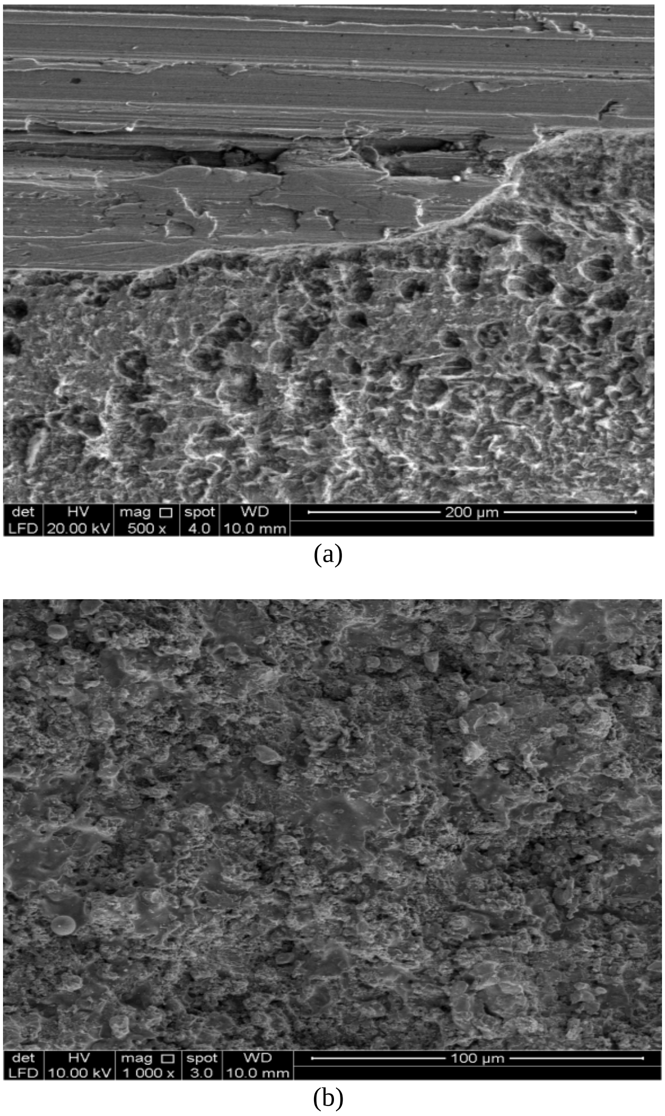
(c)

Fig. 1. Scanning Electron Microscopy of (a) carbon steel (uncoated), (b) Cr_3C_2-25%NiCr coated, (c) Al_2O_3-13%TiO_2 coated samples before corrosion testing

After immersing uncoated and coated samples in the 3%NaCl solution for 27 days, the surface of carbon steel (uncoated) sample is destroyed significantly. Figure 2(a) shows top surface of carbon steel after 27days, while Figs. 2(b) and (c) show that the surface of coated samples after a long immersion in NaCl, has still similar to that one before corrosion testing. It can be concluded that the HVOF coated samples are resistant against corrosion. However, it has been demonstrated that the electrolyte penetration through the coating defects can strongly affect the electrochemical behavior of thermal spray coatings. In this case, the electrolyte did not penetrate into the substrate and did not produce iron oxide.

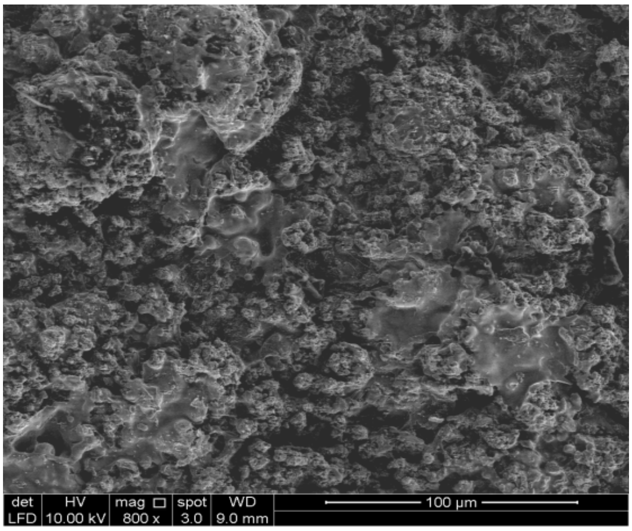
Potentiodynamic polarization results gave overall current response of the applied potential which included the current responsible for chemical reaction and current for charging and discharging of the double layer. The general corrosion ranking of different materials was established by measuring corrosion potential, corrosion current density and passive current density from polarization curves [16].

The corrosion current density (I_{corr}) and the corrosion potential (E_{corr}) are two parameters determined from the electrochemical testing. The corrosion current density and the corrosion potential were obtained by the intersection of the extrapolation of anodic and cathodic Tafel curves. Higher values of the corrosion current density or a more negative value for the corrosion potential will indicate that the system coating-substrate is less resistant to corrosion (i.e. that it is prone to electrolytic solution penetration). Regarding to this rule a polarization curves were made for uncoated and coated samples for the last day (day 27) of corrosion testing. Figure 3 shows the corrosion currency density for carbon steel, Al_2O_3-13%TiO_2 and Cr_3C_2-25%NiCr are 1.416E-4, 5.144E-5 and 2.011E-6 respectively. It also can be seen that the corrosion current I_{corr} for the coated samples are smaller than for the uncoated sample. Also the open circuit potential (OCP) of the Al_2O_3-13%TiO_2 and Cr_3C_2-25%NiCr samples with amount of -0.443 and -0.36 move toward noble potential at the end of day 27, while the corrosion potential for carbon steel is become more negative (-0.624). So the OCP values for the coated samples are nobler compared to the uncoated sample. Because the amount of OCP depends on several parameters such as the coating chemistry, the surface roughness, the coating thickness, etc. These characteristics are a function of the operating conditions. These results suggest that the HVOF coating on carbon steel offers good protection of the carbon steel substrate against corrosion and between these powders a Cr_3C_2-25%NiCr has a more durable behavior against aggressive environment.



(a)

(b)



(c)

Fig. 2. Scanning Electron Microscopy of (a) carbon steel (uncoated), (b) Cr_3C_2-25%NiCr coated, (c) Al_2O_3-13%TiO_2 coated samples after corrosion testing

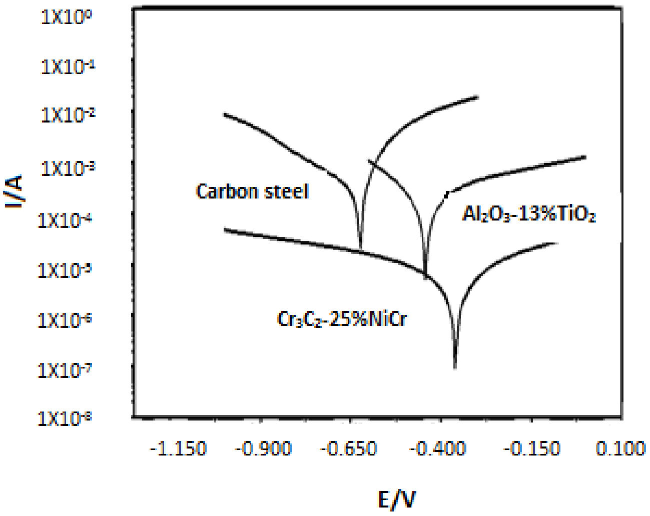


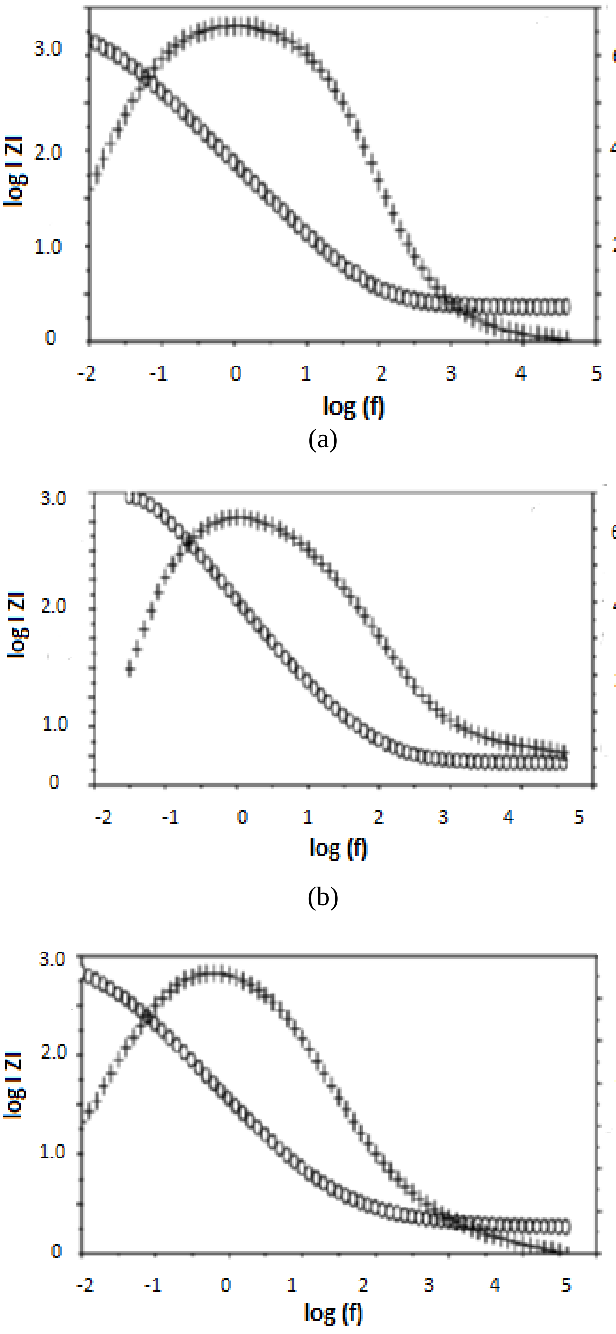
Fig. 3. Potentiodynamic polarization curves in 3%NaCl solution

Figure 4 show simultaneously a typical bode phase and Z modulus diagram evolutions for uncoated and coated samples after 27day immersion in NaCl solution. The high frequency response represents the electrical capacitance of the coated film. At very low frequency, total impedance recordings correspond to the polarization resistance at the surface of the test electrode (i.e. coating surface).

Generally the process of conduction can be schematized by (1) the displacement of the ions in the solution; (2) the phenomena of charge transfer at the interface and finally by (3) the displacement of the electrons in the electrode.

The current circulation through the solution is due to the migration of the ions. The displacement of the ions is related to the conductivity of the electrolytic solution. From this conductivity, one defines the equivalent resistance of the electrolytic solution R_s. At the interface, the phenomena are more complex. It is necessary to consider capacitive and faradic process. When a metal is immersed in an electrolytic solution, an electrochemical double layer is created at the interface metal/electrode. This double layer is materialized by a capacitance C_{dc}. A faradic process is represented by the charge transfer resistances R_{ct}.

Table II shows the calculated values of the different coated. These values were determined on the basis of the equivalent circuit using a suitable fitting procedure by Autolab Software and they are related to the diffusion of the electrolytic solution into the pores. The data are coherent with coatings that do protect the substrate clearly, i.e. electrolytic solution doesn't go through the barrier for coated samples. Also according to Fig. 4 the corrosion resistance for Cr_3C_2-25%NiCr is higher than Al_2O_3-13%TiO_2.



(a)

(b)

(c)

Fig. 4. EIS test results for (a) Carbon steel, (b) Al_2O_3-13%TiO_2, (c) Cr_3C_2-25%NiCr for day 27

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TABLE II. EIS FOR DAY 27

Symbol	Carbon steel	Al_2O_3-13%TiO_2	Cr_3C_2-25%NiCr
R_s	1.04833e+1	5.13321e-1	1.11798e+3
R_{CT}/kOhm	8.98984e-1	3.3361e+2	7.35994e+3
CPE/F	5.75421e-3	3.87149e-3	2.0752e-5
n	0.89412	0.42759	0.36357

IV. CONCLUSION

In this work, the corrosion resistance of carbon steel samples that covered with HVOF sprayed Al_2O_3–13%TiO_2 and Cr_3C_2-25%NiCr coatings was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 3%NaCl solution for 27days. The corrosion potential of samples is raised by ceramic composite coating. Coatings act as simple barriers and diminishes the probably of finding interconnected pores. HVOF sprayed coatings Al_2O_3-13%TiO_2 showed less corrosion resistance than Cr_3C_2-25%NiCr ones. In the structure of Al_2O_3-13%TiO_2 coating the inhomogeneity and local differences were observed. Alumina-titania coating had many micro pores, but the chromium carbide-nickel chromium coating is found to be more densified and exhibited the highest corrosion resistance in corroded environment. In addition, both polarization and EIS results confirm these results and the corrosion protection properties of the HVOF coatings of these ceramic composites.

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