International Journal of Latest Research in Engineering and Technology (IJLRET)
ISSN: 2454-5031
www.ijlret.com || Volume 03 - Issue 11 || November 2017 || PP. 35-42

Corrosion resistance evaluation of Ni-Al \ YSZ composite coatings by an Electrochemical Investigation

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Abstract: The composite coating is used to protect carbon steel pipeline from corrosion by Surface modification using thermal spraying technique to enhance the corrosion resistance of carbon steel. In this study the influence of sour hydrocarbon on carbon steel was investigated on samples taken from Alloys with (API 5L) that used for oil transport pipe lines in North Oil Company in Kirkuk fields and specifically from well (No. K-130) which the oil sample was brought as well. The cermets coating(Ni-Al /ZrO2-8Y_2O_3) were prepared in different mixing ratios of Yttria-Stabilized Zirconia (YSZ) with Ni-Al as a self bonding. Several mixing ratios of the binder (Ni-Al) were used to prepare the cermets for thermal spraying coating namely 15% and 50%. In order to study the effect of roughness on the binding of the cermets and hence the corrosion behavior of the carbon steel another specimen was mechanically abraded to a surface finish 800 grit by SiC paper and the cermets mixing ratio (50% YSZ+ 50% Ni-Al) .The thermal spraying gun was located in an angle of 90º in front of the carbon steel specimen and the distance between them was 16 cm. The corrosion behavior of the modified surface in comparison with untreated one was investigated by electrochemical techniques. Two electrochemical techniques (DC and AC techniques) were used. The AC technique was potentiodynamic cyclic polarization using Solatron 1287, USA) potentiostat/galvanostate. The EIS measurements for all coated specimens show enhancement in the impedance parameters (total impedance |Z|, polarization resistance (R_p) and the capacitance (C)) comparing to the uncoated one. The cermets thermally sprayed coating show improvement in the corrosion parameters.

Keywords: Corrosion, Carbon steel, Electrochemical techniques ,Thermal spraying technique, Yttria-Stabilized Zirconia (YSZ) Composites.

1. INTRODUCTION

The surface of a component is usually the most important engineering factor while, it is in use. It is often the surface of a work-piece that is subjected to wear and corrosion. In industrialized countries about 30% of energy generated is ultimately lost through corrosion [1]. Corrosion is basically an economic problem. This, the corrosion behavior of any part product is an important consideration in the economic evaluation of any project mode. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to positive value. The environment are called electrolytes since they have their own conductivity for electron transfer [2]. Petroleum product include hydrocarbons are not aggressive to alloy under ambient condition. In spite of this ,give rise to the corrosion of tanks, pipes and pumps made of mild steel[3]. In oil, many cases of extensive corrosion have occurred in production tubing, valves and flow lines from the well-head to the processing equipment. The reason for this is that various amounts of water, which can be precipitated as a separate phase in contact with the material surface, and the water contains gases such as CO2 and H2S , as well as salts can be causes corrosion[4] .

Thermal spray techniques were able to satisfy the increasing demand for thermal barrier and corrosion resistant coating systems. Today, These techniques includes a wide range of processes where coating materials, in a wire or a powder form, are heated, with an electrical current, a plasma gas or a torch, and sprayed in particle form, which can be molten, partially molten or solid, with a carrier gas onto a substrate to form a coating. [5-7]. The technique of cermet coatings is attractive for it is weak thermal and electrical properties and more resistant to oxidation , corrosion ,erosion and wear than metals in high temperature environments. This coatings is known as (thick coatings) which refers to the property of high hardness in mechanical sense with good corrosion resistance properties[8]. Mythili[9], studied the corrosion behavior and corrosion rates of carbon steel in the presence of CO2 and H2S using classical electrochemical techniques at various pH levels. It was found that in a galvanic coupling, the metal in the sulfide environment gets protection even at pH= 3, and the bare metal which is in neutral pH was corroding sacrificially.. The corrosion rate generally was higher for CO2/H2S system than for H2S system only. Diaz et al.[10], have been evaluated the H2S corrosion inhibition of X-120 pipeline steel by using carboxyethylimietazoline in electrochemical techniques which include polarization curves, linear polarization resistance. Testing solution includes H2S containing 3% NaCl with different inhibitor concentration at 50°C. They showed by adding carboxeyethylinidazoline the susceptibility to both uniform and localized corrosion decreases. Lampke et al [11], found that thermally sprayed (flame spray, arc spraying, plasma-electrolytic) of alumina coatings are widely used in a range of industrial applications to improve wear and erosion resistance, corrosion protection and thermal insulation of metallic surfaces. They found that the created Al2O3 layers show outstanding hardness up to 1600 HV0.1, good bonding strength and excellent abrasion resistance compared to atmospheric plasma-sprayed Al2O3-coatings. The results show the superior performance of coatings and demonstrate their applicability for technical components in extreme operating conditions . Lamees S. Faiq[12], studied the thermal spraying technique which employed for coating low alloy steel specimens that have been used in a derrick oil well frames. Two types of ceramic materials were used as a coating material and two groups of steel samples were prepared for coating process. The first group was coated by zirconia while the second group was coated by alumina. Ni-Al composite powder was used for bonding the coating material on the substrate surface of the steel specimens. The hardness, adhesion strength of the coating layers as well as wear rates were studied for the two steel group samples and compared with the received steel. Results showed an increase in the mechanical properties with a decrease in wear rate values for coated samples as compared to those of uncoated samples.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

In this study the influence of sour hydrocarbon on carbon steel was investigated on samples taken from Alloys with (API 5L) specifications have been used widely in oil and gas sector to reduce the impact of this harsh medium on the metal and equipments as well from the standpoint of cost, durability, good corrosion resistance and pollution . the oil transport pipe lines that used in North Oil Company in Kirkuk fields and specifically from well (No. K-130) from which the oil sample was brought as well. Using special alloy is not the solution in such harsh medium as production processes comprise liberation of H2S, CO2 and free water as well, so extra protection is required by applying other means of protection which is the subject of our study.

The aim of this paper is to prepare a protective coating on API 5L (carbon steel) alloy which is the widely used materials in oil industry and study its effect on the corrosion behavior of the carbon steel in crude oil environment.

2.2 Preparation of Substrates

Surface condition of a specimen plays an important role in coating binding and corrosion resistance. Hence, it is necessary to prepare uniform surface and requires careful specimen preparation. Specimen preparation for surface analysis and electrochemical studies involve the following steps; square carbon steel type (API 5L-GR.B PSL1) specimens of 20 mm diameter with thickness of 5 mm were cut out from the as received carbon steel. The specimens were grinded with SiC emery papers with different grits started from 80 grit, and continued by 120, 230, 400, 600, and 800 grit to get flat surface. The specimens then were cleaned with ethanol in order to enable coating detachment after spraying. Spraying was carried out immediately after cleaning. The second stage included the implementation of the bonded coating process (nickel - aluminum) and coating the main (YSZ) using a flame spray coating process was conducted in different ratio from the YSZ and Ni-Al for each model .The factors in thermal spraying become steady, which included the surface roughness of the base metal, the temperature of the surface of the base metal before the coating process, the distance between the spray gun nozzle and the surface of the form and thickness of the coating. Table (1) shows the chemical composition of carbon steel that used in the present study.

Table(1) Chemical composition of Carbon Steel

Element	C	S	Mn	P	V
Weight%	0.26	0.03	1.20	0.03	0.01

In this study it was used kirkuk oil field. Table(2) shows the chemical compositions of the crude oil .

Table 2: Kirkuk crude Oil chemical composition

API	Viscosity	H2S	Sulphur	Asphaltene	Wax
33.2	9.30 centi stock @ 80F	360 ppm	2.5 %	2.23%	3.1 %

2.2 Preparation of The Cermets (Ni-Al /ZrO2-8Y2O3)

The powders which were used to coat the carbon steel are:

2.2 .1- Nickels --Aluminum

Ni-Al binding powdered materials has a melting point of (1350C°), particle size of (50- 75)µm and gray color with chemical composition of 93%Ni and 7% Al, coatings thickness (50- 75) µm .

2.2 .2-Zirconia Stabilized Y2O3

The ZrO2 powder which was used has a tetragonal – monoclinic phase with a melting point (2680°C) having a white color obtained from Oerlikon Metco Switzerland. the powders where a particle size is about (50-75) µm, coatings thickness(250 -300) µm ,we made different ratio coatings between the (Ni-Al /YSZ). Table (3) shows the percentage of the Ni-Al /YSZ composite.

Table (3) The percentage of the Ni-Al /YSZ composite.NO. Of Sample	**Top Coat** YSZ	**Bond Coat** Ni-Al
1	85%	15%
2	50%	50%

2.3 Coating Operation

After roughing and cleaning the carbon steel specimens surface, the following steps were done:

1- Sample was fixed on the turning machine.
2- Spray gun was fixed forward sample vertical form.
3- The sample was rotates under constant velocity during spraying process.
4- The pressure of the two gases was controlled as shown in Table (4) Operating parameters during coating deposition process.
5- The sample was heated to 200°C by flame before spraying and then the bond powder was sprayed (Ni-Al) from distance of 200 mm to produce bonding layer.
6- Then (YSZ) was sprayed from distance of 200 mm to produce ceramic coat.
7-The coated sample (Ni-Al/YSZ) was heated after spraying to a temperature of 1300°C for (24) hour followed by air cooling to the room temperature. Figure(1) shows the samples after coatings with Ni-Al /ZrO2+Y2O3.

Table (4) Operating parameters during coating deposition process.

OXY – Acetylene Mixing	3:1
Spraying Distance	200 mm
Rotation Number	4
Flame spray temp	≈ 3000°C
Angel of spray	90°
Coating Time	(1-2) min
Maximum Thickness Coating	300 µm
Time between two spray prosses	5 sec
Particle size of Ni-Al powder	(50-75µm)
Particle size of YSZ powder	(50-75µm)

Oxygen pressure	4-6 bar
Acetylene pressure	1-2 bar

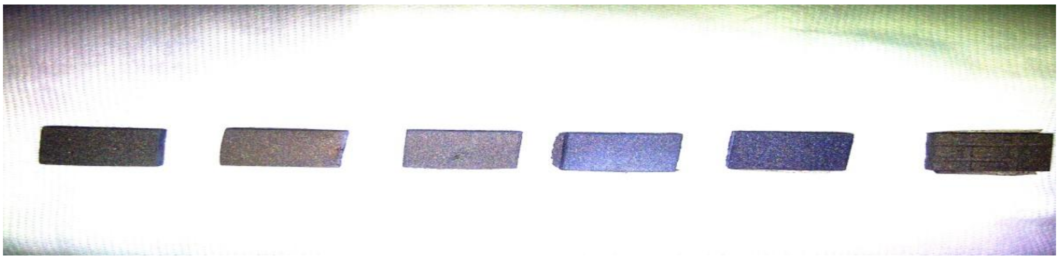
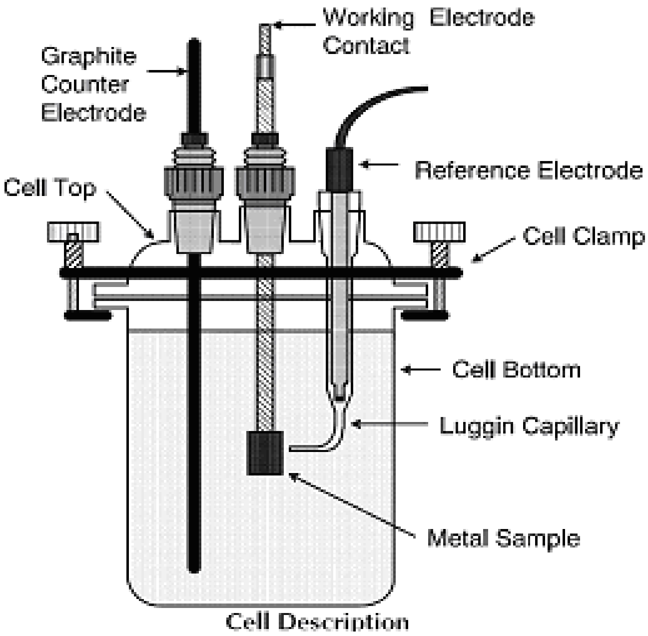


Fig (1) The samples after coatings with Ni-Al /ZrO2+Y2O3.

2.4 Electrochemical Technique Investigation

Anodic cyclic polarization was conducted on the coated specimens in comparison to the uncoated one in oil simulated solution. Three electrodes standard corrosion cell was used for corrosion measurements. Platinium foil was used as auxiliary counter electrode; saturated calomel electrode (SCE) as reference and the specimens was acted as working electrodes respectively. The samples were polarized from -0.6 V to 1.5 V with scan rate of 0.5 mV/s and then reversed until it was intersected the forward scan. Electrochemical Impedance Spectroscopy (EIS) measurements at OCP condition in 3.5 M of NaCl and Kirkuk crude oil solution (Table 2 chemical composition of Kirkuk crude oil) were carried out at the same setup used for potentiodynamic polarization. A Solartron make 1255 HF frequency response analyzer (FRA) and SI 1287 potentiostat/glvanostat electrochemical interface controlled by commercial software program Zplot, version 3.4d, (C) 1990-2015, Scribner Associated, Inc., . All experiments were done in standard corrosion cell provided with a platinum counter electrode (CE) and Saturated Calomel Electrode (SCE) as reference electrode, whereas the coated carbon steel specimen was acted as working electrode (WE). The resulted curves of the potentiodynamic polarization and the impedance spectroscopy were analyzed using CView 3.4d and ZView3.4d software from which all the corrosion parameters were predicted. Figure (2) indicate schematic representation of a similar corrosion cell used for testing.



Fig(2): Schematic representation of a similar corrosion cell used for testing[13].

3. RESUILT AND DISCUSSION

3.1 Electrochemical Investigation Techniques

3.1.1- DC Potentiodynamic Cyclic Polarization Measurements

Potentiodynamic polarization is a technique where the potential of the electrode is varied at a selected rate by the application of a current through the electrolyte. Through the DC polarization technique, information on the corrosion rate, pitting susceptibility, passivity, as well as the cathodic behavior of an electrochemical system may be obtained. In a potentiodynamic experiment, the driving force (i.e., the potential) for anodic or cathodic reactions is controlled, and the net change in the reaction rate (i.e., current) is observed. The potentiostat measures the current which must be applied to the system in order to achieve the desired increase in the driving force, known as the applied current. As a result, at the open circuit potential the measured or applied current will be zero [9].

The main parameters that can be obtained from potentiodynamic cyclic polarization curves are the corrosion potential, E_{corr} , corrosion current I_{corr} , polarization resistance R_p, corrosion rates C_R and the passivation current density I_{pass} .

The uncoated and the NiAl+YSZ coated carbon steel were tested by potentiodynamic cyclic polarization in crude oil at room temperature. Compared to the uncoated carbon steel, the open circuit potential (Eoc) of the NiAl+YSZ coating shifted to more positive direction. Figure (3) shows the polarization curves for the uncoated carbon steel and composite (NiAl+YSZ) coated with different mixing composition in crude oil solution [14].

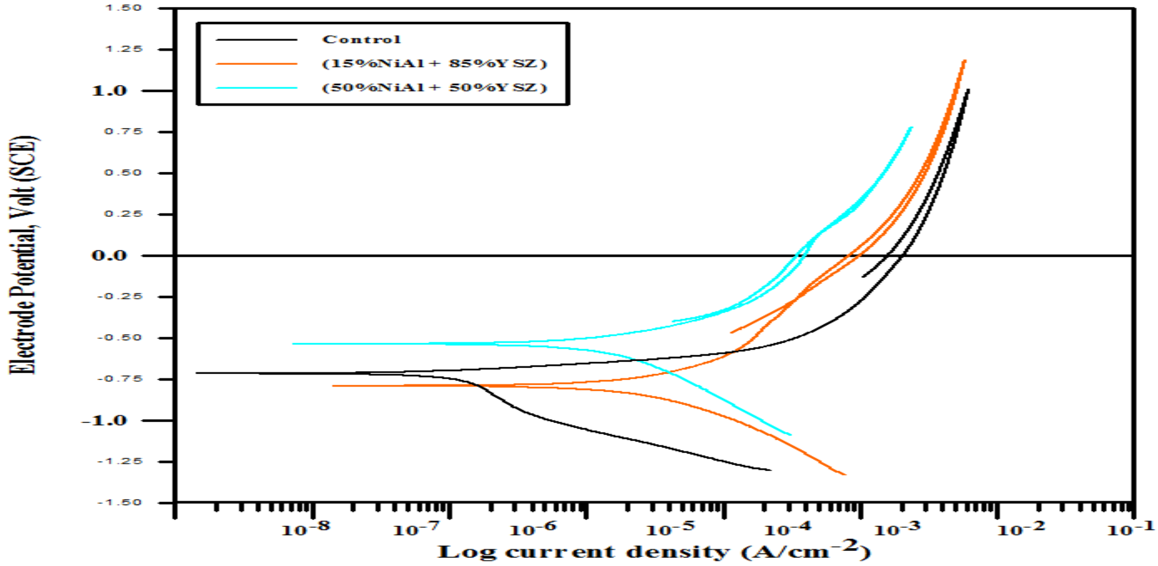


Fig 3: Cyclic polarization for the uncoated and (NiAl + YSZ) coated with different mixing ratios carbon steel in crude oil; Sweep rate 1 mV/sec.

Table 5 demonstrates the electrochemical parameters predicted from the polarization studies shown in Fig 3

Treatment conditions	OCP (V)	I_{corr} (A/cm^2)	E_{corr} (V)	CR (MPY)	I_{pass} (A/cm^2)
Control(uncoated)	-0.705	1.24 $x10^{-5}$	-0.830	5.28	3.73 $x10^{-2}$
15%NiAl+85%YSZ	-0.7324	2.85 $x10^{-6}$	-0.811	2.53	1.99 $x10^{-2}$
50%NiAl+50%YSZ	-0.7323	1.42 $x10^{-6}$	-0.535	4.13	1.50 $x10^{-2}$

Table (5) shows the electrochemical parameters obtained from the polarization curves shown in Figure (3). The results show that when the potential reversed in the end of the cathodic polarization the cycle went toward the clockwise direction and increasing the current indicating the occurrence of pitting corrosion on the surface of the specimens coated with 15%NiAl+85%YSZ and 50%NiAl+50%YSZ The passive current density in Figure (3) of the uncoated and composite coated specimens showed decrease in its values indicating the stability of the passive film formed on the surface and the lowest value of passivation current was recorded for specimens coated with 15%NiAl+85%YSZ and 50%NiAl+50%YSZ (1.99 $x10^{-2}$and 1.50 $x10^{-2}A/cm^2$,respectively) comparing to the uncoated one (3.73 $x10^{-2}A/cm^2$).

3.1.2-Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) has been used to analyze the response of corroding electrodes to small-amplitude alternating potential signals of widely varying frequency. EIS is a complex combination of solution resistance, interface capacitance, charge transfer resistance and mass transfer resistance. At high frequencies the solution resistance predominates whereas at low frequencies charge and mass transfer become the main contribution to impedance. This is normally to be analyzed using Nyquist diagrams, where the imaginary part of impedance is plotted as a function of its real part. The Bode plots show the total impedance |Z|, and phase angle θ, as a function of frequency. The impedance parameters |Z|, polarization resistance R_p and capacitance C were calculated from Nyquist and Bode plots using *Zview* software version 3.4a, (C) 1999-2015, Scribener Associated, Inc.

The Nyquist simulated experimental impedance curves with a simple circuit with CDL (double layer capacitance) in parallel with polarization resistance is not a very good overlap. So that, for this reason it is necessary to introduce an equivalent circuit Figure (4) with CPE (the capacitance element of the double layer which is dependent of the frequency because the surface is not homogenous).

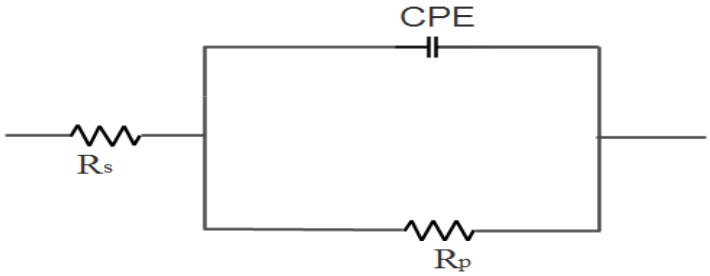


Fig4: Equivalent circuit to calculate the polarization resistance from impedance spectrum with a CPE: Rs – solution resistance between the reference electrode and the working electrode; CPE – the double layer capacity in parallel with the polarization resistance R_p.

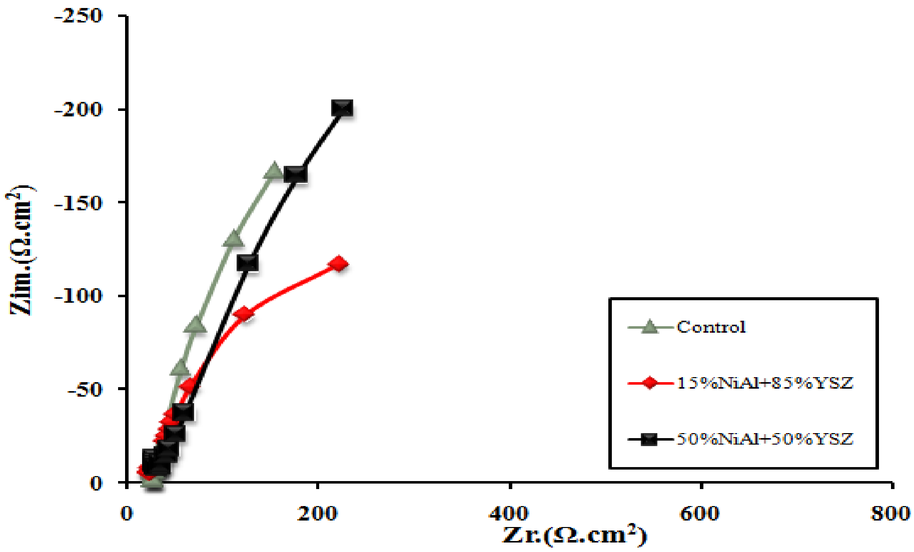


Fig 5: Nyquist diagrams of impedance spectrum for control (uncoated) and NiAl+YSZ coated carbon steel in crude oil .

It could be observed that the experimental impedance data fit very well with the equivalent circuit proposed. Equivalent circuit Re-CPE//R_p represented in Figure (4) gives a single flattened circle as can be seen in Figure (5) of the Niquist plots for the carbon steel coated with different mixing ratio of NiAl+YSZ.

The evolution of the impedance depending on the frequency in this case could be described by the following equation:

$$Z = R_e + \frac{R}{1+(jw\tau)^{\beta}} (0 < \beta \leq 1) \ldots\ldots\ldots\ldots (1) \qquad (1)$$

Ciubotariu et al [15] explain this expression as the parameter β (always smaller than 1) indicates the smoothing of the circular curves from Randles models and the experimental circuit with CPE: the line corresponding to the Randles model was found only in the value β = 1 when they studied the EIS of carbon steel X60 in different corrosion solutions. They found that in this case, the CPE is a pure capacitor.

Figure (6) shows simultaneously a typical Bode phase and Z modulus diagram evolutions for uncoated and NiAl+YSZ coated samples in crude oil solution. The high frequency response represents the electrical capacitance of the coated film. At a very low frequency, total impedance recordings correspond to the polarization resistance at the surface of the test electrode (i.e. coating surface) which are presented in Table (6).

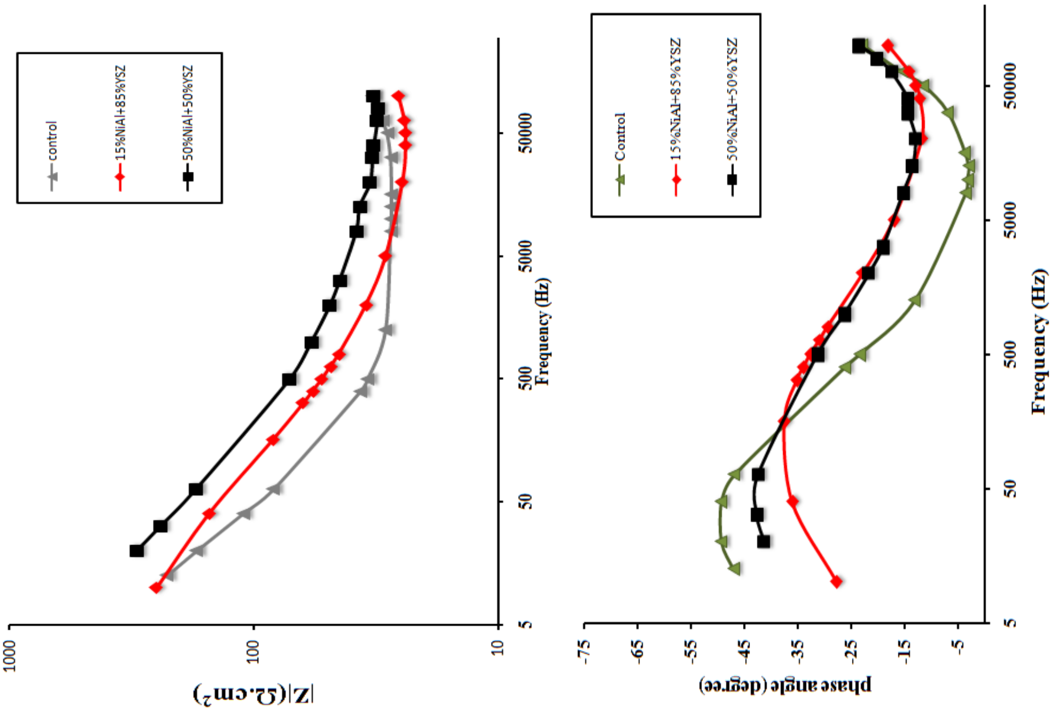


Fig 6: Bode plots of control (uncoated) and NiAl/YSZ carbon steel in crude oil (a) Impedance (b) Phase angle.

Table 6: Impedance parameters of uncoated (control) and NiAl+YSZ coated carbon steel after immersion in crude oil solution.

Treatment conditions	Rs (Ω)	CPE-T(f)	CPE-P (f)	Rp(Ω)	|Z|	C (f)
Control(uncoated)	27.36	1.2594E-4	0.7919	600	1.982 $x10^1$	1.2594E-4
15%B+85%YSZ	22.22	2.5790E-4	0.57513	517.2	2.51 $x10^2$	2.5790E-4
50%B+50%YSZ	29.36	2.4684E-4	0.54468	5094	4.15 $x10^2$	2.4684E-4

The constant phase element (CPE) is defined by CPE-T and CPE-P. If CPE-P equals one approximately, then the CPE is identical to a capacitor, Cdl [16]. If CPE-P equals 0.5, a 45 degree line is produced on the Complex-Plane graph. When a CPE is placed in parallel to a resistor, a Cole-Element (depressed semi-circle) is produced. It's very clear from Table(6) that all specimens coated with mixture of NiAl+YSZ, the CPE-P values are almost nearly 0.5 for that the complex-plane graphs in Figure 4 produced 45 degree lines.

4. CONCLUSION

All coated specimens show enhancement in the impedance parameters (total impedance |Z|, polarization resistance (R_p) and the capacitance (C)) comparing to the uncoated one.

It's very clear from that all specimens coated with mixture of NiAl +YSZ, the CPE-P values are almost nearly 0.5 for that the complex-plane graphs produced 45 degree lines. In addition, the results show that the samples coated with 15% NiAl+85%YSZ had more uniform corrosion resistance than control (uncoated) and other coated samples. The samples coated with mixing ratios 15%NiAl+85%YSZ and 50%NiAl+50%YSZ show high passivity with no pitting corrosion as the polarization cycle went anticlockwise. The cermets thermally sprayed coating even show improvement in the corrosion parameters.

5. ACKNOWLEDGEMENTS

The authors wish to acknowledge the efforts of university of Tehran / school of metallurgy & material who gave me access to the laboratories and research facilities and help me to perform several tests in time effective manner such as corrosion tests.

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