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The effect of temperature and phosphate treatment for investigation of wear and corrosion of synthesized nano-alumina coatings through sol-gel method on Inconel 718 alloy

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Nano-alumina particles were coated on phosphate surface of Inconel 718 alloy through sol-gel method in this study. morphological and fuzzy structure of coatings surface were conducted through X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) analyses, respectively. Wear properties were checked using pin-on-disk corrosion. The resistance of coated samples against corrosion was investigated by electro-chemical impedance spectroscopy. XRD results of coatings thermally treated at 300, 500 and 800˚C confirmed the amorphous nature of coatings and accordingly, weak peaks of γ-phase alumina ($\gamma - Al_2O_3$) can be only seen in thermally treated coating at 800˚C. The conducted studies by FE-SEM of coatings showed that average size of particle has been in coating of 46 Nanometer and a uniform and porosity-less structure can be only seen in thermally treated at 300˚C. The obtained results of FE-SEM of coatings indicated that the best time for immersing the samples in phosphating bath includes 60 minutes. The obtained results of wear testing depicted that the beneath surface layer phosphating increases the resistance against alumina coatings corrosion. The spectroscopy results of electrochemical impedance showed that, creating Nano-alumina coating with phosphate substrate has had a significant effect on increasing corrosion resistance of Inconel 718 alloy.

Keywords: Nano-Coatings, Alumina, Sol-gel, Inconel 718, Wear, Electrochemical impedance, Corrosion

INTRODUCTION

One of cases, in which Nano-technology has been widely used, is coating process and consequently producing Nano-structure materials. Nanometer materials have exclusive properties due to the emergence of quantum phenomena in dimensions below 100 nm. Compared to micrometric coating, coatings of Nano-structure have higher thermal expansion coefficient, higher toughness and more resistance against corrosion, wear and erosion [1, 2]. Additionally, permeability of corrosive solutions is less in this coatings than micro-structure coatings [3].

Among Nano-structure coatings, ceramic ones have been far more noticed due to high wear and corrosion resistance, dielectric properties and high thermal resistance. Ceramic coatings are deposited on metal substrate using different methods. The thickness of these coatings is provided in the scope of Nanometer to micrometer. The coatings are divided into two general groups of thick film layers and thin film layers [4]. The methods of applying these coatings are very different but two important categories of them include [4]:

1. Coating in vapor phase such as chemical vapor deposition (CVD) and physical vapor deposition (PVD)
2. Coating in soluble phase such as sol-gel method

The methods, used in high temperature and pressure, have always faced with problems such as oxidation under the layer during compressing the skin and difference in thermal expansion coefficient between coating and substrate [5]. The provided coatings in high temperature and pressure has some defects such as pores and cracks, leading to corrosion of these areas in humid environments. Many attempts have been recently conducted to create ceramic coatings, resistant against corrosion and wear, on metal sublayers using sol-gel technique. Komeil et al [6] made Nano-alumina particles of 14nm through sol-gel method. This method is easy and requires less prose temperatures. Created coatings by this method can be also used on glass, plastic and ceramic, having simple or complicated geometric shape, in addition to metals [7, 8]. The sol-gel coatings are also uniform. Sol-gel is successfully used for expanding non-crystal and crystal structures of coatings in environment temperature. Many studies have been conducted on the application of ceramic coatings such as alumina, silica and titania using sol-gel method to improve chemical corrosion resistance and resistance against oxidation of metal sublayer. Among these coatings, alumina is of a great importance due to ideal

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properties such as chemical stability, thermal stability, very high corrosion resistance and wear resistance [9, 10]. Most of alumina coatings have been employed on stainless steel substrate by multi-concentration hydrolyze and using sol-gel method. Doodman et al [11] increased corrosion resistance of stainless steel using alumina coating. Marsal et al [1] investigated tri-biological properties of alumina and silica, coated on stainless steel trough sol-gel. The results of their study showed that alumina coating is of higher corrosion resistance even in the less thickness, compared to silica coating. It is reported that skin properties of alumina coatings significantly increase by increasing the thickness of coating layer in terms of particle stiffness, corrosion resistance and electrical properties. However, the application of alumina coating is low for resistance against substrate wear due to limited power of adhesive phases. Bakous [12] and Roohi [13] observed that alumina coating increases wear resistance of substrate in the initial times of wear testing but after a while, wear rate has a sudden increase because of separating coating from substrate.

One of methods for improving alumina particles adhesion to metal substrate, the surface is phosphate treated [10]. Phosphating metal surface is because of obtaining non-Soluble coating of metal phosphate crystals, strongly stick to the base metal. This case creates a supreme base for secondary coating and improves the connection of alumina layer with base metal. Zhu et al [14] coated phosphate surface with alumina by spraying. The results of their study represented that phosphating improves the connection of coating. The roughness of metal phosphate surface is considered as an important factor for increasing the strength of connection bands and strong mechanical connection of steel coating. The current study is sought to increase corrosion and wear resistance of Inconel 718 alloy (with a phosphate surface) using sol-gel method by Nano-alumina coating.

EXPERIMENTAL ACTIVITIES

Materials

Aluminum isopropoxide (as an alumina precursor), ethanol, nitric acid, phosphoric acid, iron phosphate and oxygenated water, all made in Merck German company, are the most consumed materials in this study.

Phosphating the surface of alloy

15ml of 85% phosphoric acid was poured in a beaker of 500ml and using ionized water, it is reached to the volume of 100ml. using magnetic stirrer with heater, the temperature of solution is reached to 60˚C and meanwhile 11 grams of iron phosphate (III) were added to the solution above. pH of the solution in this phase was measured as 4 using pH meter. To increase the speed of reaction, 5ml of oxygenated water was gently titrated to the solution above. Following that, the samples of Inconel 718 alloy to the dimensions of 20×20×2mm were immersed in phosphating bath for 60 minutes through immersion coating technique and were immediately heated in heater after being taken out of phosphating bath.

Providing nano-coating and coating conditions

To make aluminum oxide sol, 0.38mol of aluminum isopropoxide (77 g) to the rate of 500ml was added to boiling water and stirred with magnetic stirrer for 60 minutes with the speed of 1000rpm. the solution is heated as follows to reach the final column of that to one fourth of initial volume. In the next step, nitric acid was added to the solution above gently to increase zeta potential and prevent particles agglomeration till pH of solution reached 3. To prevent gelling and form a sustainable and transparent sol, ionized water was added to the solution in drops by pipette and cooled in room temperature gently. In order to layer, phosphate layer entered sol solution by dip coating layering device with the fixed speed of 1mm/s and 0.5mm/s and after immersion of 60 minutes was dried in the heater of 70˚C. finally, for thermal treatment at 300, 500 and 800˚C, the samples were heated in argon atmosphere with a temperature increase of 10° C / min for 60 minutes. Figure 1 shows the flowchart of coating method and experiments.

Characterization

In order to ensure the percentage of different components of substrate, Oxford emission spectrometry device was used, according to standard of RMRC-WI-560-114-01. Chemical composite of Inconel 718 alloy, used for coatings substrate, has been shown in Table 1.

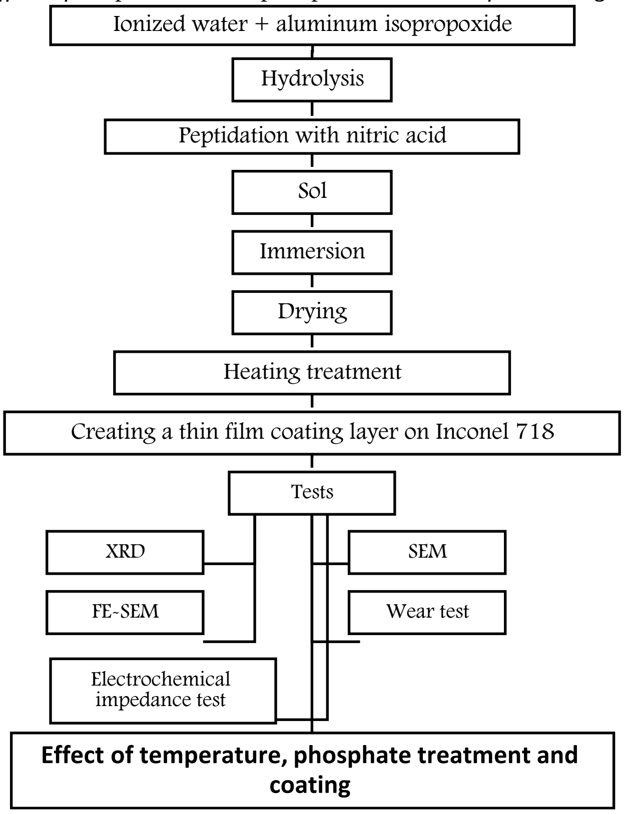

Fig. 1. The flowchart of conducting the tests

Table 1. Chemical composite of substrate (Based on weight percentage)

Nb	Al	Ti	Co	Fe	Cu	Mo	Cr	Mn	Si
4.80	0.21	0.70	0.09	4.30	0.02	3.00	20.10	0.03	0.10
Ni	W	pb	B	V	Mg	Sn	S	P	C
Base	0.005	0.005	0.005	0.02	0.04	0.04	0.003	0.013	0.02

To investigate the crystallographic structure and texture of coatings, sol-gel coating was tested by X-ray diffraction (XRD) using Philips device in the work conditions of 40KV and 30mA in the scope of 2ɵ=10-90. The container of samples is made of aluminum with copper lamp (kα=1.540598). After obtaining XRD, each phase and its consisting components were specified and determined through comparing the angle and severity of diffraction peaks with existing information in standard cards. This was done using X'pertHighScore device. In order to characterize substrate surface after phosphating and also determine the coating thickness, scanning electron microscopy (SEM) of the model TESCAN-VEGA was used. Magnification of this device is maximum 50000 times and its maximum voltage is 30kV. Morphological investigation of coating and observation of consisted Nano-structures were conducted using field emission scanning electron microscopy of the model Hitachi S4160 (Cold Field Emission). Magnification of this device is maximally 300000 times and its maximum voltage 30kV.

Coatings wear resistance was evaluated through pin-on-disk wear test, based on standard ASTMG99-95a with the pin rotation speed of 180rpm and during the distance of 50 meters. Wearing pin in this test was used with the nature of ceramic aluminum of 0.02 to the diameter of 6mm under vertical load of 15 newtons.

To investigate corrosion resistance of applied coatings on substrate, electrochemical impedance test was conducted based on electrode systems on the coatings. Referent electrode was of saturated calomel (SCE), graphite auxiliary electrode and work electrode of coated sample with Inconel alloy substrate with exposing surface of 1cm. all proposed potentials and results were evaluated with referent electrode of calomel. The scope of chosen potential was considered 250-500mw towards saturation calomel and scanning rate of 1mV/s and the room temperature as the testing temperature. Sample immersion time to reach balancing mood was chosen as 30 minutes. Frequency scope was selected 0.1HZ to 1000HZ and ZView software was used to extract data.

THE RESULTS AND DISCUSSION

Figure 2 shows the obtained images of SEM after phosphate treatment of Inconel 718 alloy in different times of immersing in phosphate bath, leading to a uniform phosphate layer on the alloy.

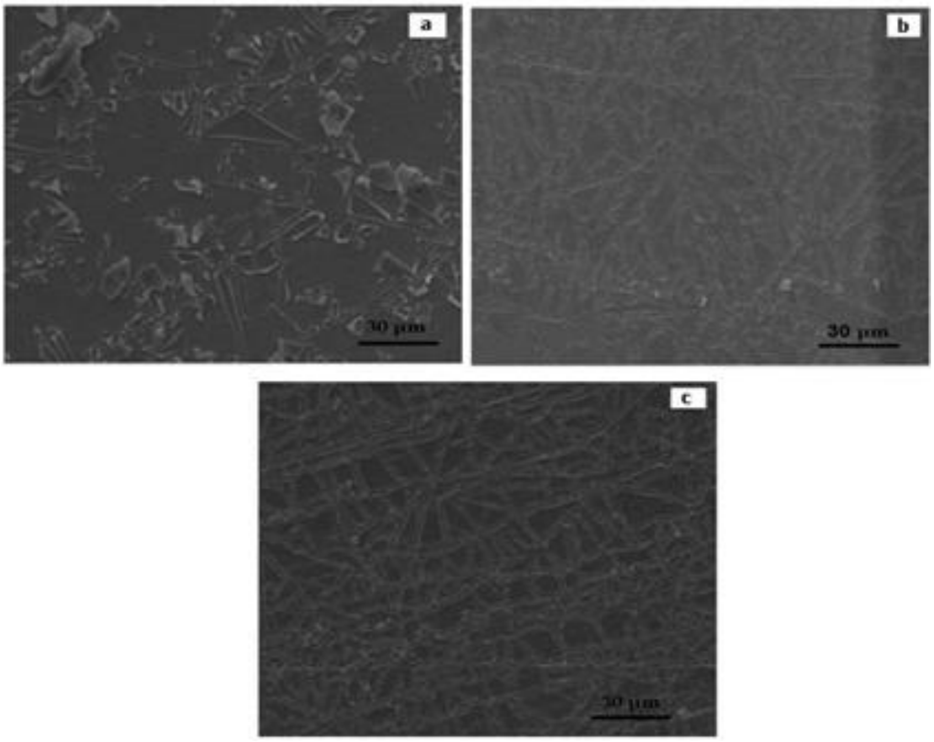

Fig. 2. The obtained images of SEM after phosphate treatment of Inconel 718 alloy in different times of immersing in phosphate bath: a) 10 minutes, b) 60 minutes and c) 120 minutes

Figure 3 shows XRD patterns of layered coating on phosphate substrate (60 minutes) of Inconel 718 alloy at different thermal treatment temperatures. Given the figure 3, in thermally treated coating at 300 and 500˚C, no diffraction peak wad observed for Al_2O_3, indicating that coating amorphous nature is synthesized (only related peaks to substrate can be seen). Coating thermal treatment at 800˚C created weak peaks in ɵ2=67˚ and ɵ2=46.2˚ of XRD. The compliance of obtained diffraction peaks at 800˚C with the standard of JCPDS:9-432 (it is related to XPert High Score software of XRD device) indicates germination of Al_2O_3 crystals in gamma-coating, aligned with the results of previous studies. Wang [15] and Doodman [11] also observed weak peaks of γ-phase alumina ($\gamma - Al_2O_3$) only in thermally treated coatings at 800˚C.

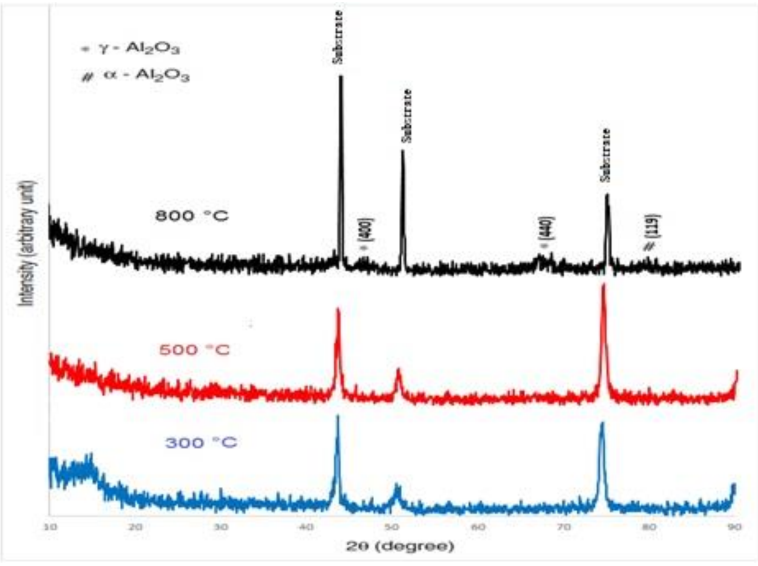

Fig. 3. XRD patterns for layered coatings on phosphate substrate of Inconel 718 alloy, thermally treated at 300, 500 and 800˚C

Figure 4 shows the images of FE-SEM, related to the coated samples with different speeds of immersion. It should be explained that both samples have been phosphate treated before coating and dried in oven with the temperature of 70˚C. Given the shape of increasing immersion speed from 0.5 to 1 mm/s increases the integrity and uniformity of coating. Coating in immersion speed of 0.5 mm/s creates micro cracks and lack of uniformity on the surface. By decreasing the immersion speed of coating, new particles will be created on the initial surface, which is inappropriate for uniform coating.

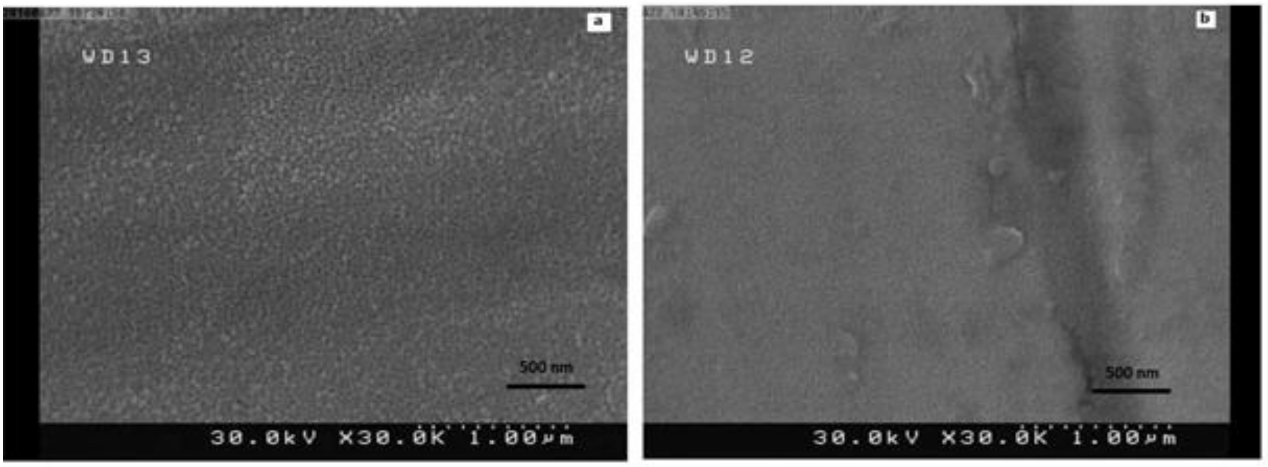

Fig. 4. The images of FE-SEM, related to the coated samples with different speeds of immersion in sol with a magnification of 30,000 times a) 1mm/s b)0.5mm/s.

Figure 5-a shows SEM image of thermally treated coating section at 300˚C. Given the image and conducted investigation, the thickness of layered coating was calculated as 2.5 micron. Figure 6-b shows the image of FE-SEM at magnification of 100000 times of the surface of same coating. It is clear from figure 6-b that the size of consisting particles under 100nm was calculated averagely as 46 nm.

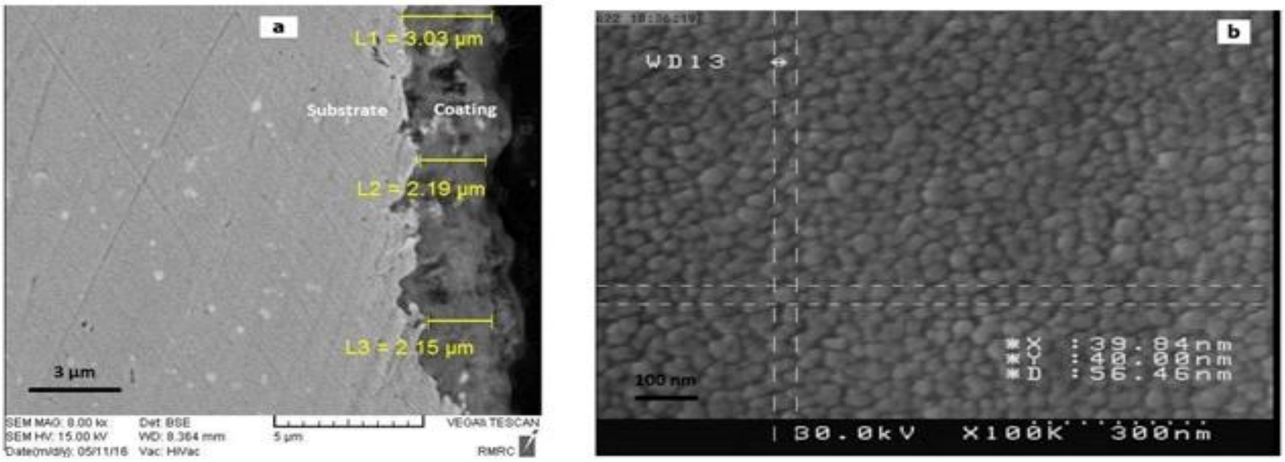

Fig. 5. a) The image of SEM from thermally treated coating section at 300˚C and b) the image of FE-SEM at magnification of 100000 times of the surface of same coating.

The amount of obtained stiffness in the current study, compared to stiffness of alumina coating in Hotor study [16] has better results. They coated a stainless steel substrate with alumina and reported stiffness of coating as 380 HV at 300˚C which is less than coating stiffness at 300˚C in this study.

Figure 6 shows the variations of wear rate for the coatings above. As it was expected the layered coating on phosphate substrate has less wear rate of not-phosphate mood, indicating good wear resistance of this coating. Lack of appropriate adhesion will cause the phenomenon of delamination [17] or the same separation of layers from the surface of substrate and severely increase the depth of penetration in the sample and wear rate.

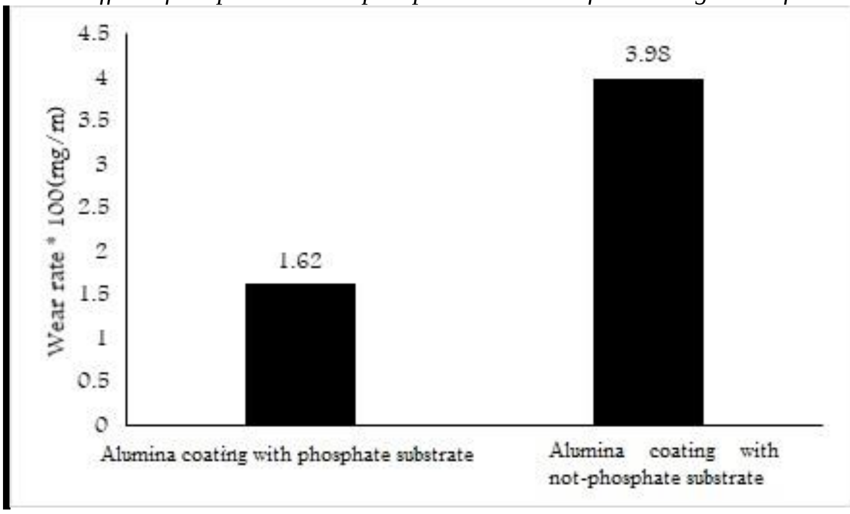

Fig 6. The variations of wear rate for the coatings, treated at 300˚C, in two modes in phosphate and not-phosphate substrate

Figure 7 shows Nyquist curve for the coatings in different conditions. Given the curve, all curves are forming a semi-circle, having a center under actual axes and representing the nature of Corrosion reaction activation control plus load transfer. Small pseudo-circle diagrams with center below the horizontal axis also indicate increasing micro-surface roughness and non-uniformity of coating during corrosion [18-22]. As it is seen, Nyquist curve shows more diameter for phosphate substrate while the dimeter of semi-circle for the samples coated at 300˚C is decreases and semi-circle is almost completed.

Additionally, the value of load transfer resistance (Rct) is equal with the diameter of Nyquist curves. In other word, the difference between actual impedance in low and high frequencies is known as load transfer resistance. This value is reversely appropriate with the speed of corrosion. Given Nyquist curves for discussed coatings, it can be seen that the value of Rct for phosphate samples without alumina coating has been less than tested samples with alumina coatings and in the sample thermally treated at 300˚C, it reaches to its maximum rate, actually shows better corrosion resistance for this sample. The results of this study are similar to the results of Roohi et al [10]. Maximum impedance in their study was 3000 ΩCm^2 while in this study the value of 700 ΩCm^2 was obtained. This difference was attributed to the different thickness of coatings. One-time immersion was used in this study for immersion.

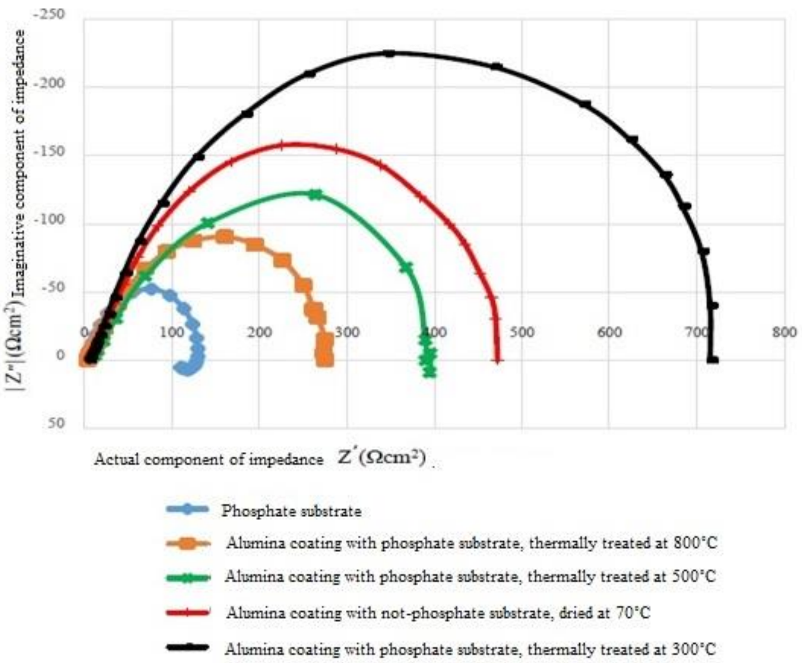

Fig. 7. Nyquist curve for heated coatings, the coating with not-phosphate substrate and phosphate substrate without alumina-coating.

Figure 8 shows bode curve for mentioned coatings. Given this curve, these graphs have 3 sections. It was observed that the value of impedance for alumina-coating samples is more than phosphate substrate (without alumina-coating). In high frequencies, log lZl tends to be zero with fuzzy angle, reaching the zero point is rapidly decreased. This behavior is natural resistance reaction and related to corrosion resistance. In middle parts of graph, a linear behavior between log lZl based on log f with the steep of near -1 and fuzzy angle, tending to -70˚. This is capacitive behavior response and of the ideal properties of a capacitive behavior response is the steep of -1 and fuzzy angle of 90 °.

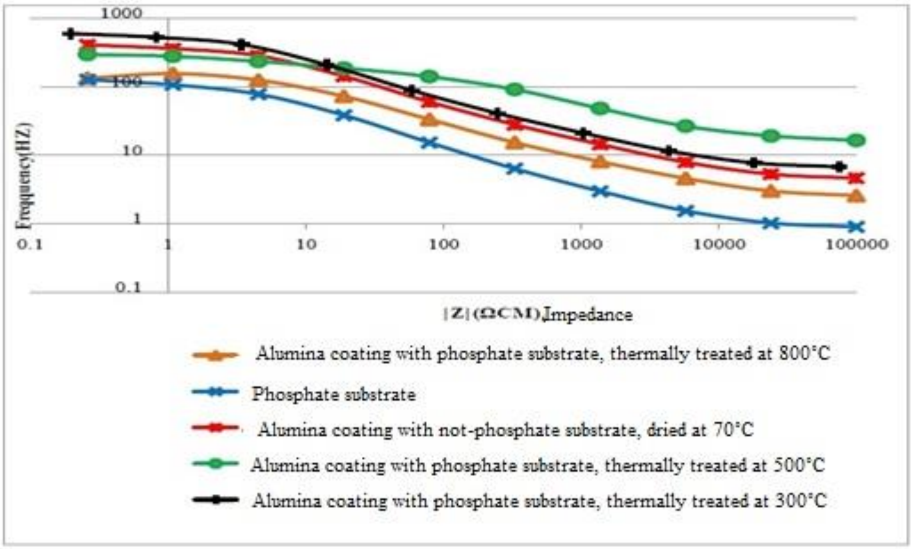

Fig. 8. Bode curves for heated coatings, the coating with not-phosphate substrate and phosphate substrate without alumina-coating

Given Bode curves, by increasing heating temperature, the curves are respectively located in lower impedance surface, indicating decrease of their corrosion resistance under the influence of increasing coatings heating temperature and this can be seen in phase-angle curve in Figure 9 by increasing the temperature of heating as reducing the thickness of capacity frequency scope which shows decreasing protection behavior. Since no change has occurred in whole view of impedance with alumina, the dissolution mechanism of electrodes (the coated samples) are considered equal [19-21].

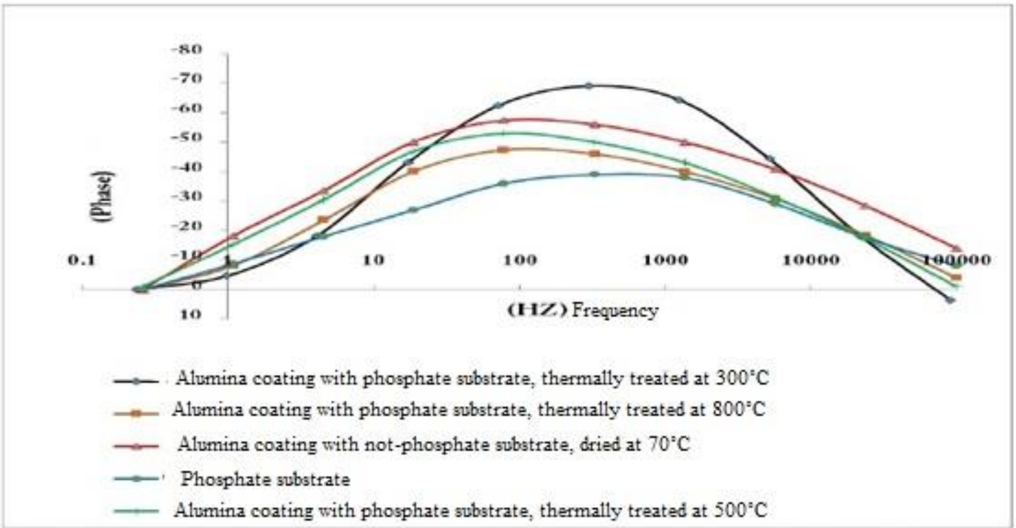

Fig. 9. Phase-angle curves for heated coatings, the coating with not-phosphate substrate and phosphate substrate without alumina-coating.

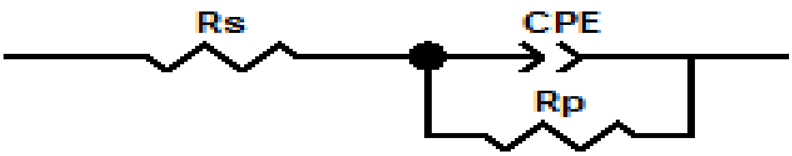

Fig. 10. Equivalent circuit used in ZView software analysis for tested samples with alumina-coating.

Equivalent circuit used in ZView software analysis for tested samples with alumina-coating in corrosion test has been shown in Figure 10.

In table 2, the obtained results of electrochemical impedance for coated samples within 30 minutes for each sample have been shown in which R_p is polarization resistance, R_s solution resistance and Cdl is the capacity of dual layer. It can be analyzed that the capacity of phosphate substrate is less than not-phosphate one and also the temperature of 300˚C is the best Cdl compared to other heating ones and 800˚C shows the weakest mood.

Table 2. The obtained results of electrochemical impedance for coated samples in different conditions

(μF)Cdl	Rs(ΩCm^2)	Rp(ΩCm^2)	The characteristics of impedance test samples
104	1.619	110	Phosphate substrate
53.6	186	550	Coating without phosphate substrate
27.1	192	1222.22	Heated coating at 300˚C
83	14.41	314.28	Heated coating at 500˚C
140	27.11	150.68	Heated coating at 800˚C

CONCLUSION

Nano-alumina coating was layered through sol-gel on phosphate Inconel 718 alloy and the following results were obtained about the effect of temperature and phosphate treatment:

1. XRD analysis of thermally treated coatings confirmed amorphous nature of coating.
2. The images of FE-SEM of coating surface showed that optimum time for phosphate treatment bath is 60 minutes.
3. By decreasing the speed of coating immersion in sol-gel solution, the new particles will be obtained on initial coating which isn’t appropriate for uniform coating.
4. The investigations showed that the average size of alumina particles is 46nm. The thickness of layered coatings was also calculated as 2.5 micron.
5. The results of wear test showed that phosphating substrate decreases friction coefficient.
6. It was specified out of electrochemical impedance test results that coated sample on phosphate and thermally treated at 300˚C substrate has the least corrosion rate compared to other samples.

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