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Synthesis of Nano-Alumina Thin Film Coating on Phosphated Surface of Inconel 718 Alloy and Investigation of its Tribological and Corrosion Properties

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ABSTRACT

In this research, Aluminum Oxide nanoparticles were made using the Sol-Gel methods, coating on phosphated substrate on Inconel 718. The study crystal structure and surface morphology respectively by FE-SEM and XRD Analysis were performed. Evaluate the properties of abrasion, by Test Pin-on-disc and calculated hardness variations by Microhardness test was performed on the coatings. The Polarization tests were used for study the corrosion resistance properties coating. The XRD results of coatings heat treated in 300, 500 and 800 °C, confirmed was amorphous nature of coatings. Just in the coating heat treated at 800 ° C can be weak peaks of gamma phase alumina (γ-Al2O3) can be seen. The FE-SEM images of the samples indicate, Coating particle size contains 46 nm and just uniform structure and free of porosity can be observed in the coating heat treated at 300 °C. The results of the test abrasion showed that phosphate substrate surface increases the wear resistance of the alumina Coating. The corrosion tests showed that the synthesis of nano-alumina Coating on phosphate surface of Inconel 718 alloy had a great effect on increasing corrosion resistance.

Keywords: alumina, inconel 718, sol-gel, corrosion

INTRODUCTION

Currently, one of the applications that extensively incorporates nanotechnology is the process of coating and subsequently the production of nanostructured materials. Nanometer materials have unique properties due to quantum phenomena at dimensions below 100 nm. Nanostructured coatings have lower thermal expansion coefficient and higher hardness, toughness and greater resistance to corrosion, wear and erosion compared to micron coatings [1, 2]. Besides, permeability of corrosives solutions in these coatings is less than the microstructured coatings [3].

Among nanostructured coatings, ceramic coatings has recently attracted the attention of many researchers due to high corrosion and wear resistance as well as dielectric properties and high thermal resistance. Ceramic coatings are deposited on metal layers using different methods. The thickness of these coatings is different and ranges from nanometers to micrometers. Generally, coatings are divided into two overall categories of thick layers and thin films [4]. Application methods of these coatings are very different, but their two major categories include [4]:

1. Vapor-phase deposition, such as CVD[1], PVD[2] methods,
2. Liquid-phase deposition, methods such as sol-gel, co-precipitation, etc.

High temperature and pressure methods always encounter problems such as oxidation of substrate during case densification and difference in thermal expansion coefficient between coating and substrate [5]. Coating which is

[1] Chemical Vapor Deposition
[2] Physical Vapor Deposition

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prepared at high temperature and pressure has some disadvantages, such as pores and cracks which lead to development of corrosion from these regions in humid environments.

Recently, many efforts are done to develop ceramic coatings on metal substrates by sol-gel technique that are resistant to corrosion and wear. Kamilet al. [6] prepared 14nm alumina nanoparticles by sol-gel method. This method is easy and requires lower processing temperature. In addition to the metals, coatings that are prepared by this method can also be applied over glasses, plastics and ceramics with simple to complex geometries [7 , 8]. Moreover, coatings produced by sol-gel method are uniform. Sol-gel is successfully being used to develop crystalline and non-crystalline coating structures at ambient temperature. A lot of researches have been conducted on the application of ceramic coatings such as alumina, silica and titania using sol-gel method to improve resistance to chemical corrosion and oxidation of metal substrates. Among these coatings, the alumina coating is very important due to its favorable properties such as chemical stability, thermal stability, high resistance to corrosion and wear [9 , 10]. Most of the alumina coatings are employed on stainless steel substrates by multi-concentration hydrolysis using sol-gel method. Doodman, et al. [11] increased the corrosion resistance of stainless steel using alumina coating. Marsal et al. [1] investigated tribological properties of alumina and silica coated on the stainless steel by sol-gel method. Results of their research showed that the alumina coating has higher wear resistance even at thicknesses less than the silica coating. It has been reported that the alumina coating properties including particles hardness, corrosion resistance and electrical properties significantly increase by enhancing the thickness of the coating layer. Nevertheless, the alumina coating application for wear resistance of the substrate is low due to limited strength of adhesive phases. Ruhi [12] and Bakus [13] observed that the alumina coating increases the wear resistance of the substrate at the start of the wear test, but has a sudden increase in the wear rate with passage of time due to separation of the coating from the substrate.

One of the methods for improving the adhesion of the alumina particles to metal substrates is surface modification using phosphate treatment [10]. Phosphating is a treatment on the metal surface to achievean insoluble coating from the phosphated metal crystals, which strongly adheres to the base metal. This develops an excellent base for secondary coating and improves the connection of the alumina layer to the metal base. Zhou et al. [14] deposited the alumina coating on the phosphated surface by spraying. Their research results indicated that phosphating improves the coating binding. Roughness of phosphated metal surfaces is an important factor to increase the strength of binding bands and to provide strong coating to the steel mechanical bonds. This study intends to enhance the corrosion and wear resistance of Inconel alloy 718 (with the phosphated surface) by the alumina nano coating using sol-gel method.

EXPERIMENTAL STUDIES

Materials

In this study, aluminum isopropoxide (as a precursor of alumina), ethanol, nitric acid, phosphoric acid, iron phosphateand hydrogen peroxide are the most important consumables, all from Merck, Germany.

Phosphating the Alloy Surface

15 ml phosphoric acid 85% was poured in a 500 ml beaker and brought to the volume of 100 ml by ionized water. Using magnetic stirrer equipped with heaters, temperature was brought to 60°C and 11 g of iron phosphate (III) was added to the above solution at the same time. At this point, the pH was measured as using a pH meter. In order to accelerate the reaction rate, 5 ml hydrogen peroxide was titrated slowly to the above solution. Next, Inconel 718 alloy samples with dimensions of 20×20×2 mm were kept in a phosphating bath for 60 min using dip coating technique and were dried in a hot dryer immediately after removing from the phosphating bath.

Preparation of Nanocoatings and Coating Conditions

For preparation of aluminum oxide solution, 0.38 mol aluminum iso-propoxide (77 g) was added to 500 ml boiling water and mixed using a magnetic stirrer for 60 min at a speed of 1000 rpm. Then, the solution was heated until the final volume reaches to one fourth of the initial volume. In the next stage and in order to increase zeta potential and prevent agglomeration of the particles, nitric acid was titrated drop wisely until the pH of the solution reached 3. To avoid gelation and formation of a stable and transparent solution, ionized water was added drop by drop to the above solution using a pipette and was slowly cooled to room temperature. In order to apply the deposition process, the phosphated substrate was immersed into the solution using an immersion device at a constant speed of 1 mm/s after 1 minute it was extracted from the solution at the speed of 1 mm/s. After the deposition process, samples were dried for 60 minutes at a temperature of 70 °C in a dryer. Finally, the samples were heated for heat treatment at 300, 500, 800 °C in argon atmosphere with temperature increase rate of 10 °C/min for 60 minutes. **Figure 1** shows the flowchart of the preparation method of the coating and experiments.

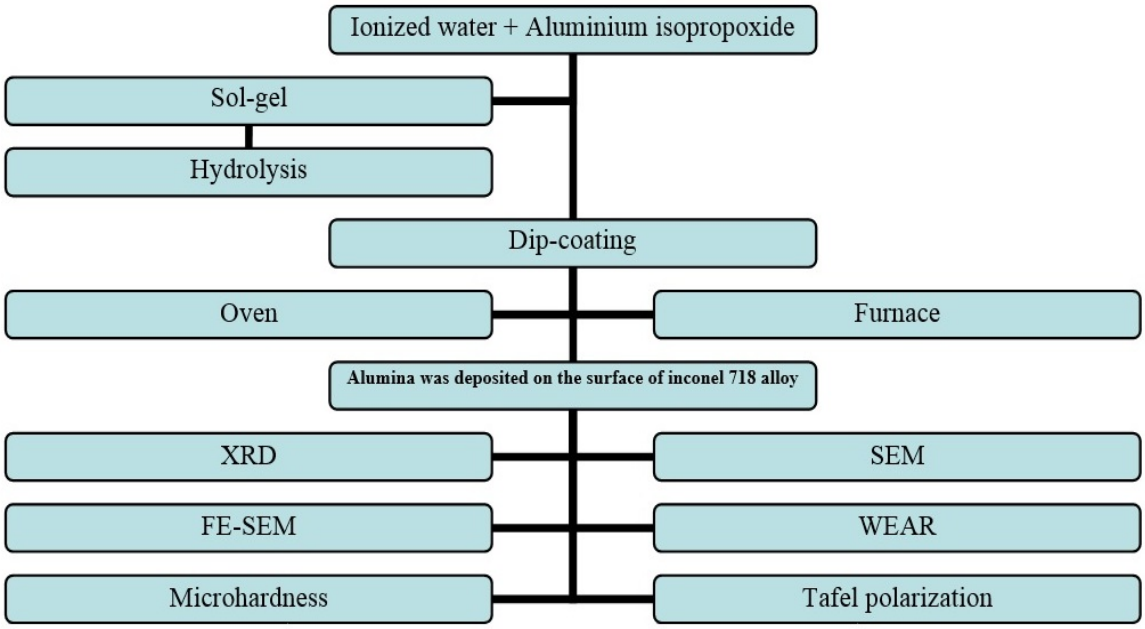

Figure 1. Flowchart of the method of testing

Table 1. Composition (wt. %) of the substrate

Si	Mn	Cr	Mo	Cu	Fe	Co	Ti	Al	Nb
0.10	0.03	20.10	3.00	0.02	4.30	0.09	0.70	0.21	4.8
C	P	S	Sn	Mg	V	B	Pb	W	Ni
0.02	0.013	0.003	0.04	0.04	0.02	0.005	0.005	0.005	base

Characterizations

In order to ensure the percentage of various elements of the substrate, Emission Spectrometry Oxford model was used in accordance with RMRC-WI-560-114-01 standard. The chemical composition of Inconel 718 alloy used for coating substrates is shown in **Table 1**.

To investigate the crystallographic structure and texture of the coatings, X-Ray diffraction (XRD) testing was performed on the sol-gel coatings using Philips instrument at working conditions of 40 kV and 30 mA in the range of 2θ=10-90. Chamber of sample holder is from aluminum, equipped with a copper lamp (K^{α}=1.540598). After obtaining the X-ray diffraction pattern, each phase and its components were determined by comparing angle and intensity of the diffraction peaks with data of the standard cards. This was done by X'Pert HighScore software. In order to characterize the substrate after phosphating and also to determine the thickness of the coating, Scanning Electron Microscope (SEM) VEGA-TESCAN model was used. Magnification of this device is at most 50000 x and the maximum voltage is 30 kV. Investigation of the coating morphology and observation of the formed nanostructures were conducted by Field Emission Scanning Electron Microscope Hitachi S4160 (Cold Field Emission). The magnification of this device is upto 300000 x and the maximum voltage is 30 kV.

Measurement of the coatings hardness was done based on Vickers microhardness test in accordance with ASTM E92 standard. In this method, the 0.05 Kgf load is applied by Wilson Tukon 1202 microhardness testing. Evaluation of the wear resistance of the coatings was carried out by pin-on-disk and according to ASTM G99-95a standard with rotational speed of 180 rpm and traveling distance of 50 m. In this test, an abrasive pin with aluminum ID of ceramic nature having 0.02 roughness and 6 mm diameter under vertical load of 15 N was used.

To evaluate the corrosion resistance of the coatings applied to the substrate, the Tafel polarization test was conducted based on three-electrode systems over the prepared coatings. The reference electrode was saturated calomel (SCE), the auxiliary electrode was graphite and the working electrode of the coated samples by Inconel alloy substrate was exposed with surface area of 1 square centimeter. All presented potentials and results were evaluated with calomel reference electrode. The selected potential range of-250 to 500 mV relative to the saturated calomel, scan rate of 1 mV/s and the test temperature equal to room temperature were considered. Dipping time of the samples for reaching an equilibrium state was chosen as 30 min by the E vs T test. Corr View software was used to extract $ß_a$, $ß_c$, E_{cor} and I_{cor}.

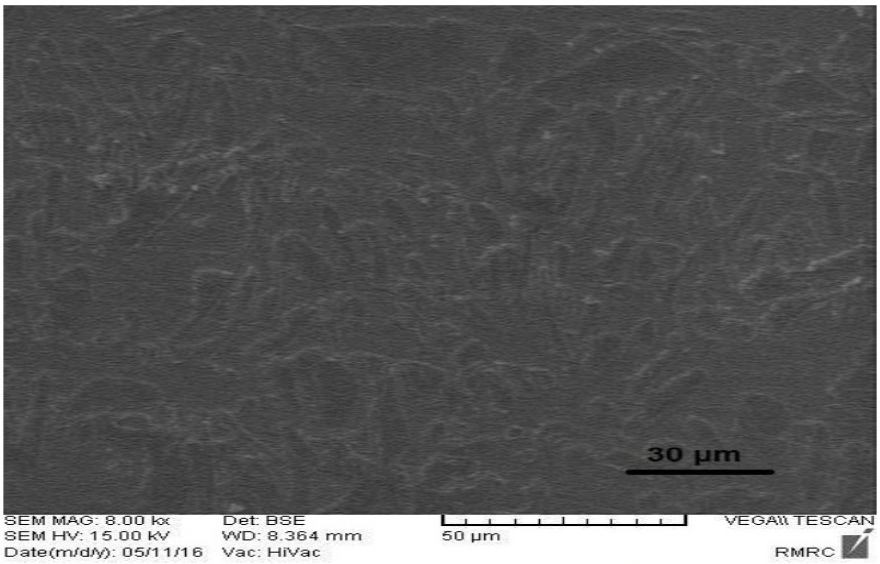

Figure 2. SEM image of Inconel 718 alloy surface after holding for60 minutes in a phosphating bath

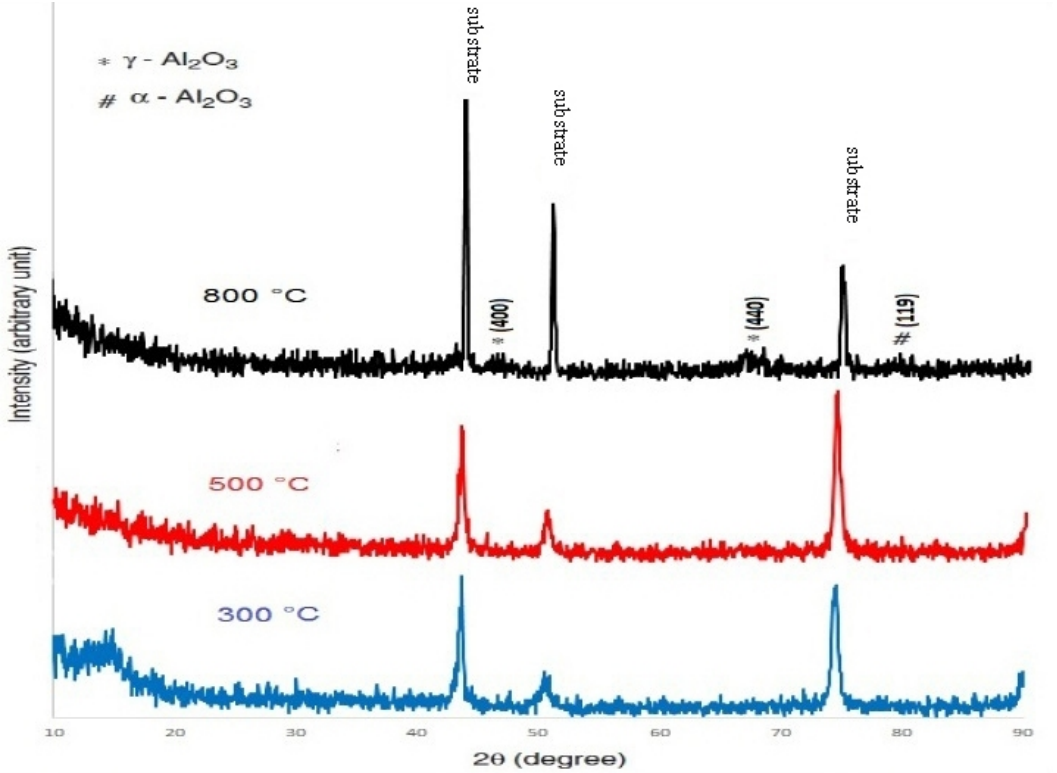

Figure 3. X-ray diffraction patterns coatings deposited on phosphated substrates of Inconel 718 alloy heat treated at 300, 500 and 800 °C

RESULTS AND DISCUSSIONS

Figure 2 shows SEM image of Inconel 718 alloy surface after the phosphating process. According to **Figure 2**, holding of the substrate in a phosphating bath for 60 min causes the formation a uniform phosphated layer on the surface of the alloy.

Figure 3 indicated the X-ray diffraction patterns of deposited coating on the phosphated substrate of Inconel 718 alloy at different heat treatment temperatures. According to **Figure 3**, in the heat treated coating at 300 and 500°C, no diffraction peak was observed for Al_2O_3 that represents the amorphous nature of the synthesized coating (only peaks related to substrate are seen). Heat treatment of the coating at 800 °C caused to appear poor peaks at 2θ=67° and 2θ=46.2° on X-ray diffraction pattern. Conformity of the obtained diffracted peaks at 800 °C with JCPDS:

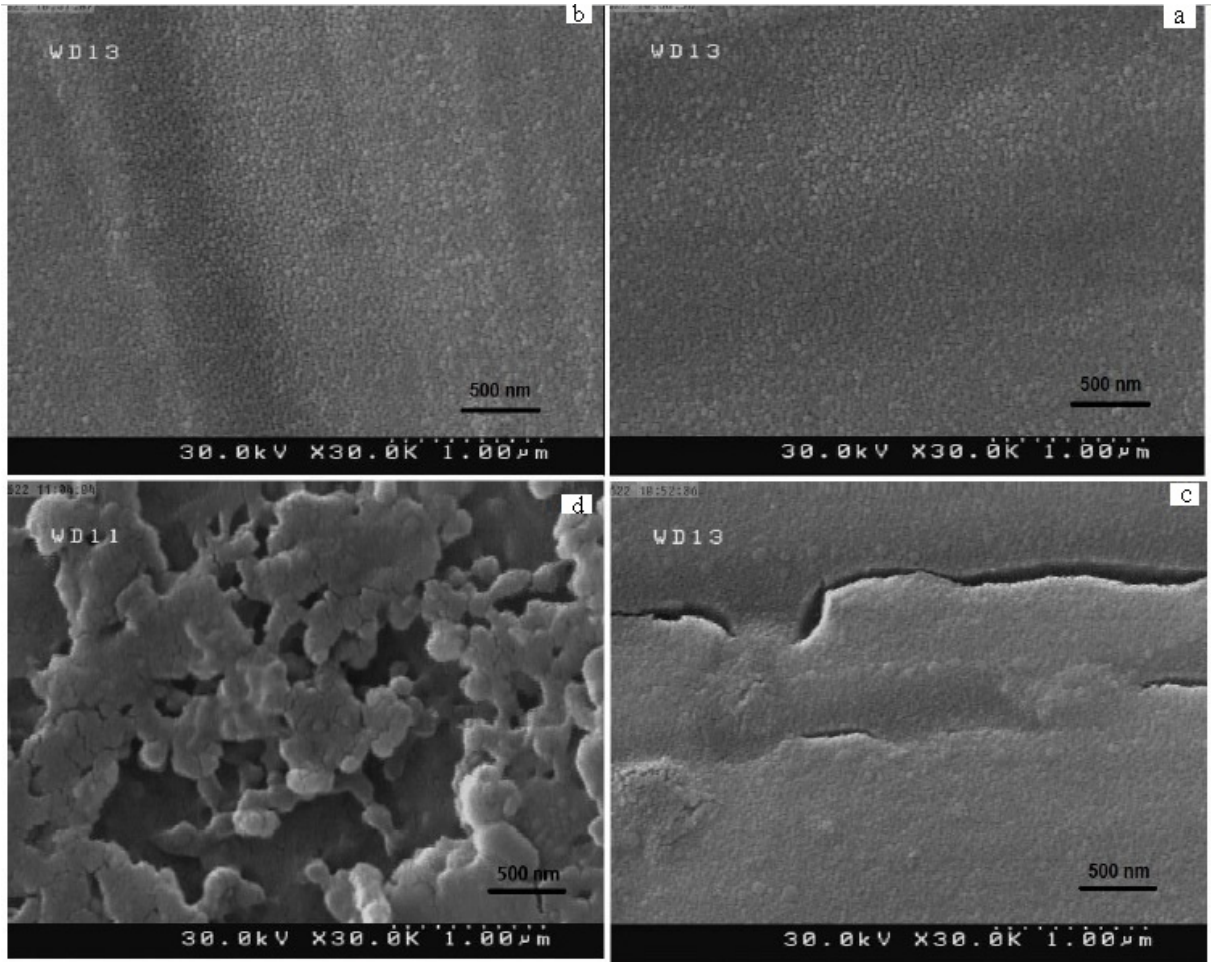

Figure 4. FE-SEM images of the surface of the heat treated coatings at magnification 30000 x: (a) before heat treatment, (b) heat treated at 300 °C, (c) heat treated at 500 °C and (d) heat treated at 800 °C

9-432 standard (This standard is related to X'Pert High Score Software of XRD device) represents nucleation of Al_2O_3 gamma crystals in the coating that is in accordance with the results of previous studies. Wang [15] and Doodman [11] also observed poor peaks of gamma alumina phase (γ-Al_2O_3) only in the coating heat treated at 800°C.

Figure 4 shows the effect of the heat treatment temperature on the morphology of the produced coatings. According to images obtained from FE-SEM, increasing the heat treatment temperature from 300 to 500 °C causes porosity in the coating. Only in the sample heat treated at 300 °C (**Figure 4-b**), a uniform structure can be seen. Development of porosity in the coating mainly occurs for two reasons; burning and evaporation of hydrates present in the coating because of sol-gel process and emerging of water vapor present in the coating that develops porosity in the coating while exiting [16, 17]. It should be noted that the difference in thermal expansion coefficient of the coating and the substrate is also another important factor that leads to cracking during heat treatment of the coating. The cracks can be reduced by applying multilayer coatings; however, the presence of microcracks in the alumina coatings intensifies local losses in the substrate. According to the investigations, the increase in the heat treatment temperature increases porosity and causes the formation of microcracks in the alumina coating. The heat treatment results of alumina coating are similar to Doodman [11] and Ruhi [12]. They also observed that by increasing the heat treatment temperature, the porosity in the coating becomes higher.

Figure 5-a shows the image of the prepared coating with the phosphate substrate and **Figure 5-b** represents the image of the coating with non-phosphated substrate after drying at 70 °C. It is clearly identified in the images that phosphating of the surface causes coating sintegrity and uniformity. Phosphating of the surface is a reason to increase surface roughness and the roughness is considered as an important factor for increasing the strength of binding bands and strong mechanical linking of the coating with the substrate alloy [14].

Figure 6-a shows SEM image of the cross-section of the heat treated coating at 300°C. According to the image and conducted surveys, the thickness of the deposited coating was measured as 2.5 microns. **Figure 6-b** represents

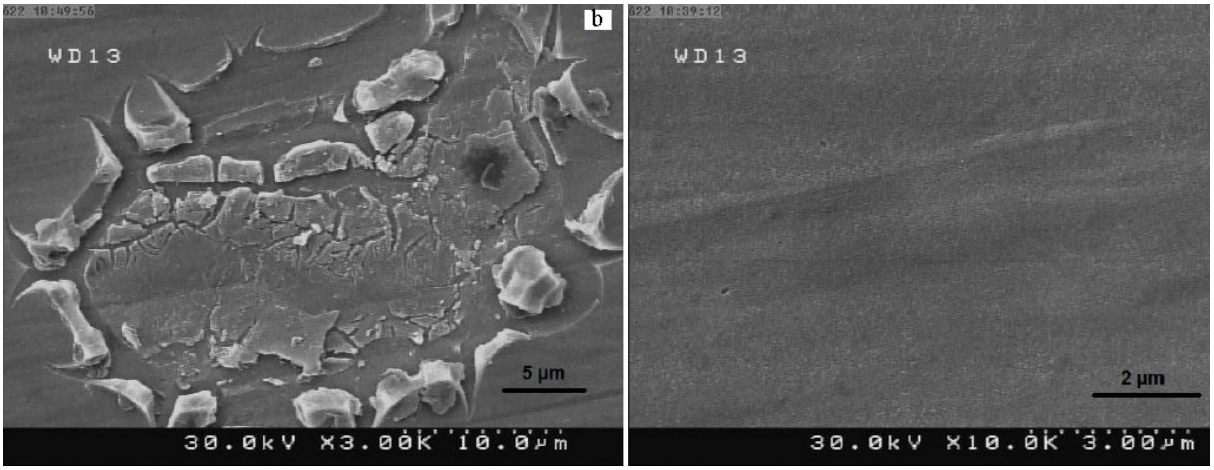

Figure 5. FE-SEM images of Al2O3 coating with phosphated substrates and Al2O3 coating with non-phosphated substrates: (a) coating phosphated substrate, (b) coating without phosphated substrate

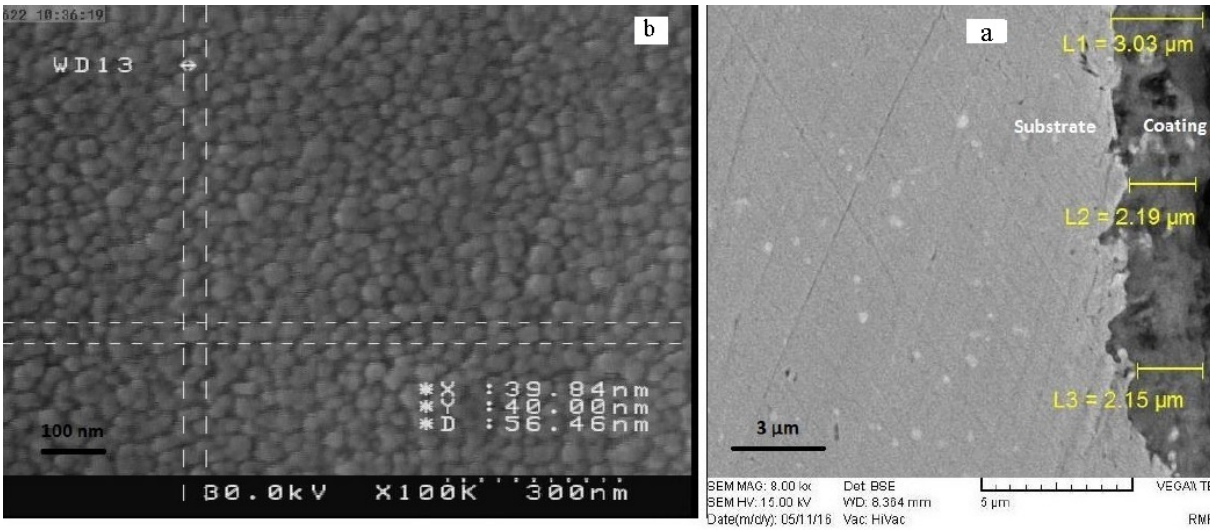

Figure 6. a) SEM image of the cross-section of the coating heat treated at 300 °C and b) FE-SEM image of the same coating surface at 100000x magnification

FE-SEM image of the same coating surface at 100000 x magnification. It is clear from **Figure 6-b** that the calculated size of the constituent particles of the coating is below 100nm and has an average value of 46 nm.

The microhardness testing results of the heat treated coatings at different temperatures are shown in **Figure 7**. According to the Figure, the hardness of the untreated coating is less than the other samples (The coating that was dried at 70 °C). Reason of this issue is the presence of organic compounds and water molecule in the amorphous coating structure [18]. The maximum hardness is related to the heat treated coating at 300 °C. Increasing the heat treatment temperature from 300 to 800 °C results in decreasing the coating hardness. The reason for the hardness reduction with increasing the heat treatment temperature can be found in FE-SEM images of the coatings as shown in **Figure 4**. It was found that increasing the heat treatment temperature leads to an increase in porosity and microcracks caused by the difference in thermal expansion coefficient of the coating and the substrate. The developed porosity and microcracks in the heat treated coatings at 500 and 800 °C is the main reason for the hardness decline in these coatings compared to the coating heat treated at 300 °C.

The hardness values obtained in the present study have better results compared to the hardness of the alumina coating in the Hawthorne study [18]. He deposited the alumina coating on a substrate of stainless steel and reported the hardness value of 380 HV for the coating at 300 °C that is less than the hardness value of the coating at 300 ° C in this research.

Figure 8 represents friction coefficient variations for the two deposited coatings on the phosphate and non-phosphated substrate surfaces. It should be noted that both samples were heat treated at 300 °C for 60 minutes. According to **Figure 8**, the friction coefficient of the phosphated coating remains constant after passing a 50 m distance of the abrasive pin which reflects the high adhesion of the alumina particles to the phosphate substrate

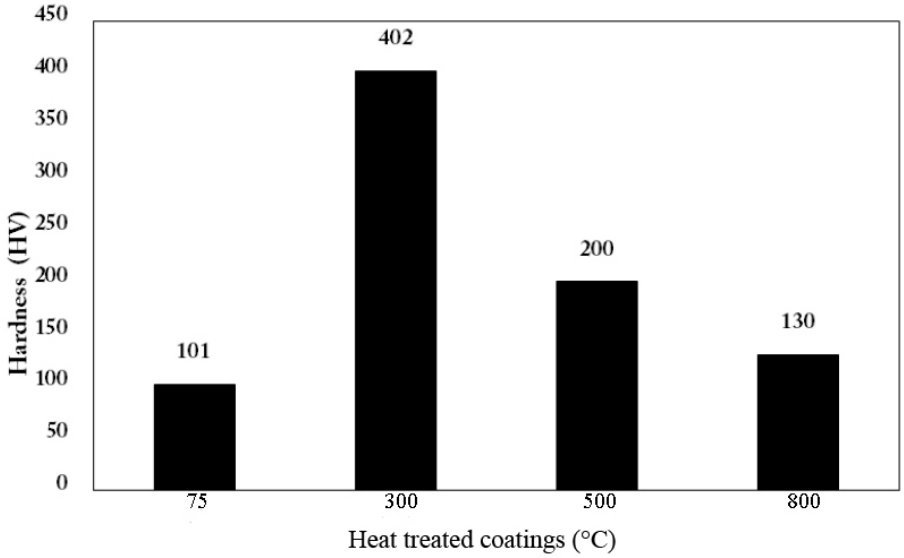

Figure 7. The obtained results of the microhardness testing of the samples

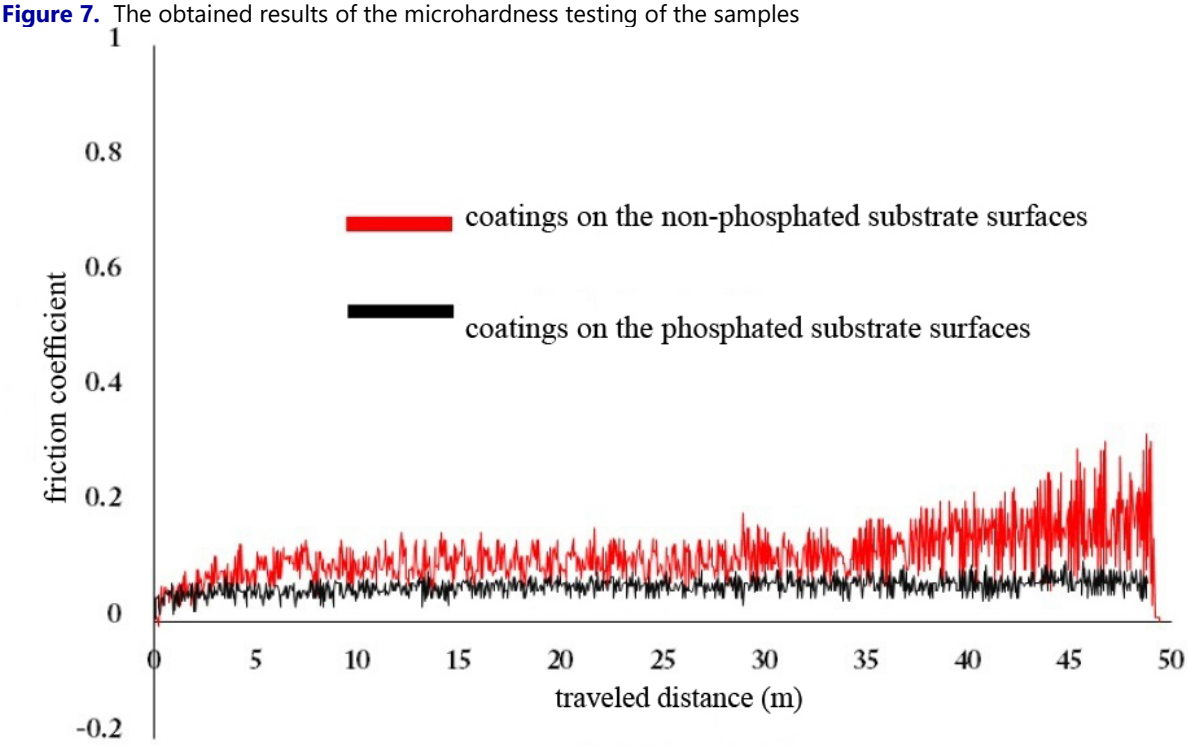

Figure 8. Variations of friction coefficient in terms of traveled distance for the coatings heat treated at 300 °C

and uniformity of the coating. In case of poor binding of alumina particles with substrate, these particles act as a third body and increase the friction coefficient between the abrasive pin and the coating that this has not occur in the phosphated coating regarding to the constancy of the friction coefficient. The friction coefficient of the coating with non-phosphated substrate after passing a distance of 35 m has experienced a sudden increase. As stated above, the reason of this issue is separation of the alumina particles and acting as an abrasive material and consequently increasing the friction coefficient.

Figure 9 shows the Tafel polarization curves of the coated samples on the phosphated substrate, the coated samples on the non-phosphated substrate and also samples without coating (phosphate substrate) in NaCl 3.5% solution. By comparing the diagrams it can be seen that the corrosion current density has decreased due to coating. The corrosion potential has also tended to more noble (positive) values. **Table 2** shows the results of samples Tafel polarization test. According to the mentioned topics the coated samples on the phosphated substrate (heat treated at 300 ° C) has better performance to increase the corrosion resistance of the substrate. In the coated sample on the

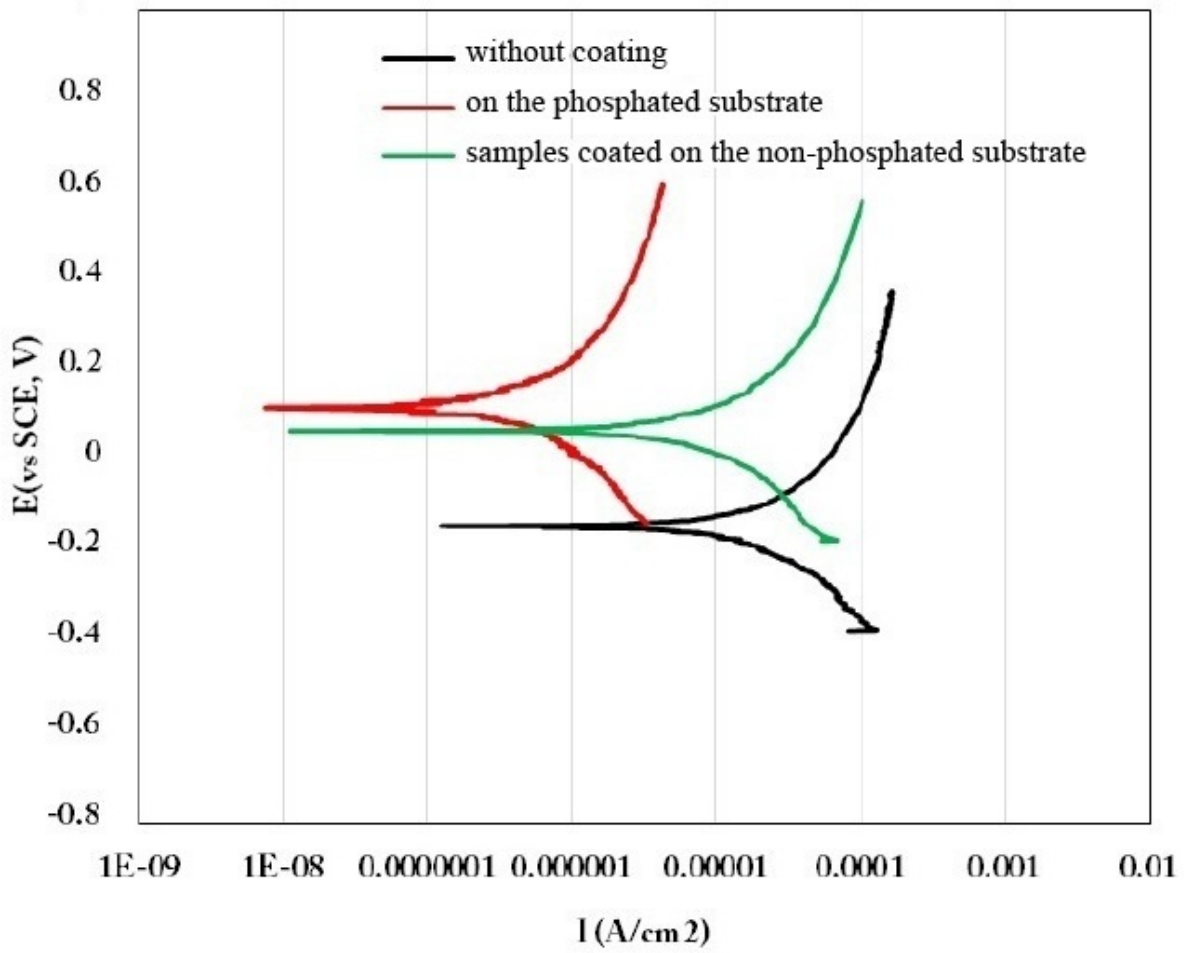

Figure 9. Polarization curves of the samples coated on the non-phosphated substrate, on the phosphated substrate and sample without coating in NaCl 3.5% solution

Table 2. Results of polarization test of the coated samples and the substrate

Samples detail	Corr.Rate (mpy)	β_c (mv.dec^{-1})	β_a (mv.dec^{-1})	I_{corr} (A / cm^2)	E_{corr} (mV)
The phosphated substrate whitout coating	3.10	60.620	59.420	3.4250×10^{-6}	-0.14
Coated on the phosphated substrate heat treated at 300 °C	0.21	31.203	12.452	3.0825×10^{-7}	0.181
Coated on the non-phosphated substrate	0.40	25.026	39.343	6.8293×10^{-7}	0.091

phosphated substrate, with 3.0825×10^{-7} mA.cm^{-2} corrosion current density and 0.181 mV corrosion potential, the corrosion rate has reached the minimum value compared with other samples.

CONCLUSIONS

In this study, the alumina nano coating prepared by sol gel method was deposited on the surface of Inconel 718 alloy and the following results were obtained:

1. FE-SEM images of the surface of the coatings showed that increasing the heat treatment temperature above 300 °C causes to develop porosity in the coating and only the heat treated coating at 300 °C has uniform and porosity free structure.
2. Investigations indicated that the average particle size of alumina is 46 nm. Also, the thickness of the deposited coating was measured equal to 2.5 microns.
3. Wear test results showed that phosphating of the substrate reduces the friction coefficient.

4. Micro hardness test results demonstrated that the heat treated coating at 300 °C has the maximum hardness compared to other coatings.
5. It was found from Tafel polarization test results that the sample coated on the phosphated substrate and heat treated at 300 °C has the minimum corrosion rate compared to other samples.

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