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## Alumina nanostructured coating for corrosion protection of 316L stainless steel

### ABSTRACT

**P. Doodman**<sup>1</sup>  
**M. A. Faghihi-Sani**<sup>1</sup>  
**N. Barati**<sup>2,\*</sup>  
**A. Afshar**<sup>1</sup>

<sup>1</sup>Department of Material Engineering,  
Science and Research Branch,  
Islamic Azad University, Tehran,  
Iran.

<sup>2</sup>Department of Materials Science and  
Engineering, Sharif University of  
Technology, Azadi Street, P.O. Box  
11365-9466, Tehran, Iran.

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Nanostructured alumina thin films were coated on stainless steel by Sol-Gel dip coating method. In order to prevent crack formation, Al<sub>2</sub>O<sub>3</sub> films were kept in a solvent bath immediately after coating to reduce the rate of drying. Effects of calcination temperature and withdrawal speed on structural properties were analyzed using XRD and SEM. Topography and thickness of coatings were analyzed by AFM. Effects of the above parameters on anticorrosion performance of coats have been evaluated through electrochemical polarization technique. The results indicated that the optimum calcination temperature to achieve the best corrosion protection was 400°C. The thickness of one time coating with 1mm/s withdrawal speed was about 146 nm.

**Keywords:** Alumina; Nanostructured coating; Sol Gel; Dip-coating; Corrosion resistance; Polarization.

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### INTRODUCTION

316 L stainless steels are used in different applications such as bone surgeries due to their mechanical and corrosion properties. However due to auto passivation properties, they undergo local corrosion in chloride ion containing media [1]. Alumina is one of the important technical ceramics because of its useful properties especially hardness, thermal, chemical and dielectric properties. Alumina films have received considerable attention as high temperature engineering material. There is an increasing technological need to protect metals in aggressive environments such as acidic or oxidizing environments. Corrosion resistance of metals may be improved through various surface engineering techniques such as depositing protective ceramic coating (nitrides, carbides, silicides or transition metal oxides) on metal surface. Main deposition methods are usually PVD or CVD [2, 3] and sol-gel [4].

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\* Corresponding author:

N. Barati  
Department of Materials Science  
and Engineering, Sharif  
University of Technology, Azadi  
Street, P.O. Box 11365-9466,  
Tehran, Iran.  
Tel +98 9122350804  
Fax +98 2166006277  
Email [n\\_barati@alum.sharif.edu](mailto:n_barati@alum.sharif.edu)

In comparison with other deposition techniques such as chemical vapor deposition and plasma spraying, sol-gel deposition has several potential advantages, including cheap deposition technology, ability to cover complex shapes of a variety of materials (plastics, glass, metal) and application of multi component oxides [5]. Based on this technique the films can be deposited by spin coating, spray coating and dip coating [6, 7].

Application of  $ZrO_2$  [8, 9],  $SiO_2$  [10],  $TiO_2$ - $SiO_2$  [11],  $SiO_2$ - $Al_2O_3$  [11] and  $TiO_2$  [12] films on stainless steel and their aqueous corrosion properties have recently become of interest. Among those oxides,  $Al_2O_3$  is frequently used as protective coating [13, 14]. T. Lampke et al. have been demonstrated the protective characteristic of alumina coatings prepared using different methods on metallic substrates [15].

In this work we prepared a uniform alumina coating on 316 stainless steel using sol-gel dip coating method. Effects of calcination temperature and withdrawal speed on structural properties of coated samples have been studied. Corrosion resistance of samples coated with different coating conditions have been evaluated through electrochemical polarization technique in 1 molar sulfuric acid solution.

## EXPERIMENTAL

Coating of alumina film was carried out by dipping of stainless steel substrate inside aluminum hydroxide sol through hydrolysis and poly condensation of an aluminum alkoxide solution. Figure 1 shows flow chart of experimental procedure.

The sol was prepared by adding aluminum isopropoxide ( $Al [OCH (CH_3)_2]_3$ ) powder (Merck) to a boiling water under vigorous stirring for 30 min. After sol preparation Final concentration of aluminum was 0.95mol/l.

The solution was heated under stirring until the total volume of solution reached to one fourth of the volume of starting solution, Then concentrated nitric acid (Romil) was added to the solution to reduce the pH of solution to 3 to increase its zetta potential in order to prevent agglomeration. To obtain a proper sol and prevent gelation, the solution was diluted by adding enough

water before cooling to room temperature. Table 1 presents chemical analyses of the stainless steel substrates. The surface of 316L stainless steel substrates were first ultrasound in acetone solution. Then, they were dip coated inside the final sol with different withdrawal speeds of 0.7 and 1.0 mm/s. The samples were heated at various calcination temperatures from 400 to 800°C for 30 min to find the optimum calcination temperature.

Moreover, the prepared bulky gel was dried and calcined at various temperatures (from 400 to 800 °C) and evaluated by XRD using CuK $\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ) with a scanning rate of 18 °/min, ranging  $2\theta$  from 10° to 70°. Microstructure of the coated substrates, heat treated at various temperatures, were investigated using a scanning electron microscopy (XL30, Philips). Surface topography and thickness of the coated substrates, with different withdrawal speeds (0.7 and 1 mm/s) after heat treating at 400 °C for 1 h, were characterized by Atomic Force Microscopy (Mahar Fan Abzar Co, Dualscope<sup>TM</sup> DS95-200) with 0.1 nm accuracy in Z-axis direction.

Corrosion analysis was conducted using EG&G Electrochemical measurement system connected to a corrosion analysis software program (EG&G Princeton Applied Research). The test was carried out potentiostatically in a three-electrode cell at room temperature using a saturated calomel reference electrode (SCE), a coated sample as working electrode and a bear 316L Stainless Steel electrode. The potentiodynamic measurements were taken within the range of -100 mV to 400 mV versus SCE at a rate of 1 mV/s. Each sample was immersed in 1 molar sulfuric acid solution for at least 15 min prior to the test. The cohesive property of coatings was evaluated through scratch test (ASTM D3359).

**Table 1.** Chemical analysis of the stainless steel substrate

Impurities	Si	S	Mn	C	Mo	Ni	Cr
Weight percent	0.46	0.004	1.43	0.03	2	11.26	16.69

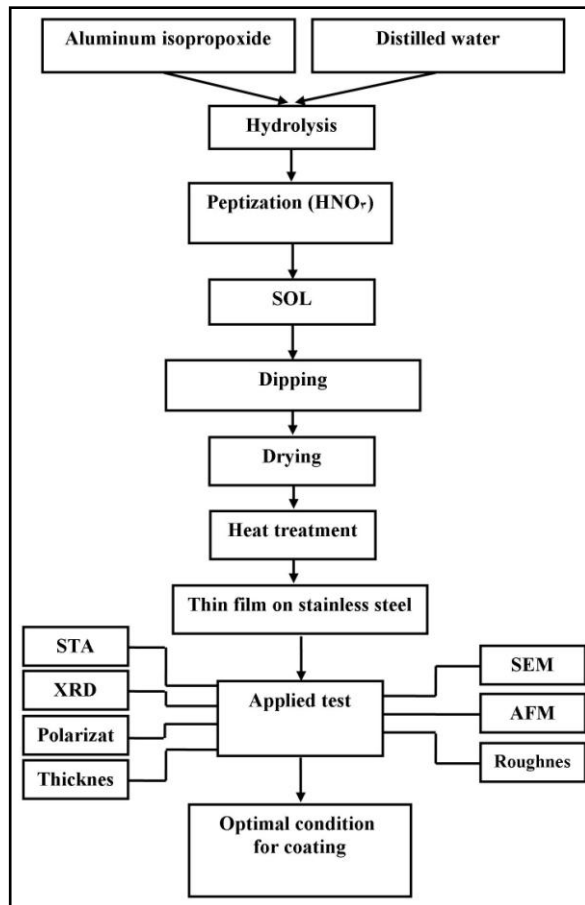


Fig. 1. Flow chart of the experimental procedure

## RESULTS AND DISCUSSION

There are numerous parameters that affect the quality of coatings. Among them drying is an important stage after coating. In this regard, coated samples were first dried in solvent bath to reduce the rate of solvent removal and therefore prevent cracking. Figure 2 illustrates the coated substrates, a) after drying in air, the created cracks are clear because of elevated rates of drying, and sample b free from any cracks, after drying in solvent bath at room temperature and in oven at 100 °C for 1 hour,.

Moreover, the calcination temperature can also significantly affect the structural and corrosion properties of the coats. Figure 3 shows XRD patterns of the calcined gel at various temperatures for 1 hour in air. It is clear that there isn't any peak in these patterns, demonstrating that Al<sub>2</sub>O<sub>3</sub> coating is amorphous, even after calcination at 800°C.

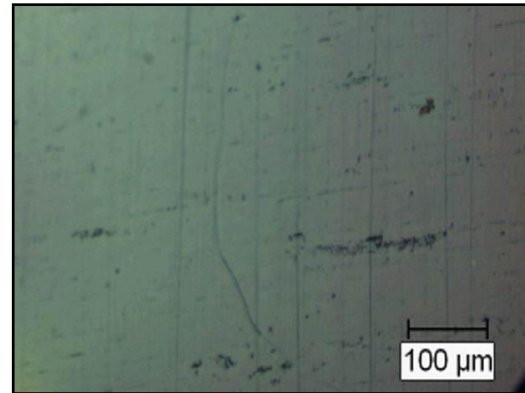


Fig. 2. Optical microscope image of coating after drying in solvent bath and oven

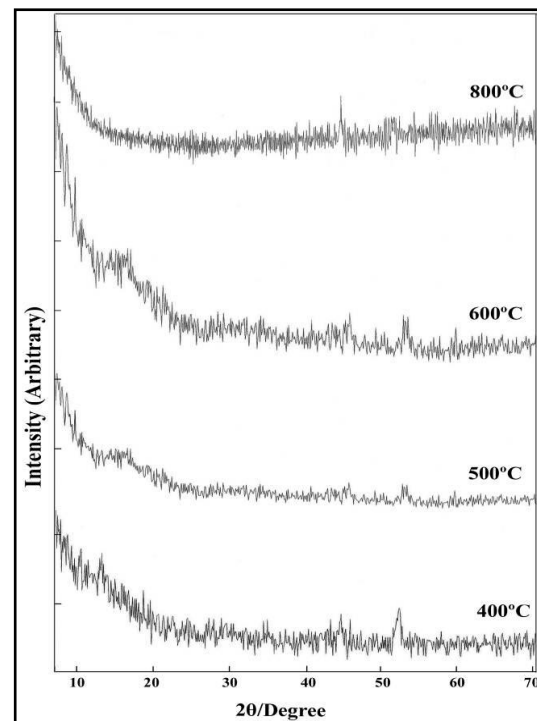


Fig. 3. Diffraction patterns of the calcined bulky gel at various temperatures in air for 1 hour

On the other hand the SEM images in Figure 4 indicate formation of more uniform coating at lower calcination temperature. These images also reveal that uniform, homogeneous and crack-free coating on stainless steel substrate was readily obtained at 400°C for 30 min.

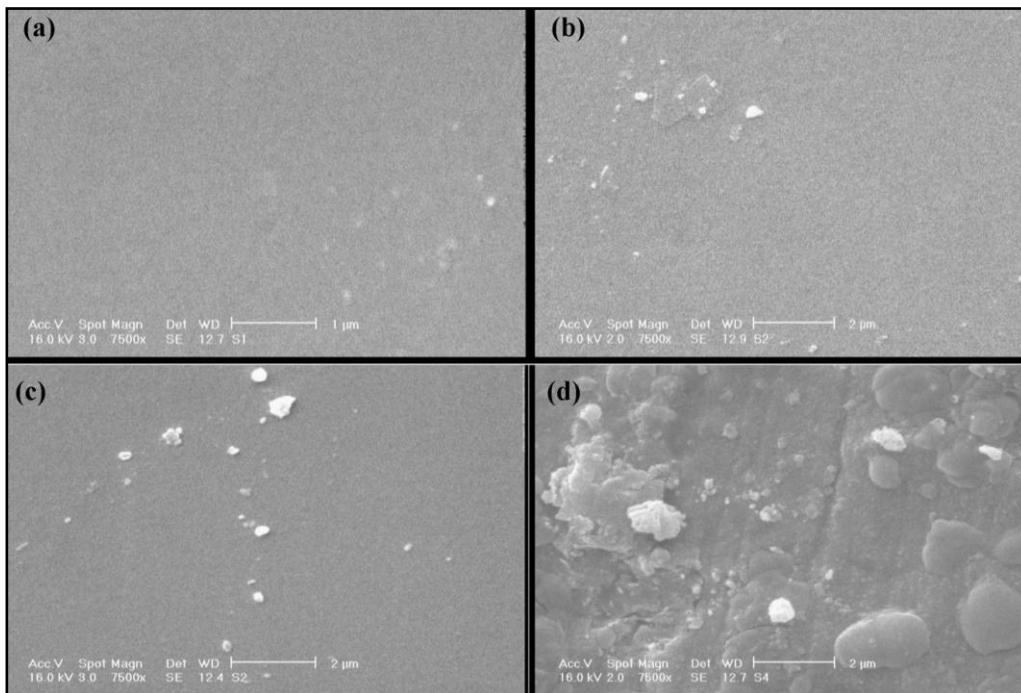


Fig. 4. SEM images of coating after heating at a) 400, b) 500, c) 600, d) 800°C for 1 hour

Figure 5 shows the potentiodynamic polarization curves of the coated 316L stainless steel substrates, heat treated at 400, 500, 600 and 800°C. The electrochemical corrosion parameters;  $i_{corr}$  (corrosion current density),  $E_{corr}$  (corrosion potential) of tafel slope in Figure 5 were calculated by power suite software from tafel slope and presented in Table 2.

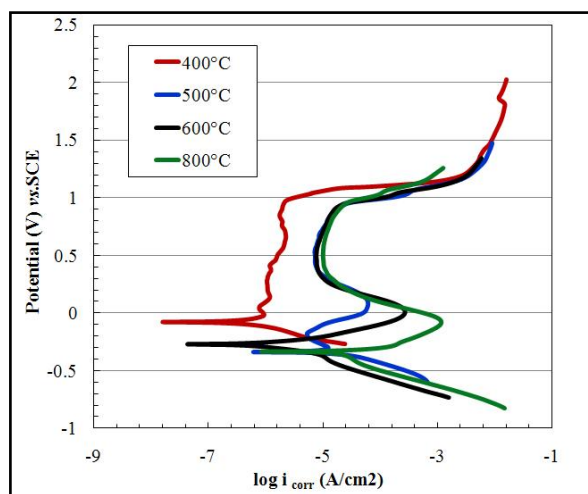


Fig. 5. Polarization curves of alumina coated 316L stainless steel in 1 M H<sub>2</sub>SO<sub>4</sub> at 400, 500, 600 and 800°C

Table 2. Electrochemical corrosion parameters of alumina coated 316L stainless steel in 1 M H<sub>2</sub>SO<sub>4</sub> derived from the polarization curves given in Figure 5.

Calcination Temp. (°C)	Log ( $i_{corr}$ )	$E_{corr}$ (V)	$i_{corr}$ (A/cm <sup>2</sup> )	$R_p$ (KΩ.cm <sup>2</sup> )
400°C	-6.513	-0.075	3.07E-07	68.725
500 °C	-5.281	-0.343	5.24E-06	2.152
600 °C	-5.594	-0.268	2.55E-06	11.225
800 °C	-4.670	-0.334	2.14E-05	0.945

These data show that increase of calcination temperature results in decrease of  $E_{corr}$  and increase of  $i_{corr}$  values, indicating a decrease in corrosion resistance. It is known that heat treating austenitic stainless steel at temperatures between 425 and 815°C causes precipitation of carbides at the grain boundaries [16], resulting in decrease of the corrosion resistance. Changes of  $R_p$  versus calcination temperature in Figure 6 demonstrate that corrosion resistance of the coated sample at 400°C is the highest.

In the next step, effect of withdrawal speed on thickness and corrosion behavior of the coats was studied. AFM results in Figure 7 indicate the morphological differences between bare and coated samples, in coated samples thickness of the film increases with increase in withdrawal speed. The thickness of coatings was 91

and 146 nm and the roughnesses of coatings were 4.98 and 6.38nm, when withdrawal speeds were 0.7 and 1 mm/s, respectively. Meanwhile the roughness of bare sample was in the range of millimeter. It shows the effect of alumina nanostructure coating on improvement of 316l stainless steel.

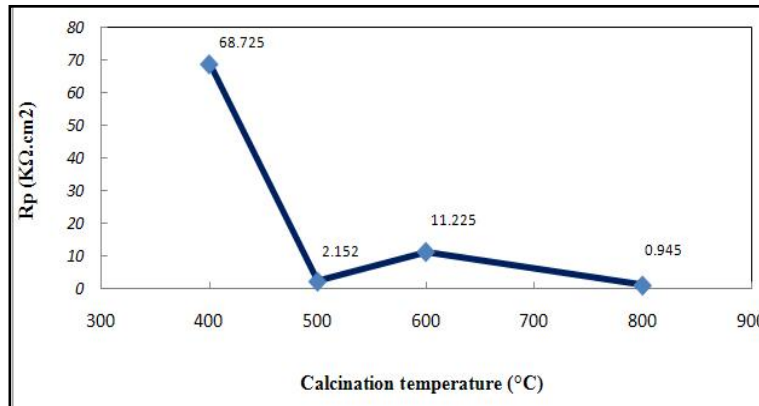


Fig. 6. Relation between  $R_p$  and heat treatment

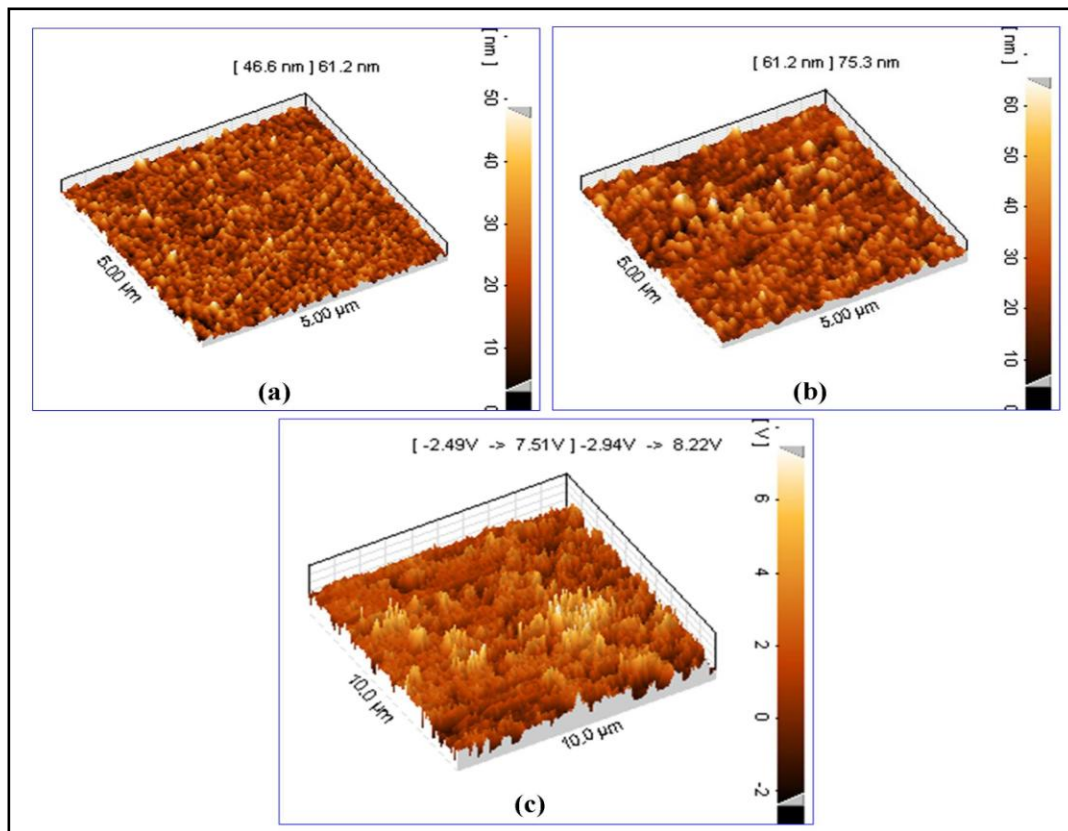


Fig. 7. AFM images of alumina coats with different withdrawal speeds a) 0.7 and b) 1 mm/s c) bare sample

Polarization curves of the coated samples, with withdrawal speeds of 0.7mm/s and 1mm/s (after heat treating at 400°C) in Figure 8 and the related results in Table 3 show that the corrosion resistance increases when withdrawal speed increases, resulting from increase in coating thickness. Increase in withdrawal speed results in lower  $i_{\text{corr}}$  and higher  $E_{\text{corr}}$  values, leading to an increase in the corrosion resistance.

Comparison of the polarization curves of coated and bare samples in Figure 8 and Table 3 confirms that the coated samples consistently have a lower passivation current by approximately one order of magnitude due to the formation of a film on the surface of substrate. Polarization curves indicate that the heat-treated sample at 400°C presents an active/passive behavior while the bare sample shows transpassive behavior. Generally the quality of adhesion between a coating and substrate depends on the condition of the interfacial layer between them. A scratch test gives information about the adhesion of the coating as well as different stages of its failure under applied load. The test result of class 5B for all coated substrates shows higher adhesion between substrate and alumina coat. Adhesion mechanism between alumina coat and substrate can be combination of penetration and chemical bond [17].

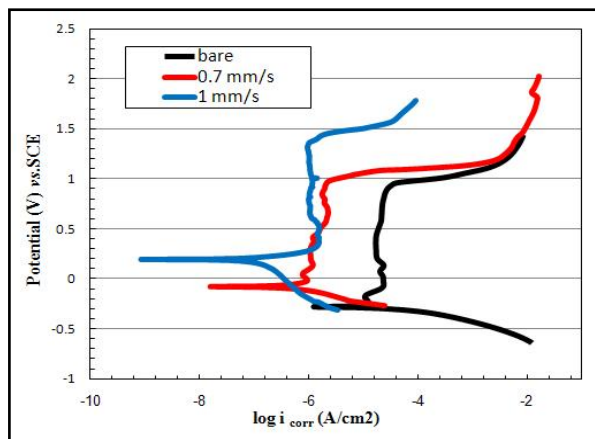


Fig. 8. Polarization curves of alumina coated samples with withdrawal speeds of 0.7 and 1 mm/s and bare 316L stainless steel at 400°C in 1 M H<sub>2</sub>SO<sub>4</sub>

## CONCLUSIONS

In this work a uniform nanostructured alumina coating has been prepared on 316L

stainless steel by sol-gel dip coating method. The results indicated that the optimum calcination temperature to achieve the best corrosion behavior was 400°C. The thickness of coating with withdrawal speed of 1mm/s was about 40nm. Polarization curves showed that the Al<sub>2</sub>O<sub>3</sub> coating on stainless steel can exhibit an excellent corrosion resistance. The optimum corrosion protection was achieved with withdrawal speed of about 1mm/s.

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