Chemical and Mechanical Characterization of Thermal-Multilayered Al₂O₃ Atomic Layer Depositions on AISI 316L Stainless Steel

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Abstract In this work, three different nanometric, multilayered Al₂O₃ coatings, obtained by alternating two different deposition temperatures, have been applied on AISI 316L stainless steel by atomic layer depositions. The coating morphology has been investigated using atomic force microscopy (AFM) and scanning electron microscopy. Thickness analysis has been performed using AFM and glow discharge optical emission spectrometry (GDOES). In-depth compositional profiles have been performed using GDOES. The corrosion protection has been investigated using polarization curves in aggressive NaCl electrolyte. All variations of the coatings appeared to be adherent to the substrate with thickness in the range of the nominal values. Compositional analysis confirmed the presence of the Al₂O₃ layers. Vickers indentations used to evaluate coating adhesion showed that all coatings have a good adhesion to the substrate and in particular the amorphous/crystalline 20-nm-thick coating showed almost no sign of coating delamination. All samples show a higher corrosion resistance when compared with bare AISI 316L.

Keywords ALD · Al₂O₃ · Corrosion protection · GDOES · AISI 316 stainless steel

Introduction

Currently, stainless steel is one of the most used and important materials at an industrial level, thanks to the extremely convenient balance between high mechanical

resistance (600 MPa of ultimate strength) and high resistance to environmentally induced corrosion in many common atmospheres. This ability is imparted by the presence of a nanometric chromium oxide layer, usually for a total thickness of less than 10 nm, which acts as a perfectly conformal ceramic barrier coating, completely insulating the substrate [1]. This protective layer also shows self-healing ability, as the chromium oxide layer is spontaneously re-formed in the presence of oxygen if removed or scratched away. Even so, stainless steels could show insufficient corrosion resistance in strongly aggressive media containing, for example, Cl[−] and/or S^{2−} ions, in particular at high temperature or extreme pH values, above 12 or below 2 [2–4].

For all these reasons, it is possible that even stainless steel may need a further improvement in its corrosion protection. The most common treatment, painting, is hardly applicable to stainless steel due to the lack of chemical adhesion between the oxide layer and paint, as observed different times in the literature [5] when an opportune pretreatment has not been applied on the stainless steel surface [6–8]. A very large number of different technologies are under intensive study in order to improve stainless steel corrosion resistance, including laser surface melting [9], plasma nitriding [10, 11], plasma detonation techniques [12], arc-ion plating [13], sol–gel deposition [14, 15], chemical conversion layers of cerium [16] chromium [17] or other elements, chemical vapor deposition (CVD) [18], high-velocity oxy-fuel spray [19], and atomic layer deposition (ALD) [20].

ALD is a self-limiting deposition process, meaning that the amount of film material deposited in each reaction cycle is constant. A sequential deposition procedure produces conformal thin-films of materials onto substrates of varying compositions. ALD is similar to CVD, except that

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the ALD process breaks the CVD reaction into two half-reactions, keeping the precursor elements separate during the deposition. By keeping the precursors separate throughout the coating process, atomic layer control of film growth can be obtained as fine as $\sim 1 \text{ \AA}$ (100 pm) per monolayer. Separation of the precursors is accomplished by pulsing a purge gas (typically nitrogen or argon) after each precursor pulse to remove excess precursor from the process chamber and prevent “parasitic” CVD deposition on the substrate.

ALD had been developed and introduced worldwide with the name atomic layer epitaxy in the late 1970s [21]. For thin-film electroluminescent flat-panel displays, high quality dielectric and luminescent films were required on large-area substrates [22]. Interest in ALD has increased stepwise in the mid-1990s and 2000s, with the interest focused on silicon-based microelectronics [23]. ALD can be used to deposit several types of thin-films, including various oxides, nitrides, sulfides, and metals.

In this work, characterization of ALD-coated AISI 316L has been carried out, in order to determine the possible use of nanometric ceramic ALD coatings for the corrosion protection of stainless steel. Preliminary results on the corrosion protection on stainless steel by Al_2O_3 layers were already obtained by Matero et al. [24], which supposed that the conformal ALD coatings could improve the corrosion resistance of different metal alloys. In 2007, Shan et al. [20] used TiO_2 ALD layers to protect an undefined stainless steel, obtaining only a limited effect. In 2011, Marin et al. [25], Díaz et al. [26], and Potts et al. [27] clearly showed that the porosity amount of ALD layers is a decreasing monotone function of the thickness of the deposited coating. In most cases the nanometric ALD layers clearly showed a corrosion protection similar, if not superior to conventional protective techniques and thicker coatings, even if common industrial tests (salt spray) performed on plasma-enhanced ALD by Potts et al. [27] clearly showed a time-limited corrosion protection [25–28].

The aim of this work is to investigate the effect of thermal multilayer configurations in sealing residual porosities without increasing the coating thickness and thus reducing the deposition times and costs.

Experimental

Sheets of cold rolled, standard AISI 316L ($C = 0.035$; $P < 0.04$; $S < 0.03$; $Mn = 2.0$; $Si = 0.75$; $Cr = 16.0$ – 18.0 ; $Ni = 10.0$ – 15.0 ; $Mo = 2.0$ – 3.0) were obtained from an industrial producer. Sheets were then mechanically cut in $10 \times 10 \text{ mm}$ samples and polished (SiC paper from 500 to 4000 grit, then diamond suspensions of 9, 6, and $3 \text{ }\mu\text{m}$

diameter) to obtain a surface roughness of about 20 nm average roughness (R_a). Samples surface was then cleaned using ethanol in ultrasonic bath for 10 min and dry heated at a temperature of $50 \text{ }^\circ\text{C}$ for 15 min. Some samples were then partially masked with heat-resistant Kapton polyimide laboratory tape to prevent ALD deposition on part of the substrate. The samples were then coated with three different ALD configurations: Sample AC was coated with 50 ALD cycles of tri-methyl-aluminum (TMA) and water (H_2O) at $120 \text{ }^\circ\text{C}$ followed by 50 ALD cycles of TMA and H_2O at $300 \text{ }^\circ\text{C}$. Sample CA was coated with 50 ALD cycles of TMA and H_2O at $300 \text{ }^\circ\text{C}$ followed by 50 ALD cycles of TMA and H_2O at $120 \text{ }^\circ\text{C}$. Sample CAC was coated with 50 ALD cycles of TMA and H_2O at $300 \text{ }^\circ\text{C}$ followed by 100 ALD cycles of TMA and H_2O at $120 \text{ }^\circ\text{C}$ followed by 50 ALD cycles of TMA and H_2O at $300 \text{ }^\circ\text{C}$.

Morphological

Morphological characterization was carried out using an atomic force microscope (AFM) and a scanning electron microscopy (SEM) on the stainless steel substrate and on coated surface of the samples, and in particular:

- $25 \times 25 \text{ }\mu\text{m}$ square maps were obtained by tapping mode AFM and scanning kelvin probe force microscopy (SKP-FM) using SCM-PIT tips in tapping mode (0.01 – 0.025 Ohm/cm Antimony (n)-doped Si, coated with 20 nm PtIr, typical frequency 60–100 kHz) on the coated regions in order to obtain information about the surface roughness and the presence of defects;
- $10 \times 10 \text{ }\mu\text{m}$ square maps were also obtained by tapping mode AFM at the interface between coated and uncoated regions, using a Kapton high temperature adhesive tape to partially mask the substrate during deposition;
- Secondary and backscattered electron SEM images were obtained at the samples surface in order to search and identify local defects or inclusions on both substrates and coatings.

Compositional

In-depth compositional analyses were carried out using RF–GD Profiler glow discharge optical emission spectrometry (GDOES). GDOES was at first calibrated using conventional standard materials of known composition (setting-up samples and certificate reference materials). The calibration and the plasma parameters were then adjusted measuring with a high-precision stylus profilometer the crater depth on ALD-coated mirror-polished samples at different sputtering times.

Fig. 1 AFM $25 \times 25 \mu\text{m}$ square maps of (a) sample AC, (b) sample CA, (c) sample CAC measured on the surface of the coatings

Mechanical

Mechanical characterization of the coatings was performed using a Vickers microhardness tester on the coated substrate at different loads ($\text{HV}_{0.1}$, $\text{HV}_{0.2}$, $\text{HV}_{0.3}$, $\text{HV}_{0.5}$, HV_1 , HV_2). Delaminated areas caused by each indentation were then measured and the delaminated area over load ratio was then plotted as a function of the applied load for the different coatings, obtaining a rough estimation of the coating resistance to delamination.

Electrochemical

Electrochemical characterization of the different samples was performed using Polarization Curves in three electrodes configuration. The reference electrode was Ag/AgCl and the counter electrode was a 99.99% pure Platinum wire. A 9 g/l NaCl physiological solution was used. All polarization curves were obtained after 10 min of free immersion of the samples, in order to stabilize the open circuit potential (OCP).

Contact Angle

Water drop contact angle measurements were also performed on the surface of the different samples in order to evaluate the capability of the coatings to “remove” drops of electrolyte in humid environments and thus delay corrosion when not directly immersed in fluids. Static sessile drop method was used. The tests were performed using a volume increment of $2 \mu\text{l}$.

Results and Discussion

Morphological

Figure 1 shows the morphology of the surface for sample AC on AFM $10 \times 10 \mu\text{m}$ maps. As surface morphological features were homogeneously distributed on the surface, R_a was measured and considered representative for the different surfaces. For samples AC and CA, the morphology resulted to be flat and the roughness quite low (about $20 \text{ nm } R_a$), similar to the roughness of the AISI 316L substrate. Sample CAC showed a slightly lower surface roughness (about $15 \text{ nm } R_a$), due to the higher thickness of the total deposit, which resulted in a more efficient smoothing effect of the substrate roughness features. In all cases, smooth, oriented linear scratches due to the polishing procedure were evident in the AFM maps. Few spot-like spikes caused by small dust particles were present on the maps and no cracks or other delamination phenomena were found on the samples during AFM analysis.

Deposition rates were then verified for both TiO_2 and Al_2O_3 dividing the overall average coating thickness of samples A and B for the number of different precursors cycles. In the case of 100°C layer, the real deposition rate was about $1.35 \text{ \AA/cycle}$, while in the case of the 300°C layer, the real deposition rate was about $1.68 \text{ \AA/cycle}$. The deposition rate of Al_2O_3 at 300°C has been double checked using AFM measurements at different numbers of deposition cycles.

The coating thickness measurements obtained by AFM are presented in Table 1. It can be observed that the AFM

Table 1 Thickness values for the different samples, nominal, measured using AFM at the interface between coated and uncoated substrate, measured using GDOES

Sample	Nominal thickness (nm)	AFM thickness (nm)	GDOES thickness (nm)
AC	15.2	16.7 ± 1.3	16.4 ± 3.1
CA	15.2	16.2 ± 2.0	17.6 ± 2.2
CAC	30.4	32.8 ± 5.3	37.7 ± 5.2

Average values (ten measurements)

results are close to the nominal thickness values, with a relatively limited data dispersion between 16 and 8% depending on the coating thickness.

Figure 2 shows the SEM images obtained on the three different samples, at 10,000 magnifications (Fig. 2a for sample AC, Fig. 2b for sample CA, Fig. 2c for sample CAC). No defects could be found on the surface of the sample, the ALD coatings seem to be conformal, without any crack or sign of delamination. Some small residual dust particles can be observed on the images, and their composition was confirmed by EDS analysis.

Compositional

GDOES accuracy was strongly related to the sharpness of the interface region between coating and substrate. In this work, the coating thickness has been measured between the top surface and the intersection point between oxygen and iron signals. Signals overlapping between Fe and Al are mainly due to the surface roughness of the samples which is on the same order of magnitude of the single layer thickness.

Figure 3a shows the GDOES graph for the first 30 nm of sample AC. The thickness of the coating was approximately 17 nm, even if coating signals are still present for more than 30 nm. This is caused by the surface roughness of the sample and the sputtering rate differences between ceramic coating and steel substrate. The coating composition resulted to be around 73 wt.% oxygen and 20 wt.% aluminum in weight for the first layer, which is far away from the 53 wt.% aluminum and 47 wt.% oxygen nominal composition of Al_2O_3 . This strong oxygen overestimation is due to the absence of reliable standards for ceramic materials in the GDOES calibration method and thus GDOES results must be considered only qualitative for compositional analyses. For the second layer, the ratio is still not stoichiometric, with 68 wt.% oxygen and 28 wt.% aluminum. A small chromium peak corresponding to the pristine Cr_2O_3 protective layer spontaneously formed by stainless steel.

In the case of sample CA (Fig. 3b), the thickness of the coating resulted to be around 18 nm, even if, as for sample

Fig. 2 SEM images of (a) sample AC, (b) sample CA, (c) sample CAC measured on the surface of the coatings

AC, coating signals are present in the analyses for more than 30 nm. As before, this is caused by the surface roughness of the sample and the difference in sputtering rates between ceramic coating and steel substrate. Again, the coating compositions of both layers detected with GDOES show a strong overestimation of the oxygen signal.

Fig. 3 GDOES profile for (a) sample AC, (b) sample CA, (c) sample CAC, signals of Al, Fe, Cr, and O

In the case of sample CAC (Fig. 3c), the overall coating thickness of the coating resulted to be 38 ± 5.2 nm. In contrast with the previous samples, the three different layers could not be discriminated.

Both in the case of samples CA and CAC, it is not possible to clearly spot the presence of a Chromium peak at the interface between coating and bulk stainless steel substrate.

The GDOES analysis clearly evidenced a difference between the layers deposited at different temperature. It is not possible to state if this phenomenon is really caused by a difference in the stoichiometric ratio between oxygen and aluminum or it is caused by differences in the crystalline structure and/or grain dimension, which may influence the GDOES results. From this analysis, it is only possible to state that the layers have physical differences and GDOES technique has the capability to discriminate between the two different deposition temperatures. Discrimination can only be obtained by GDOES comparing the results with reliable “thick” ceramic standards with different stoichiometry and finally confronting the results with XRD low angle specters to confirm the crystalline structure.

Mechanical

Vickers indentations performed on the coated sample surface were observed using SEM, as the optical microscope field depth resulted to be too small to contemporarily resolve different points, due to the intense local plastic deformation and curvature of the substrate. The results obtained for the three different samples are presented in Fig. 4. All coatings showed an increase of the delaminated Area/Load ratio which remains almost constant only at the highest indentation loads ($9.8 \text{ N} = \text{HV}_1$ and $19.6 \text{ N} = \text{HV}_2$). For the overall investigated load interval, sample CAC showed the worst behavior, with delaminated areas almost three times higher than the other samples at every load interval. This behavior was initially speculated to be caused by a difference in the adhesion properties between the layers deposited at 120 and 300 °C, as confirmed by the results obtained on sample CA, which showed a worse behavior when compared with AC. For CAC, the relatively low adhesion can be explained with the increased thickness of the deposited layer. All samples have almost flat graphs after 10 N, as already reported before in previous publications [29, 30]. The best behavior is shown by the AC

Fig. 4 Delamination graph for the different samples. Delaminated areas over load versus applied load

sample, on which the delaminated areas were almost impossible to discriminate around the indentations.

Electrochemical

Polarization curves for the different samples are shown in Fig. 5. Uncoated AISI 316L shows a passive behavior in the 9 g/l NaCl solution, with a corrosion current density between 10^{-6} and 10^{-7} A/cm² and a passive region from 0.1 to 0.4 V with respect to Ag/AgCl. The OCP for uncoated AISI 316L steel resulted to be about 0.1 V with respect to Ag/AgCl. Uncoated AISI 316L and sample CA showed the same corrosion potential of about -0.05 V with respect to Ag/AgCl. Both samples AC and CAC showed a decrease in the corrosion potential, to about -0.2 V for AC and -0.3 V for CAC. All three ALD-coated samples showed a shift of the corrosion current density to lower values. In particular, samples AC and CA showed a decrease of corrosion current density from about 2×10^{-7} A/cm² to about 2×10^{-9} A/cm². Sample CAC showed a stronger decrease in corrosion current density from about 2×10^{-7} A/cm² to about 3×10^{-10} A/cm². OCP was -0.3 V with respect to Ag/AgCl. The uncoated substrate showed a corrosion current density of about 2×10^{-7} A/cm² and a passive region from -0.3 to 0.2 V with respect to Ag/AgCl. Samples B, C, and D showed a stronger corrosion current density reduction, to less than 10^{-10} A/cm² with wider passive regions and a shift of the breakdown potential to about 1.3 V with respect to Ag/AgCl. The protective properties against localized corrosion of the stainless steel are clearly proven by the polarization curves. The improved behavior obtained with the sample CAC may be caused by a combination of two effects: the increased thickness of the deposit and the presence of three different layers on the surface of the sample, creating a multilayer structure in which defects are not continuous

Fig. 5 Polarization curves obtained for the different samples and bare AISI 316

through the overall coating thickness [29]. Using the same procedure already applied in the literature by Potts et al. [26] and Diaz et al. [27], it is possible to estimate the overall amount of defects as a ratio between the corrosion current density of the coated samples and the substrate, obtaining a residual amount of defects of about 1.5% for sample CA, about 1% for sample AC, and 0.13% for sample CAC.

Contact Angle

Table 2 resumes the contact angle values measured on the three different samples and on uncoated AISI 316L stainless steel. It is possible to state that the layers deposited at 120 °C and the pristine stainless steel surface are in the range of high wettability ($0^\circ < \theta < 90^\circ$), while both the layers deposited at 300 °C, on the surface of samples AC and CAC, are in the range of the low wettability ($90^\circ < \theta < 180^\circ$). Similar differences in results were obtained in the literature on different oxide morphologies [31] (high wettability for porous anodized alumina, low wettability for alumina nanowires pyramids) and thermal treating α -Al₂O₃ at different temperatures [32]. A correlation between surface wettability and corrosion resistance has been proposed in the literature, for different materials and testing conditions, for example in the case of pipelines for transportation of oil and gas [33], or in the case of Benzotriazole-treated copper [34]. This property has also been investigated for metallic glasses [35]. In the case of 7075-T6, a strong dependency of corrosion resistance to surface wettability was found when tested with accelerated cycling testing over a period of 60 days [36]. The beneficial effect of a low surface wettability for corrosion resistance is the capability to obstruct the formation and permanence of electrolyte droplets for extended periods of

Table 2 Water contact angle measurements for the different samples and the bare 316L substrate (average values on five measurements)

Sample	Contact angle θ (°)
AISI 316L	48.3 ± 1.1
AC	74.2 ± 4.7
CA	112.1 ± 4.3
CAC	109.6 ± 7.1

time that provide a constant potential gradient needed for the initiation of pits or other corrosion phenomena.

Conclusions

Three different multilayer configurations of ALD coatings were successfully deposited on polished AISI 316L stainless steel substrates. No deposition discontinuities or cracks were observed by AFM and SEM analysis on the coated samples.

AFM analysis at the coating/substrate interface showed that all three depositions are close to their nominal thickness values, with a deviation of less than 20%.

GDOES proved to be a useful tool for thickness evaluation of ALD, although it was not reliable for compositional analysis, giving only qualitative results. GDOES showed the capability to discriminate between layers deposited at different temperature, by utilizing difference in the ratio between Al and O signals.

Adhesion tests performed using Vickers microhardness indentations proved to be a simple and reliable method for the evaluation of mechanical/adhesion properties of the ALD coatings. Due to the limited thickness of the coatings, all configurations showed a good resistance to delamination, AC (amorphous/crystalline) being the best.

Contact angle measurements showed that Al_2O_3 deposited at 300 °C has a low wettability, further promoting the protection of the stainless steel substrate against aggressive moistures and environments.

All three ALD coatings proved to be effective in the corrosion protection of the stainless steel substrate, reducing the corrosion current density from about 10^{-6} to about 10^{-8} (samples AC and CA) or even 6×10^{-10} A/cm² (samples CAC). Sample CAC also evidenced a large increase in the passive region range of potential.

Similar results on corrosion protection and adherence were obtained in a previous work, using Al_2O_3 and TiO_2 layers at the deposition temperature of 120 °C [30]. TMA and TiCl_4 were used as precursors. The main objective of the present paper was to completely remove the TiCl_4 precursor from the process, due to the potentially dangerous presence of chlorine, which has a deleterious effect on

the passivity of metals and metallic alloys [1]. A residual presence of chlorine in ALD deposited layers was in fact found by other research groups [26, 27]. Using a thermally multilayered Al_2O_3 structure, superior corrosion resistance results were obtained with less thick deposits, completely avoiding the presence of TiCl_4 in the deposition process.

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