Electrochimica Acta 203 (2016) 404–415

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical characterization of atomic layer deposited Al_2O_3 coatings on AISI 316L stainless steel

M. Fedel*, F. Deflorian

Department of Industrial Engineering, University of Trento, Via Sommarive 9, 38123 Trento, Italy

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 15 February 2016
Accepted 16 February 2016
Available online 18 February 2016

Keywords:
Atomic Layer Deposition (ALD)
AISI 316L
Al_2O_3
Electrochemical Impedance Spectroscopy (EIS)

ABSTRACT

In this work the potential of the Atomic Layer Deposition (ALD) technique to deposit thin and compact ceramic films to shield AISI 316L stainless steel against corrosion is investigated. Al_2O_3 films were applied onto mirror polished AISI 316L by means of Atomic Layer Deposition to increase its durability. The effect of a different number of self-terminating gas–surface reactions in the ALD chamber (which lead to different thickness of the deposits) was investigated. The physical properties of the coatings were explored by means of FT-IR exploiting the ATR geometry. The corrosion protection properties of the Al_2O_3 deposits were investigated by means of electrochemical techniques such as potentiodynamic curves and electrochemical impedance spectroscopy (EIS). In particular, the electrochemical response of the coated substrate was investigated for prolonged immersion time (up to 1000 hours of continuous immersion) to assess the corrosion resistance of the coatings in this condition. Relatively long term EIS measurements revealed that a monitor of the corrosion protection properties during time provides useful information related to the effective corrosion protection of the coatings, integrating the commonly employed short term test (such as polarization curves and short term EIS) to study ALD ceramic coatings.

1. Introduction

Among the existing coating technologies, the interest in Atomic Layer Deposition (ALD) is increasing in the recent years since it can be used as an alternative method to produce corrosion resistant films [1–3]. Atomic layer deposited coatings have been recognized to be suitable for a wide range of applications such as microelectronics, optoelectronics, catalysts, electroluminescence as well as different areas of nanotechnology [4]. ALD can be exploited not only to apply coatings on materials surface, but also to precisely coat nanoparticles, nanowires and nanotubes [5]. However, only recently these coatings have been considered for corrosion protection purposes thanks to the capability of ALD technique to deposit thin and compact ceramic films onto different metallic substrates. From both scientific and technological point of view, ALD is an evolution of traditional chemical vapour deposition (CVD) technique: it consists in a series of self-terminating gas–surface reactions controlled by a separate pulsing of precursors [6]. Choosing the proper precursors, by means of ALD technique it is possible to control the growth of thin and conformal inorganic films onto many metals such as stainless steel [7–9], carbon steel [10], magnesium alloys [11], silver [12,13] as well as a few polymeric substrates [14]. With respect to traditional vacuum deposition techniques such as CVD processes, ALD shows enhanced conformality, uniformity and a relatively simple control of the thickness (as it is determined by the number of pulse of the different gas reagents) [15]. Comprehensive and detailed overviews of the deposition mechanisms as well as the potential of ALD technique can be found in literature [4–6].

In this work, atomic layer deposited Al_2O_3 films have been studied for the protection against corrosion of AISI 316L stainless steel. ALD deposited alumina films, whose formation mechanisms have been object of a comprehensive review by Puurunen [16], are recognized to be effective to protect metals against corrosion [8,17]. However, very often the corrosion protection properties of the coatings are investigated by means of polarization curves and Electrochemical Impedance Spectroscopy (EIS) collected only after very short immersion time, in the order of a few hours [2,8,10,18–20]. This approach provides relevant and significant information related to the corrosion protection properties of the film as well as on its dielectric characteristics. However, to provide some insight into the fundamental mechanisms for the performance differences understanding of the corrosion resistance of the ALD coatings as well as to better understand their long term durability, it is necessary to monitor the electrochemical response of the coated substrates for prolonged immersion time. In fact it is

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* Corresponding author. Tel.: +39 0461 282403, fax: +39 0461 281977.
E-mail address: michele.fedel@unitn.it (M. Fedel).

http://dx.doi.org/10.1016/j.electacta.2016.02.107

believed that this approach would be helpful to obtain a more comprehensive knowledge to forecast the long term corrosion behavior. In addition, the failure mechanism of the coatings can be also better understood with time monitoring of the electrochemical properties of the coated substrates for prolonged immersion time. For this purpose, this work is devoted to the investigation of the long term electrochemical response of atomic layer deposited Al_2O_3 films immersed time in a NaCl containing solution. ALD coatings object of the experimental tests were applied onto mirror polished AISI 316L plates: the effect of a different number of self-terminating gas–surface reactions (i.e. different thickness) employed to produce layers Al_2O_3 was investigated for relatively long immersion time (about 1000 h of continuous exposure to the electrolyte).

The structure of the coatings was explored by means of Attenuated Total Reflectance (ATR) infra-red spectroscopy. Polarization curves and electrochemical impedance spectroscopy (EIS) measurements carried out in a 0.2 M NaCl solution were employed to investigate the initial corrosion protection properties of the different inorganic layers as well as their evolution during time. 0.2 M NaCl solution has been widely employed by other authors to investigate ALD coatings [2,8–11,17,20]. This fact is related to two main reasons: (1) as it contains chlorides, it is suitable to promote localized corrosion on passive metals and (2) it is close to the physiological solution (i.e. 0.9 wt%), which is commonly used as corrosive mean as many research study are devoted to the application of ALD coatings in the biomedical field. As the present work deals with ALD coatings on stainless steel, a 0.2 M NaCl solution was employed also to allow an easier comparison with previous work carried out on similar systems. After collection of the EIS spectra, analysis and discussion of the possible and suitable electrical equivalent circuits have been carried out. Based on the present literature and on the shape of the experimental spectra obtained, a possible model to interpret the EIS spectra has been proposed. The experimental results highlighted that relatively long term exposure (in the order of thousands of hours) can be exploited to better differentiate the corrosion protection properties of the investigated coatings compared short term electrochemical test (such as polarization curves or EIS in the very first hours of immersion).

2. Experimental

Mirror polished (i.e. grinding with 800, 1200, 4000 emery papers and then polished with 3 μm and 1 μm diamond paste) AISI 316L stainless steel plates (supplied by Ronda S.p.A, Italy) were used as substrate to coat. The composition is reported in Table 1. Prior to entering the deposition chamber, the substrate were cleaned with ethanol under sonication for 8 minutes and finally dried under nitrogen flux. Atomic layer depositions were carried out on a commercially-built Beneq TFS-500 equipment. Trimethyl aluminum (TMA, $Al(CH_3)_3$) and water (H_2O) were employed as precursors and alternately injected via nitrogen carrier gas. The depositions were performed at temperature of 350 °C in a 33 mm height–20 mm diameter large deposition chamber. The evaporation of TMA and H_2O was conducted at room temperature while the the ALD reactor operated with a pressure of about 10 mbar.

The deposition rate was expected to be in the order of about 0.1 nm $cycle^{-1}$ [21]. A cycle consists of a single series of self-terminating gas–surface reactions controlled by a separate pulsing of precursors. The sequence consisting of (1) a gas pulse of the first film precursor (TMA in this case), (2) the consequent gas pulse of the second precursors (H_2O in this case) and (3) the final purging of the by-products, constitutes one single "cycle". Nitrogen was used as carrier gas as well as purging gas. In order to analyze the effect of the thickness on the final properties of the ALD films, 500 and 1000 cycles films were produced. The labels Al_2O_3–500 and Al_2O_3–1000 refer to the coating obtained employing 500 and 1000 cycles, respectively while the label "SS316L" is related to the bare substrate. The thickness of the coatings was determined by means of Secondary Ion Mass Spectrometry (SIMS). Dynamic SIMS analyses were performed on Cameca SC-Ultra equipment using 37 nA, 1 keV O_2^+ primary ion beam in a chamber maintained at about $\sim 10^{-9}$ mbar. The beam was scanned across areas of 300 μm × 300 μm. Positive secondary ions were accepted from circular analysis areas limited to a diameter of about 100 μm. In order to calibrate the sputtering rate of the coating layers, the eroded craters were analyzed "ex situ" using a Tencor P6 profilometer. The average of three profile measurements was employed. The structure of the coatings was characterized by means of an ATR infra-red spectroscopy equipment (Varian 4100 Excalibur Series). A diamond internal reflective element (IRE) was exploited to collect the experimental spectra. The wavenumber range was 500–4000 cm^{-1} and the resolution 4 cm^{-1}. The appearance of the coatings was investigated by means of a JEOL 7000 Series SEM. The electrochemical response of the different samples was monitored in order to define the protective properties of the films and to evaluate the effect of the different number of cycles. Both direct and alternate current methods were exploited. Electrochemical tests were carried out using a three electrodes arrangement with an AUTOLAB 302 N equipment. A platinum ring and a Ag/AgCl electrode (3 M KCl, +0.205 V vs Standard Hydrogen Electrode, SHE) were used as counter and reference electrode, respectively, while the AISI 316L plate was the working electrode. All the electrochemical measurements were collected in 0.2 M NaCl. A funnel like polypropylene cell was glue to the surface of the sample under investigation by means of silicon glue. Thus, the electrochemical tests were performed on a horizontally oriented surface. The analysed circular area was about 1 cm^2. Prior to the electrochemical tests, the investigated samples were carefully cleaned with ethanol under continuous sonication and finally dried under nitrogen flux. The electrochemical investigation was carried out over the investigated coating as well as on a mirror polished bare AISI 316L sample used for comparison. Also the mirror polished AISI 316L samples were carefully cleaned with ethanol under continuous sonication and finally dried under nitrogen flux prior to performing the electrochemical tests. Open circuit potential vs time measurements were collected during 1000 hours of continuous immersion in the electrolyte. Polarization measurements were carried out to investigate the protection properties of the performed coatings. The polarization rate was set to 0.166 mV/s, scanning in the anodic direction from −50 mV vs OCP. The experimental curves were collected after a 600 seconds delay to stabilize the potential prior to starting the measurements. EIS measurements were performed to assess the corrosion protection properties and the degradation mechanisms of the coatings for relatively long immersion time (1000 h). As previously indicated, the same electrodes arrangement employed for the polarization measurements was used. Electrochemical impedance spectra were collected at OCP, which was measured before each single measurement and potentiostatically maintained during spectra acquisition. The AC perturbation amplitude was 15 mV (rms), the frequency range between 10^5–10^{-2} Hz. Five points-per-decade were collected. The electrochemical results were obtained from at least two testing samples to

Table 1
Chemical composition of AISI 316L (wt%, from the technical datasheet).

	C	Pb	Sb	Mn	Si	Cr	Ni	Mo
wt%	0.035	0.04	0.03	2.0	0.75	16.0–18.0	10.0–15.0	2.0–3.0