

Interface control of atomic layer deposited oxide coatings by filtered cathodic arc deposited sublayers for improved corrosion protection



Emma Härkönen ^{a,*}, Sanna Tervakangas ^b, Jukka Kolehmainen ^b, Belén Díaz ^c,
Jolanta Świątowska ^c, Vincent Maurice ^c, Antoine Seyeux ^c, Philippe Marcus ^c,
Martin Fenker ^d, Lajos Tóth ^e, György Radnóczy ^e, Mikko Ritala ^a

^a Laboratory of Inorganic Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland

^b DIARC-Technology Inc., Espoo, Finland

^c Laboratoire de Physico-Chimie des Surfaces, CNRS (UMR 7075) – Chimie ParisTech (ENSCP), F-75005 Paris, France

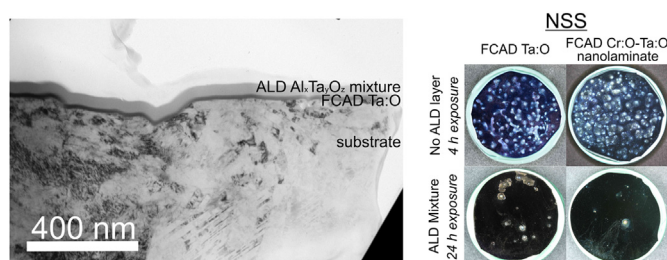
^d FEM Research Institute, Precious Metals and Metals Chemistry, D-73525 Schwäbisch Gmünd, Germany

^e Research Centre for Natural Sciences HAS, (MTA TKK), Budapest, Hungary

HIGHLIGHTS

- Corrosion protection properties of ALD coatings were improved by FCAD sublayers.
- The FCAD sublayer enabled control of the coating-substrate interface.
- The duplex coatings offered improved sealing properties and durability in NSS.
- The protective properties were maintained during immersion in a corrosive solution.
- The improvements were due to a more ideal ALD growth on the homogeneous FCAD oxide.

GRAPHICAL ABSTRACT



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ABSTRACT

Sublayers grown with filtered cathodic arc deposition (FCAD) were added under atomic layer deposited (ALD) oxide coatings for interface control and improved corrosion protection of low alloy steel. The FCAD sublayer was either Ta:O or Cr:O–Ta:O nanolaminate, and the ALD layer was Al₂O₃–Ta₂O₅ nanolaminate, Al_xTa_yO_z mixture or graded mixture. The total thicknesses of the FCAD/ALD duplex coatings were between 65 and 120 nm. Thorough analysis of the coatings was conducted to gain insight into the influence of the FCAD sublayer on the overall coating performance. Similar characteristics as with single FCAD and ALD coatings on steel were found in the morphology and composition of the duplex coatings. However, the FCAD process allowed better control of the interface with the steel by reducing the native oxide and preventing its regrowth during the initial stages of the ALD process. Residual hydrocarbon impurities were buried in the interface between the FCAD layer and steel. This enabled growth of ALD layers with improved electrochemical sealing properties, inhibiting the development of localized corrosion by pitting during immersion in acidic NaCl and enhancing durability in neutral salt spray testing.

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* Corresponding author. Tel.: +358 294150215; fax: +358 294150198.

E-mail address: emma.harkonen@helsinki.fi (E. Härkönen).

1. Introduction

Corrosion protection of engineering metals and alloys with atomic layer deposited (ALD) oxide coatings has gained increasing attention during the last years. Protective layers have been deposited on stainless steel [1–6], steel [7–14], aluminium alloy [7], magnesium alloy [15], magnesium–lithium alloy [16], copper [17,18] and silver [19]. Because ALD is based on alternating precursor pulses separated by inert gas purging, film growth occurs only on surfaces [20,21]. This leads to high conformality and uniformity even on challenging surface morphologies. Therefore ALD grown protective oxide layers offer significant advantages over ceramic coatings deposited on e.g. steel by many other methods [22–28]. Morphological heterogeneities, which pose a problem for physical vapour deposition (PVD) [23,24], do not influence the quality of the coating and even complicated 3D objects can be coated conformally with ALD. Moreover, because complete burial of surface heterogeneities is not necessary, the ALD coatings can be considerably thinner than PVD coatings. Post-deposition annealing treatments, which are usually necessary with solution deposition techniques like sol–gel and can lead to crack formation [26], are not needed in ALD. Also intrinsic defect formation during the coating process, which is typical for instance for plasma electrolytic oxidation (PEO) [28], is not an issue for ALD. Thus very low pinhole and other defect densities can be accomplished. Furthermore, combining two or more materials into nanolaminates or mixtures allows easy modification of the composition and architecture of the coatings for the best combination of properties.

The ALD thin film materials that have been considered as corrosion protection coatings on steel are Al_2O_3 , TiO_2 and Ta_2O_5 [1–14]. The best sealing properties in electrochemical measurements were achieved with Al_2O_3 [1,4,7–9]. With 50 nm thin films deposited at 250 °C a three orders of magnitude decrease in passive current density of a stainless steel was obtained [4]. Similarly, on a low alloy steel a 50 nm Al_2O_3 coating deposited at 160 °C decreased the corrosion current density by two orders of magnitude [8]. More moderate sealing properties were observed with the TiO_2 and Ta_2O_5 coatings [1–6,10–12]. Unfortunately, Al_2O_3 was observed to dissolve from a steel surface at a rate of 7 ± 1 nm per hour even in neutral NaCl solutions [9]. The dissolution was attributed to cathodic reduction of dissolved oxygen at the bottom of pinholes resulting in a local increase of pH. The stability of the coatings could be improved by combining the insulating properties of Al_2O_3 with the chemical stability of TiO_2 or Ta_2O_5 [1,3–6,10,12,13]. The best long-term corrosion protection properties were achieved with Al_2O_3 – TiO_2 nanolaminate, Al_2O_3 – Ta_2O_5 nanolaminate and $\text{Al}_x\text{Ta}_y\text{O}_z$ mixture coatings.

The ALD film growth begins with chemical reactions between the precursors and the substrate surface [20,21]. Therefore the chemical species on the surface have an effect on the quality of the film deposited on top: a lack of appropriate surface species for the film growth can induce nucleation delays and poor adhesion, impurities and weakly attached particles can induce defect formation, and hydrocarbon impurities can lead to poor adhesion and sealing properties [7,13,14,29,30]. The compositionally and morphologically heterogeneous industrial metal alloys do not offer the best starting surfaces for ALD film growth. Impurities and loose particles are hard to avoid and often the surfaces contain some type of a hydrocarbon layer. It has been observed that coatings deposited with thermal ALD on steel substrates that have been cleaned only by degreasing in organic solvents have problems with adhesion [7,13,14]. Pre-treatment with H_2 –Ar plasma was found to have a beneficial effect on the coating–steel interface, and thus both adhesion and electrochemical barrier properties of the coatings could be improved [14]. Additionally, the stability of the coatings

has been shown to improve with decreasing substrate roughness [13]. As ALD growth occurs uniformly and conformally over all surfaces, the improvement was most likely due to a reduction in the number of weakly attached particles, which upon detaching can create a pinhole defect in the coating. However, even better properties can be expected when the ALD films are grown on clean, well-defined surfaces with appropriate starting points for the film growth.

Filtered cathodic arc deposition (FCAD) is a PVD technique [31,32]. It is based on a low-voltage, high-current plasma discharge between two metallic electrodes. The plasma discharge brings forth an arc current composed of high-energy ions and electrons. A part of the ion flux is directed to a substrate after magnetically filtering away macroparticles formed in the plasma. The film deposition occurs through bombardment of the substrate with the high-energy ion flux. This leads to films with excellent adhesion, high density and hardness. The process can also involve an *in situ* pre-cleaning step that removes impurities like hydrocarbons and oxide layers from the substrate surface. FCAD coatings are widely used as hard protective coatings for reducing mechanical wear [33,34]. The characteristics of FCAD make it an ideal candidate to be combined with ALD for resolving the challenging aspects of the solely ALD-based protective coatings on metallic substrates.

In this study, we have combined the advantageous properties of FCAD with ALD films by preparing thin (≤ 120 nm) FCAD/ALD duplex coatings for corrosion protection of steel. Careful attention was given to the effect of the FCAD sublayers on the morphology, composition, electrochemical properties, stability and long-term corrosion protection properties of the ALD coatings. Two FCAD sublayers, 10 nm Ta:O and 50 nm Cr:O–Ta:O nanolaminate, were employed [11,35]. The top ALD layers were 50 nm Al_2O_3 – Ta_2O_5 nanolaminate and $\text{Al}_x\text{Ta}_y\text{O}_z$ mixtures with either homogenous or graded composition as selected based on previously published results [10,12].

2. Experimental

Low alloy steel (AISI 52100, DIN 100Cr6) hardened and tempered (at 180 °C) to 805 HV hardness was used as a substrate material. The composition of the steel was (in wt.%) C (0.95–1.1), Cr (1.5), Ni (max. 0.30), Mn (0.25–0.45), Cu (max. 0.30), Si (0.15–0.35), P (max. 0.030), S (max. 0.025) and Fe (balance). The substrate surfaces were tumble polished, ground by planar grinding, lapped in a water based diamond suspension (6 μm) and brushed.

The FCAD coating process was carried out in a DIARC-Technology Inc. coating equipment. The deposition sequence was the same as presented in previous publications [11,35]. Before coating the samples were wiped with acetone, ultrasonicated in isopropanol for 5 min, rinsed with isopropanol and blow-dried with compressed air. Then they were etched *in situ* in the FCAD chamber with 350 eV Ar ions at 0.5 mA cm^{-2} current density for 30 min. The metal oxide coatings, Ta:O and Cr:O, were produced from Cr and Ta plasma in presence of low partial pressure of oxygen. The deposition temperature was below 100 °C.

Prior to ALD the samples were once more wiped with acetone, ultrasonicated in acetone and isopropanol for 5 min, rinsed with ethanol and blow-dried with compressed air. Further purification of the surface was done by H_2 –Ar plasma at 160 °C in a Beneq TFS-200 ALD reactor according to methodology detailed in a previous publication [14]. The plasma was generated by a capacitively coupled 13.56 MHz rf power source. The reactor was operated in a remote plasma configuration, i.e. the plasma was separated from the substrates by a metal grid. The plasma gases Ar (>99.999%) and H_2 (>99.999%) were purified on site with Aeronex Gatekeeper and Entergris Gatekeeper purifiers. The gas flows were maintained

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