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ScienceDirect
Surface & Coatings Technology 202 (2008) 4047–4055
www.elsevier.com/locate/surfcoat

# Mechanical and corrosion properties of dc magnetron sputtered Al/Cr multilayers

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Received 5 December 2007; accepted in revised form 21 February 2008
Available online 4 March 2008

**Abstract**

Mechanical and corrosion properties of Al/Cr multilayer coatings deposited by dc magnetron sputtering are investigated and compared to pure Al and Cr coatings. The objective of this study is to increase the mechanical properties of sacrificial Al-based coatings. The results indicate that mechanical and corrosion properties depend on the architecture organisation. The reduction of the layer thickness allows an increase of the coating hardness. The nanolayer architecture leads to a "hard and tough" material compared to the other architectures. Moreover, the intrinsic corrosion resistance is enhanced, as the corrosion and the pitting corrosion potentials are progressively shifted towards positive values. The nanolayer coating presents the highest intrinsic corrosion resistance but multilayer and nanolayer Al/Cr coatings become nobler than the steel substrate. The corrosion resistance of the coated steel is then strongly dependent on the microscopic coating defects which act as preferential pathways for the corrosive solution. So the nanolayer architecture organisation improves the mechanical properties but does not permit to conserve the sacrificial behaviour of the aluminium based coating, which is harmful for the corrosion protection of coated steel.
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*Keywords:* Multilayer; Corrosion; Mechanical properties; Aluminium; Chromium

## 1. Introduction

Aluminium coatings are interesting candidates for the cathodic protection of construction steel due to their good corrosion resistance in aggressive media. However, the mechanical properties of aluminium (hardness around 180 HV), as well as its pitting corrosion sensitivity in chloride media, have often limited its application.

Different alternatives have been investigated in order to improve the mechanical resistance and/or sacrificial behaviour of Al-based coatings deposited on steels. Al coatings reinforced by addition of transition metals such as chromium or titanium have already been studied [1–3]. The best compromise between mechanical and corrosion properties is obtained for amorphous Al-Cr alloys deposited by dc magnetron sputtering with approximately 20 at. % of chromium. Is has been reported that the addition of elements like molybdenum or magnesium could limit the sensitivity to pitting of Al coatings [4–9]. Incorporation of magnesium induces an increase of the sacrificial coating reactivity but does not modify the mechanical resistance. A significant modification of mechanical properties could be achieved for alloys with high molybdenum contents but those alloys do not present sacrificial character anymore. So, the association of a sacrificial protection with improved mechanical or tribological properties is rather difficult to achieve through a monolayer Al alloy coating.

Another alternative is the use of multilayer metallic coatings [10]. The recent evolution of coating technology allows deposition of multilayer coatings with enhanced mechanical and corrosion behaviours [11]. It was reported that materials with nanoscale structures presented enhanced characteristics, very different from the bare materials [12].

A study of the behaviour of cathodic arc evaporation Al/Ti multilayer coatings was carried out. It was shown that the intercalation of Ti layers limits the propagation of pits, which

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doi:10.1016/j.surfcoat.2008.02.021

Table 1
Deposition conditions on AISI 4135 steel

| | |
|---|---|
| Target to substrate spacing (mm) | 70 |
| Al-Cr targets spacing (mm) | 400 |
| Pre-sputtering time (min) | 15 |
| Residual pressure (Pa) | $10^{-4}$ |
| Working pressure (Pa) | 0.3 |
| DC U(V)/I(A) (Al and Cr) | 600/1.6 |
| Ar flow rate (sccm) | 35 |
| Bias voltage (V) | −100 V |

improves the sacrificial behaviour of the architecture. Setoyama [13] reported that the hardness of a nitride superlattice considerably increased when the multilayer periodicity decreased from 30 nm to 3 nm. In the case of cathodic coatings on steels, such as carbides or nitrides, the main problem is the presence of microscopic or macroscopic (like droplets if cathodic arc evaporation is used as deposition technology) defects which expose the substrate to the aggressive solution. The electrolyte infiltrates through the coating defects by capillary action, inducing a localised corrosion of the substrate which leads to partial coating spallation. It was reported that reducing the periodicity of nitride superlattice allows enhancement of coatings corrosion resistance by limiting the infiltration of the electrolyte through the defects [14–21]. Nakayama [22] studied the corrosion behaviour of metallic Al/Si and Fe/Zr superlattices deposited on glass substrates. The Al/Si superlattice films, deposited by magnetron sputtering were composed of crystalline Al layers and amorphous Si layers with a periodicity varying between 3 and 35 nm. As the periodicity was reduced, the corrosion potential shifted towards more positive values, which was also observed for nitride or carbide superlattices [15,23–25]. Nakayama found that the pitting potential of aluminium strongly depended on the periodicity, and that the corrosion resistance was considerably increased when the periodicity was reduced. He also observed that the aluminium layers were preferentially corroded through the defects of the silicon layers, which were delaminated due to the voluminous aluminium corrosion products.

The dependence of the corrosion resistance with periodicity is linked to the diffusion of the solution through the pores of the coating. A decrease in periodicity reduces the size of the pores, and the increase of the number of interfaces prevents the electrolyte infiltration, and thus increases the corrosion resistance. The same trends were reported for sputtered Fe/Zr deposits, and for nitride-based superlattice [12,23].

The objective of this study was to improve the mechanical properties of aluminium based coatings, conserving a sacrificial protection for these new alternatives. In this paper, Al/Cr multilayer architectures, deposited by dc magnetron sputtering, have been tested. 3 architectures, composed of a bilayer, a multilayer and a nanolayer were compared. The mechanical properties and corrosion resistance in saline solution were discussed and compared to single Al and Cr coatings. Architecture effects on hardness, Young's modulus and friction coefficient were also investigated. The corrosion resistance of the coatings deposited onto glass slide and steel substrate was also studied and finally the protective efficiency of Al/Cr multilayer coatings was examined during extended immersion tests.

## 2. Experimental procedure

### 2.1. Depositions

All aluminium and chromium coatings were deposited by dc magnetron sputtering at low pressure (0.3 Pa) and low temperature (floating temperature < 200 °C) from pure Al or Cr targets (200 × 90 mm). The main process parameters are summarised in Table 1. The substrate holder is kept fixed in front of each cathode (Al and Cr) for single, double and multilayer coatings deposition whereas it turns at 3 rpm for nanolayer coatings synthesis (dynamic mode). A simple geometrical calculation allows to predict the thickness of an elementary layer in the nanolayer coatings. Glass slides and AISI 4135 construction steel plates were used as substrates. All substrates were ultrasonically cleaned in a heated alkaline solution followed by acetone and rinsed with alcohol before being dried and placed into the PVD deposition chamber.

Three multilayer architectures for which the total thickness was constant at around 7-8 µm were characterised. Table 2 presents the specific deposition parameters and the total thickness of the coatings. The first architecture was a bilayer coating of aluminium (the outer layer) and chromium (the inner layer). The second was a multilayer coating composed of 26 alternated layers of aluminium and chromium (interlayer thickness of 0.3 µm). The outer layer in contact with the solution was aluminium. The last architecture was a nanolayer coating composed of 600 alternated layers of aluminium and chromium with an interlayer thickness of 12 nm. The top layer in contact with the solution was also an aluminium one. Al and Cr single layer coatings were also characterised as references.

Table 2
Description of the specific deposition parameters and thickness of the different coating configurations

| Specific coating parameters | | Deposition method | Deposition time (min.) | Deposition rate (µm/hr) | Layer thickness (µm) | Total coating thickness (µm) |
|---|---|---|---|---|---|---|
| Al | | Fixed | 30 | 14.6 | 7.3 | 7.3 |
| Cr | | Fixed | 30 | 14.2 | 7.1 | 7.1 |
| Al/Cr bilayer | Al | Fixed | 15 | 12.4 | 3.1 | 7 |
| | Cr | Fixed | 20 | 11.7 | 3.9 | |
| Al/Cr multilayer | Al | Fixed | 13 × 1.15 | 14.6 | 13 × 0.28 | 7.9 |
| | Cr | Fixed | 13 × 1.54 | 14.3 | 13 × 0.33 | |
| Al/Cr nanolayer | | Rotation 3 rd/min | 100 | 4.32 | 0.012 | 7.2 |

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