Corrosion Behavior of Al-based PVD Multilayer Sacrificial Coatings

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Introduction

Aluminum-based coatings deposited by Physical Vapor Deposition (PVD) are known as an alternative friendly solution to pollutant corrosion protection systems. However, aluminum-based coatings present a localized corrosion associated to a pitting corrosion [1] and do not present good mechanical properties. In order to have a slow dissolution of the coating, a uniform corrosion is preferable [2-4]. This can be obtained by incorporating some elements which change the electrochemical behavior of the aluminum-based coating (e.g. Zn, Y, Gd or Mg). Moreover, a multilayer structure including hardener elements (Mo, Mn) can also be proposed as a way to improve mechanical resistance.
This paper is dedicated to the description of the mechanical and electrochemical properties of different multilayer coatings based on Al-Mn and Al-Mo alloys. The influence of the period evolution is discussed and the results deduced from the different architectures are compared in order to evaluate the best configuration.

Experimental

Multilayer coatings have been deposited by magnetron sputtering onto glass slides and steel substrates. The deposition parameters are constant except for the deposition time of each alloy. Al-Mo and Al-Mn alloys at respectively 18 and 7 or 9 at.% were selected for their mechanical properties, whereas Al-Mg and Al-Y at respectively 11-15 and 18 were selected for their sacrificial character. Five multilayer configurations: Al-Mn/Al-Mg, Al-Mo/Al-Mg, Al-Mn/Al-Y, Al-Mn/Al-Gd and Al-Mo/Al-Y were investigated, the last layer in contact with the aggressive environment is always the alloys selected for their sacrificial character. The period was changed between 15 to 120 nm in order to study its effect on the multilayer properties. The argon pressure is 20 sccm and all the coatings have a total thickness of 5 µm. The coating morphology is observed using a scanning electron microscope (SEM). Cross-section observations were performed in order to evaluate the interface between the inner layers, and TEM observations were necessary for period close to 15 nm. Microstructure was also studied through X-ray diffraction (XRD). Energy Dispersive X-ray Spectroscopy (EDS) analysis were used in order to measure the surface composition of the coatings. The hardness of the coatings was evaluated with a Nano Hardness Tester (CSM instruments), and the value given is an average of ten measures.
Electrochemical investigations were realized in an aerated and stirred NaCl 5 wt.% solution with pH adjusted to 7 at (25.0 ± 0.1)°C. The electrochemical experiments were carried out using a conventional three electrode glass cell with samples as working electrode, connected to a Perkin Elmer EG&G 273A potentiostat. The potential is referred to a saturated calomel electrode (SCE) and the counter electrode is a large platinum grid. The corrosion behaviors of coatings deposited onto glass slide were evaluated through potentiodynamic experiments after one hour of immersion and through immersion test of 48h in saline solution. The potentiodynamic polarization curves were plotted after an initial potential stabilization of 1 h from -150 mV (vs. Open Circuit Potential) in the cathodic side, up to a potential corresponding to a current density threshold of 100µA/cm² in the anodic side, using a sweep rate of 0.2 mV/s. The current density threshold is used to limit the pitting degradation. The corrosion potential Ecorr and current density jcorr were estimated by using Tafel extrapolation.

Results and Discussion

Figure 1 presents the cross section SEM observations of Al-Mn/Al-Mg multilayer coatings with a period respectively at 120 and 60 nm. The other configurations present similar cross section observations. For the 120 nm period, the succession of the different layers is clearly observed. Adherence between layers is very good. A columnar structure was observed for the configurations with a period varying between 30 and 60 nm, and a compact and dense structure is obtained for the lowest period at 15 nm.

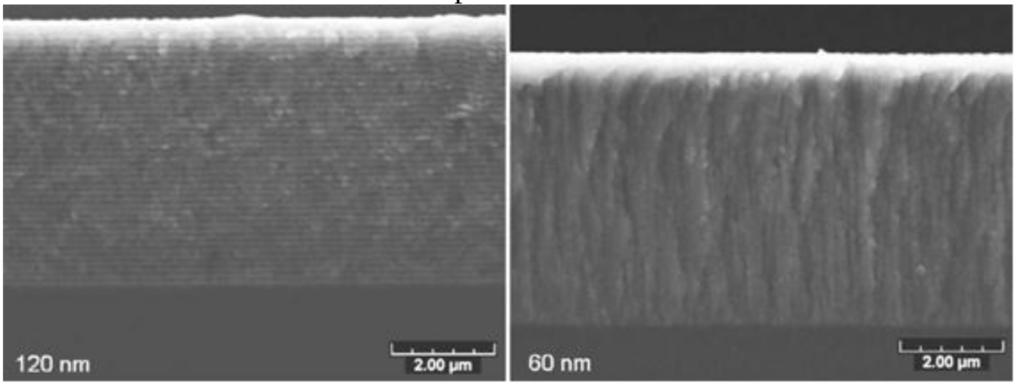

Figure 1: Cross section SEM observations of Al-Mn/Al-Mg coatings

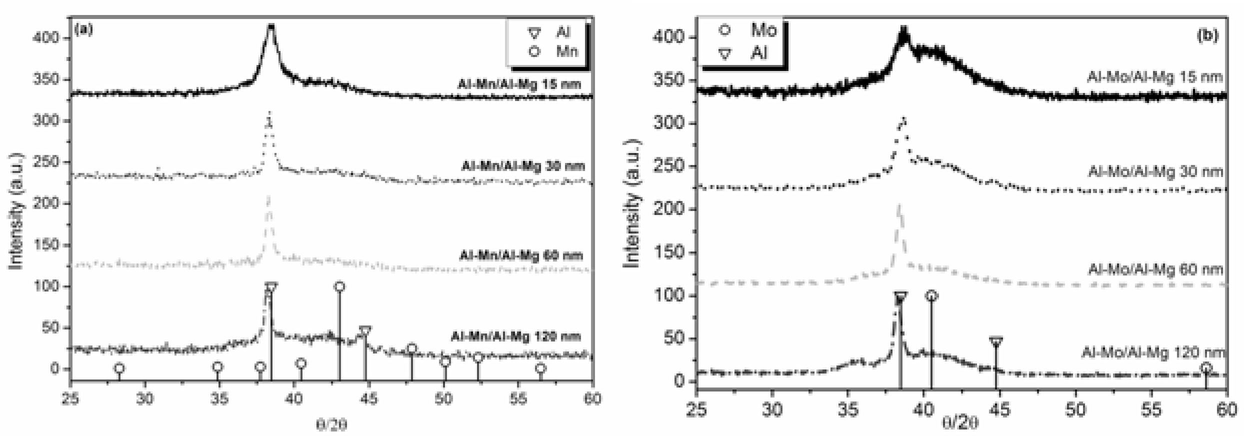

Figure 2: XRD patterns for: (a) Al-Mn/Al-Mg system, (b) Al-Mo/Al-Mg system

Fig 2a and 2b present the XRD patterns of multilayer coatings of Al-Mg combined respectively to Al-Mn or Al-Mo. In both cases, the (111) diffraction peak of aluminum at 38° is obtained, suggesting the presence of α-Al solid solution. Furthermore, very small shoulders are observed at around 41-42° suggesting the presence of amorphous phases inside the multilayer configurations. The microstructure of the multilayer coatings are in perfect agreement with the microstructure of the binary Al-X (X: Mg, Mn or Mo) alloys [5].

Electrochemical behavior was investigated in 5% NaCl solution. Figure 3 presents the polarization curves of the different multilayer configurations including the influence of the period decrease on the coating reactivity. The shape of the polarization curves is not modified when the period of the multilayer evolves. Fig. 3a and 3b correspond to multilayer configurations with Al-Mg sacrificial layers combined respectively with Al-Mn or Al-Mo layers. An ennoblement of the pitting potential of the Al-Mn/Al-Mg multilayer system is effectively observed when the period is decreased meaning that the corrosion resistance to localized degradation is improved by the nanostructuration of the coating. The dependence of the corrosion resistance with period is probably related to the diffusion of the solution through the pores of the coating. A decrease in period reduces the size of the pores, and the increase of the number of interfaces prevents the electrolyte infiltration, and thus increases the corrosion resistance.

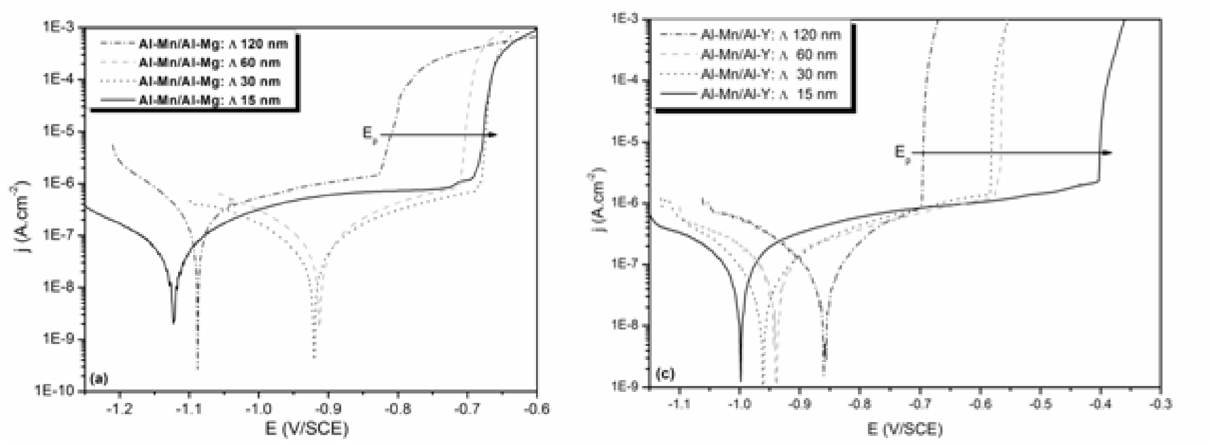

Figure 3: Polarization curves of the different multilayer coatings after 1h of immersion in saline solution

The increase of the number of interfaces can not only explain the improvement of the corrosion resistance to localized degradation. It seems that the nature of the alloying element affects the corrosion behavior of the multilayer configurations. Indeed, alloying elements could be classified [6] into two categories affecting either the dissolution of aluminum or the passivation of the alloy. Molybdenum was reported to reduce the dissolution of the aluminum base alloys, whereas manganese or rare earth elements seem to favor the passivation. So the role of these species during the initiation and growth of pits in the architecture is an important parameter. Furthermore, magnesium was reported as an element that permits to destabilize the passive films on aluminum, so the effect on pitting potential evolution when period is reduced should be quite limited.

Conclusions

Multilayer coatings are interesting alternative in order to improve mechanical properties and to preserve sacrificial character for the protection of steel structures in saline environment. Use of binary aluminum alloys do not permit to combine both characteristics, so different multilayer configurations with alloys devoted to mechanical properties and alloys ensuring sacrificial character were investigated. Decrease of the period of the multilayer permits to improve the properties of the architecture. This improvement is related to the smaller size of pores when the number of interfaces increases. The nature of the alloying elements also affects the corrosion behavior essentially when the architecture is sensitive to localized degradation. The Al-Mn/Al-Mg system with a 15 nm period configuration permits to preserve sacrificial character with enhanced mechanical properties.

Acknowledgements

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References

[1] Z.Szklarska-Smialowska, Corrosion Science, **41** (1999), 1743

[2] J.Creus, C. Berziou, C. Rébéré, A.Perez, S.Touzain, A. Billard. « Influence of rare earth element incorporation on the behaviour of magnetron sputtered Al based alloys». ICMCTF 2010. San Diego (CA, USA): 26-30 april 2010.

[3] A. Perez, A.Billard, S. Touzain, J.Creus « Corrosion behaviour of Al-Zn coatings in 5%wt NaCl solution » CORROSION NACE 2010. San Antonio (TX, USA) :14-18 march 2010

[4] A.Perez, A.Billard, S. Touzain, J.Creus « Comparison of the properties of Al-Ti and Al-Mg EBPVD coatings» ICMCTF 2010. San Diego (CA, USA): 26-30 april 2010.

[5] M. Reffass, C. Berziou, C. Rébéré, A. Billard, J. Creus. Corros. Sci., **52** (2010) 3615.

[6] P. Marcus. Corros. Sci., **36** (1994) 2155.