UMS Al-Mo coatings as an alternative to electro-plated cadmium

Mariusz BIELAWSKI and Jean-Pierre IMMARIGEON
NRC Institute for Aerospace Research, 1200 Montreal Road, Bld. M-3, Ottawa, Ontario K1A 0R6
Canada TEL:x613-998-8970 FAX:x613-990-6870 e-mail: mariusz.bielawski@nrc.ca
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For most aerospace applications, replacing cadmium plating requires sacrificial coatings having excellent adhesion to steel and that can be deposited using non-embrittling processes. Aluminum-based coatings, deposited using the Unbalanced Magnetron Sputtering (UMS) deposition process, meet these requirements. This paper discusses the development of UMS Al-Mo coatings from the perspective of their potential use as cadmium alternatives in applications requiring good corrosion resistance along with high lubricity. Results of microstructural examination and tribological and electrochemical tests are presented for a series of UMS Al-Mo coating produced over the composition range from zero to 100% Mo. The coatings have uniform thickness, a fully dense, featureless or slightly columnar structure and good adhesion to 4340 steel. The passivating effect of increasing molybdenum content resulted in a gradual increase of the corrosion and pitting potentials, indicating increasing resistance to pitting corrosion and decreasing sacrificial corrosion properties. The coefficients of friction of Mo rich coatings (with Mo contents between 90 and 100%) were found to be comparable to that of cadmium.

Keywords: Cadmium plating, Alternative coatings, Al-Mo system, Unbalanced magnetron sputtering

I. INTRODUCTION

The use of electro-plated cadmium is prohibited in many countries, except for aerospace, mining, offshore and nuclear sector applications, where high safety standards, reliability and performance are required. In these critical applications, cadmium is used to provide corrosion resistance, lubricity and/or electrical conductivity to plated components.

It is well known that metallic cadmium is a highly toxic element. It is a cytotoxic heavy metal with a long biological half-life, so it tends to accumulate in body tissues. High cadmium levels in the human body can cause severe health problems and cumulative effects can be deadly. In addition, the cadmium-plating process utilizes baths containing cyanides, which are toxic as well.

For these reasons, environmentally and technically viable alternatives are needed to replace electro-plated cadmium in industrial applications, including those in aerospace. For most aerospace applications, replacing cadmium plating requires developing coatings (i) with good sacrificial properties and (ii) deposited using non-embrittling processes. The first requirement can be met by zinc- or aluminum-based coating systems and there are many examples of such coatings. These coatings are generally deposited by electro-plating. The second requirement limits the range of deposition techniques to the so-called dry methods like PVD (Physical Vapour Deposition) or CVD (Chemical Vapour Deposition). However, the capabilities of these methods are limited basically to deposition of pure aluminum coatings. A good example here is IVD aluminum, a well known alternative to cadmium besides electrodeposited zinc alloys and some metallic-ceramic coatings. The wide use of Al coating is limited, mainly due to poor tribological properties and insufficient corrosion resistance of pure aluminum. If required, additional surface finishing like glass bead penning and/or chromating can be used to enhance the corrosion resistance of these coatings. However, chromating is also targeted by environmental regulations. Thus, the only remaining way to improve the corrosion and tribological properties of aluminum coatings seems to be alloying using one of the dry deposition methods. This can be done most efficiently by using Unbalanced Magnetron Sputtering (UMS). The UMS process provides great flexibility in varying coating composition and allows grading and multilayering of the coatings at the micro and/or nano scale, which are features not readily available from other deposition techniques.

The selection of alloying element is critical to coating performance. The most promising alloying element for improving sacrificial corrosion
properties of aluminum coatings seems to be magnesium. However, this alloying element does not improve the tribological (anti-galling) properties of Al-Mg coatings.\textsuperscript{3} A good candidate for improving the corrosion performance and simultaneously enhancing tribological properties, up to the level offered by cadmium, appears to be molybdenum.\textsuperscript{4-5} Al-Mo alloy system can be produced by sputter deposition across the full binary range. The resulting microstructure is a non-equilibrium single phase that is either nanocrystalline or amorphous.\textsuperscript{6} As an alloying element to Al, Mo causes little, if any, distortion of the lattice due to similarity in size of both atoms.\textsuperscript{6} Mo additions have a passivating effect, thus delaying the progress of pitting corrosion in aluminum alloys.\textsuperscript{7} Al-Mo alloys also show high resistance to sulfidation and oxidation at high temperature.\textsuperscript{8}

In this paper, the results of development work on deposition and characterization of UMS Al-Mo coatings are presented and discussed.

II. METHODS AND MATERIALS

II-A. Coating deposition
The coatings were deposited using a Teer UDP-650 unbalanced magnetron sputtering system employing four magnetrons in a closed field configuration. All coating runs were performed in an argon atmosphere with gas flow control. Coating stoichiometry was controlled by selective adjustment of the electrical power applied to the Al and Mo targets. The substrate material was a heat treated (52-54 HRc) and polished (Ra≈0.3 μm) AISI 4340 high-strength steel. A standard cleaning procedure involving degreasing and ultrasonic cleaning, followed by ion cleaning prior to coating, was used.

II-B. Coating evaluation
Coating microstructures and compositions were tested using a Philips high resolution scanning electron microscope (model XL FEG) equipped with an EDX microanalyser. All coating compositions are expressed in wt.%.

Microhardness tests were carried out using a standard Knoop indenter at a load of 15 g. Coatings adhesion was measured by scratch testing using a Teer ST2200 instrument. Coating adhesion was quantified by measuring the critical load Lc (in N) at which the coating fails by cracking or spallation. Coefficients of friction were measured using an instrumented pin on disc machine (model Teer PD-1) incorporating a data acquisition system. Corrosion properties of the coatings were evaluated by standard potentiodynamic polarization tests in a 3.5% NaCl solution at room temperature using an EG&G Model 173 potentiostat equipped with standard polarization cell and a SCE reference electrode. Potential scans were performed at a rate of 1mV/sec.

III. RESULTS AND DISCUSSION

III-A. Microstructure and hardness
Coating microstructures were examined on polished cross-sections and on fracture surfaces. Aluminum rich coatings seem to have fully dense fine grained metallic structures (as shown in Fig.1), while molybdenum rich coatings (above approx. 70% Mo) have a tendency to columnar growth.

Fig.1. SEM micrographs of Al rich (72% Al, 28% Mo) coating.

Figure 2 shows an example of microstructure of Mo rich (95% Mo) coating.

Fig.2. SEM micrographs of polished (a) and fractured (b) Al5-Mo95 coating. Both figures show the coating’s full thickness of 8.4 μm.

The columnar transverse structure is very distinctive and so is the nodular texture of the top surface of the coating (Fig 2b). This type of surface texture usually results in very low coefficient of friction, which was confirmed later by the POD tests.

The results of microhardness testing over the full compositional range of 0-100% Mo are presented in Fig.3. As expected, the lowest hardness was obtained for a pure Al coating (89 HK). Other Al rich phases (up to approx. 70% Mo) are also relatively soft (HK values below 400). Pure Mo is marginally harder...
while the highest hardness (above 1000 HK) was recorded for Mo rich (above 80% Mo) coatings.

Fig.3. Coating microhardness vs. Mo content.

The sudden increase in coatings’ hardness, appearing at approx. 70% Mo composition, seems related to a change in coating microstructure. However, more detailed examinations (involving XRD measurements) are needed to confirm this finding.

III-B. Adhesion

The adhesion values obtained in scratch tests have been used to optimize the deposition parameters of the coatings. This optimization was performed for one of the hardest and the most brittle 95% Mo composition.

It was found that argon gas flow and substrate bias influence the coating adhesion the most. Figures 4 and 5 show coating adhesion (expressed by critical load) dependence on gas flow and substrate bias.

Fig.4. Coating adhesion vs. argon gas flow.

As evident from Fig.4, the coating’s adhesion strongly depends on gas flow with maximum adhesion achievable at 12 sccm. The adhesion (A) sensitivity to gas flow (F) change can be quantified by a ratio of \[ \frac{\Delta A}{\Delta F} \], which can be as high as 12. Coating adhesion depends on bias voltage, but not as significantly as in the case of gas flow. The coating adhesion (A) sensitivity to bias (B) change, as quantified by a ratio of \[ \frac{\Delta A}{\Delta B} \] is typically below 2.

Fig.5. Adhesion vs. substrate bias.

Maximum coating adhesion is achievable at approximately 30 volts of bias. The adhesion map shown in Fig.6 was produced by plotting adhesion values (critical scratch test loads) versus gas flow and bias voltage, the two process parameters that were found to have the strongest influence on coating adhesion. The map reveals a processing window centered around a bias value of 30 V and a gas flow of 12 sccm.

Fig.6. Adhesion map showing the processing window for deposition of Al5-Mo95 coating.

III-C. Coefficient of friction

The addition of molybdenum to aluminum during the UMS deposition process results in a significant change in the coating coefficient of friction (COF), as shown in Fig.7. Depending on coating composition, the COF value can vary from 0.9 (for pure Al) to 0.19 (for Al-95Mo).

It is important that potential cadmium alternatives have tribological properties similar to that of cadmium, particularly if they are to be used on threaded hardware like fasteners. All PVD coatings developed so far (IVD Al, UMS Al and UMS Al-Mg) have coefficients of friction between 0.56 and 0.79, even if chromated, while cadmium has a COF of 0.27. Thus, the UMS Al-Mo coatings with Mo content above 90%, that have COF’s between 0.2
and 0.3 are expected to have similar lubricity (torque-tension characteristics) as that of cadmium.

Fig. 7. Coefficient of friction vs. Mo content.

III-D. Corrosion properties

The potentiodynamic polarization technique permits a rapid assessment of the effects of alloying element additions on corrosion open circuit potential (OCP), pitting potential (PIT), and corrosion current density (ICOR). The results of potentiodynamic polarization measurements are shown in Fig. 8.

Fig. 8. Corrosion properties of Al-Mo coatings in a 3.5% NaCl solution.

In general, the higher the pitting potential the better the coating resistance to pitting corrosion, which is the main form of corrosion attack in aluminum alloys. Also, low values of corrosion current density are beneficial for the coating long-lasting barrier protection. Figure 8 shows, that adding molybdenum to aluminum clearly increases the pitting potential, while keeping corrosion current practically at the same level. This means that with increased Mo content, coatings shift towards more noble materials, thus improving their barrier properties. However, if sacrificial protection is required, the corrosion potential (OCP) of the coating has to be lower than the OCP of the substrate (i.e., the coating needs to be more electronegative than the substrate). The typical value of OCP for mild steel is \(-0.67\) V, while cadmium has OCP of \(-0.75\) V, thus cadmium is more electronegative and sacrificially protects the steel substrate. Since, as evidenced from Fig.8, the corrosion potential of Al-Mo coatings increases with increased Mo content, at some point the coating OCP may exceed the substrate OCP. In the case of a 4340 steel substrate (OCP= \(-0.62\) V as marked by a dashed line in Fig.8) this happens at molybdenum content of approximately 14%.

This finding has significant practical implications. It means that Mo rich coatings with the best tribological properties do not provide sacrificial protection to steel substrates. Thus, in order to produce coating with both corrosion and tribological properties similar to those of cadmium, a multilayered or compositionally graded coating needs to be designed.

IV. CONCLUSIONS

The test results revealed some extremes in properties of UMS Al-Mo coatings resulting from differences in levels of alloying. Aluminum rich coatings offer better corrosion properties, while molybdenum rich coatings provide higher lubricity. These extremes in properties can be exploited to produce coatings “by design” that meet application-specific requirements. Particularly, by grading and multilayering different Al-Mo phases, new coatings with functional properties comparable to that of electro-plated cadmium can be engineered.

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