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Influence of surface pretreatments on the quality of trivalent chromium process coatings on aluminum alloy

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ABSTRACT

The effects of surface pretreatments (degreasing and pickling) on the characteristics of the Trivalent Chromium Process (TCP) coating on pure aluminum and on AA2024-T351 aluminum alloy were investigated here by means of surface sensitive techniques: X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The XPS and ToF-SIMS results evidence that the TCP coating homogeneity is strongly dependent on the pretreatment process used. The TCP coverage factor, calculated from XPS results, is significantly lower, on both pure aluminum and AA2024-T351 alloy surface, when a pickling step is applied. One of the main effects of pickling pretreatment is strong metallic copper enrichment at the surface of the 2024 alloy, associated with chemical dissolution of Al-Cu intermetallic particles. However, it is evidenced here, that the copper enrichment is not detrimental for the quality of the TCP coating. The coating failure, observed when the pickling step is applied, can be assigned to a faster kinetics of the coating growth leading to formation of thicker conversion coating more susceptible to cracking or to the localized presence of aluminum fluoride species leading to the appearance of coating defects or detachment.

1. Introduction

High strength aluminum alloys are widely used in the aircraft industry. To improve their mechanical properties, alloying elements such as Cu, Fe or Mg are added into the aluminum matrix. These alloying elements precipitate and create the intermetallic particles (IMPs) [1,2]. On the other hand, the IMPs, which can be either cathodic (Al_2Cu) or anodic (Al_2CuMg) with respect to the surrounding aluminum matrix, can be at the origin of lower corrosion resistance of the aluminum alloys [3,4]. Therefore, in most industrial applications, these alloys need to be protected by coatings. The alloy can be coated by an oxide conversion layer, which provides improved corrosion protection and allows subsequent deposition of an organic coating (such as a primer and a top-coat) [5]. Until today, chromate conversion coatings (CCC) have been widely used because of their outstanding corrosion properties: besides creating a homogenous Cr^{III} oxide layer, a small amount of leachable Cr^{VI} incorporated into the coating can be reduced in case of defects in the coating, allowing for its healing [6–9]. The mechanism of self-healing properties of the CCC coatings is well documented [10]. However, the use of hexavalent chromium species is highly restricted in Europe and in the United State because of the carcinogenic effect of chromate (Cr^{VI}), and will be forbidden by 2024 by the European Community with respect to the Registration, Evaluation, Authorization and Restriction of Chemicals (REACh) directive [11,12].

Recently, the NAVAIR (the U.S. Naval Air Systems Command) has developed and patented a new conversion coating system based on trivalent chromium species (Cr^{III}) known as the Trivalent Chromium Processes (TCP) [13,14]. The TCP bath, typically containing hexafluorozirconate, chromium sulfate and pH-adjusters, allows the deposition of a coating providing good corrosion properties [15,16]. The TCP layer thickness on the AA2024 is between 40 and 120 nm depending on the immersion time in the conversion bath as reported by Guo and Frankel [17] and confirmed by Dardona et al. [18]. The structure of the TCP layer is composed of zirconium and chromium oxides in the outer part and aluminum oxide and fluoride in the inner part [17,19,20]. The mechanism of deposition is based on the local raise of pH at the surface of 2024 alloy induced by combined aluminum oxidation and proton or dioxygen reduction that leads to the deposition of chromium and zirconium species [21]. Nevertheless, there is still a lack of thorough under-

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standing of the deposition mechanisms of the TCP layer, and on the role of the pretreatments of aluminum alloys applied before the TCP deposition. Classically, a conversion coating deposition is preceded by a two-step pretreatment, starting with (i) a degreasing in a weakly-aggressive bath (often alkaline), to remove the organic pollutants from the surface of the alloy, and followed by (ii) a pickling (also called deoxidation in some other works) in an aggressive acid bath with the aim to remove the IMPs and the native oxide layer present on the aluminum alloy surface. Recently, it has been showed that long immersion times in a pickling bath is detrimental for the TCP deposition due to dissolution of IMPs and the formation of pits leading to high surface roughness [22]. It was also shown that the coating had different thicknesses on the intermetallic particles (IMPs) that on the aluminum matrix of AA 2024-T3 [23].

The complexity of the microstructure and the chemical composition of the industrial aluminum alloys make difficult the complete understanding of the processes and, in particular, the link between pretreatments and TCP coating deposition conditions and the coating properties. The aim of this work was to characterize the chemical and morphological homogeneity of the TCP coating and to understand the influence of the surface chemistry of a given substrate (pure Al and Al alloy) after different stages of pretreatments. This paper, in the first part, presents the pretreatment effects on the surface chemistry and morphology of pure aluminum and 2024-T351 alloy) and, in the second part, the pretreatments effects on the structure and composition of TCP. High sensitive surfaces techniques such as X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) were used for the surface and in-depth chemical characterization, and combined with Secondary Electron Microscopy (SEM) for studies of the TCP coating morphology.

2. Experimental

2.1. Sample preparation

Pure aluminum specimens (99.999% purity, GoodFellow) were cut into 8 × 8 mm^2 pieces, 3 mm in thickness. AA 2024-T351 specimens (after machining) with a thickness of 3 mm obtained from the IRT-M2P were also cut into 8 × 8 mm^2 pieces. The composition of the AA 2024-T351 alloy was (in wt.%) Al, 3.8–4.9% Cu, 1.2–1.8% Mg, 0.3-0.9% Mn, 0.5% Fe, 0.5% Si, 0.25% Zn, 0.15% Ti and 0.15 % other elements.

The samples were first mechanically polished up to 2400 grade SiC paper, and then with water-based ESCIL® alumina suspension up to 0.3 μm. After polishing, the samples were rinsed ultrasonically in ultrapure water, isopropanol and ethanol for 2 min in each solution. After cleaning, the samples were degreased at 45 °C during 6 min in a bath of 10% (v/v) Sococlean A 3431™ solution (a weak base with pH ≈ 10) provided by Socomore. Then, the samples were pickled at 45 °C during 5 min in an acidic Turco SmutGo NC™ (225 g/L) solution (pH ≈ 0) provided by Henkel Corp., containing ferric sulfate, nitric acid and sodium bifluoride. Finally, the samples were immersed for 4 min at 40 °C in the TCP (conversion coating) solution Surtec 650™ (20% v/v, pH ≈ 4), mainly composed of fluorozirconate and chromium sulfate and provided by Surtec.

Ultra-pure Milipore® water with a resistivity of 18.2 MΩ cm was used for the preparation of all solutions. All experiments were conducted in beakers of 100 mL with approximately 75 mL of solution. The samples were systematically rinsed with ultra-pure water (around 75 mL) during 1 min after each pretreatment, and also after coating deposition in the conversion solution. The baths were used 4 times at most and were systematically renewed every day. All samples were stored overnight in the laboratory air before surface analysis. The samples after polishing and degreasing will be denoted “degreased” and the samples after polishing, degreasing and pickling will be denoted “pickled”.

2.2. Chemical and morphological characterization

An XPS Thermo Electron Escalab 250 spectrometer, operating at 2×10^{-9} mbar or less with an Al Kα monochromatized X-ray source (hν = 1486.6 eV) was used for surface chemical analysis. Survey spectra and high resolution core level spectra (Al 2p, Al 2s, Cr 2p, Zr 3d, Cu 2p) were recorded with a pass energy of 100 eV and 20 eV, respectively. XPS analyses were done at take-off angle of 90°. The spectrometer was calibrated using Au $4f_{7/2}$ at 84.1 eV. Peak fitting was performed with the Avantage™ software (Thermo Electron Corp.) using a Shirley type background and Lorentzian/Gaussian 30/70 peak shape. The binding energies were corrected if needed by setting the C 1s hydrocarbon component peak at 285.0 eV and are given with a ±0.2 eV uncertainty. Inelastic mean free path values (λ) were determined with the Tanuma Powell and Penn formula [24] except for aluminum, which were adapted according to Marcus et al. [25]. For the aluminum alloy, the Al 2 s core level was chosen instead of Al 2p due to the superposition of Al 2p and Cu 3p binding energies.

ToF-SIMS images and depth profile analyses were performed using a ToF-SIMS V™ spectrometer (Ion ToF GmbH). The spectrometer was run at an operating pressure of around 10^{-9} mbar. The surface chemistry images were obtained with a Bi^+ primary ion beam delivering a 0.1 pA current in order to keep a good lateral resolution (≈ 150 nm). The depth profiles were performed using a dual beam mode: a pulsed 25 keV Bi^+ primary ion source (LMIG) as the analysis beam delivering a 1.2 pA current and rastering an area of 100 × 100 μm^2 and a 2 keV Cs^+ ion beam as the sputtering beam delivering a 100 nA current and rastering an area of 300 × 300 μm^2. Negative ion profiles were recorded because of their higher sensitivity to fragments coming from oxide matrices. Data acquisition and post-processing analyses were performed using the Ion-Spec software.

SEM imaging was performed with a ZEISS Ultra-55 field emission scanning electron microscope (FE-SEM). One FIB (Focused Ion Beam) cross-section cut was performed at the IMPMC (UMR 7590–UPMC/CNRS) with a FIB Zeiss Neon 40 EsB equipped with a Ga^+ ion gun from Orsay Physics with an accelerating voltage of 30 kV and current of 2 nA. SEM images were performed *in situ* with a Gemini column. To protect the substrate, platinum deposition was performed in two steps: the first one with the electron gun of the SEM (“electronic” Pt in Fig. 10) and the second one with the ionic source (“ionic” Pt in Fig. 10).

3. Results and discussion

3.1. Effects of pretreatments

Fig. 1 presents the effects of pretreatments ((A) polishing, (B) degreasing and (C) pickling) on the pure aluminum (Al 2p) and on the 2024 alloy samples (Al 2s and Cu $2p_{3/2}$). As aforementioned in the experimental part in the case of the 2024 alloy, the Al 2s core level instead of Al 2p has been recorded due to the interference of Cu 3p and Al 2p core levels.

In the case of pure aluminum (Fig. 1, Al 2p), the peaks at 72.6 eV and 76.0 eV correspond to the metallic aluminum (Al^0) and to the Al^{3+} species, respectively. The presence of Al^{3+} species can be attributed to the aluminum oxide and possibly to the aluminum oxy-hydroxide [26,27]. Similarly, in the case of AA2024, the most intense peaks corresponding to Al^0 and Al^{3+} can be found in the area of Al 2s (Fig. 1, Al 2s). A peak at higher binding energy observed for the pickled samples (Al 2p C for pure Al and Al 2s C for AA2024) cor-