Surface & Coatings Technology 203 (2009) 2927–2936

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Factors influencing the deposition of Ce-based conversion coatings, part I: The role of Al^{3+} ions

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ARTICLE INFO

Available online 18 March 2009

Keywords:
Cerium
Rare earths
Raman
SEM
Peroxo species
Conversion coatings
Aluminium

ABSTRACT

The mechanism of deposition of cerium-based conversion coatings and the influence of Al^{3+} ions was modeled using titrations of cerium-based conversion coating solutions with and without added Al^{3+} ions. Precipitates resulting from these titrations were characterised by Raman spectroscopy and thermogravimetric analysis. Cerium peroxo species and precipitated aluminium compounds were detected in the precipitates. The titrations indicated that cerium and aluminium compounds precipitate independently. The coating deposited onto AA2024-T3 was studied using Raman spectroscopy and optical and scanning electron microscopy. Similar species were observed to those in the precipitates. Changes to the properties of the coating during ageing were monitored using contact angle measurements and Raman spectroscopy. A model is presented that proposes a mechanism for the deposition of the coating over the matrix of AA2024-T3.

1. Introduction

The cerium-based conversion coating (CeCC) process has been explored as an alternative to chromate-based conversion coating (CrCC) processes in aluminium metal finishing [1–18]. The corrosion resistance has been reported to be similar to CrCC under paint for aluminium extrusions [16] and silicate or phosphate sealed versions of the CeCC have been reported to have similar neutral salt spray performance to the CrCC on high strength aluminium alloys used in the aerospace industry [8,15]. Paint adhesion for the CeCC is similar to that of the CrCC in PATTI adhesion tests [15,17].

CeCC deposition is proposed to occur during a local pH rise at cathodic sites on the aluminium surface due to the reduction of hydrogen peroxide (H_2O_2) in solution:

$$H_2O_2 + 2e^- \rightarrow 2OH^-. \quad (1)$$

H_2O_2 is added as an accelerator to the coating solution [15]. In the absence of H_2O_2, the coating process relies on the reduction of dissolved O_2 and can take several days at room temperature [15,19–23]. In the presence of H_2O_2, coating formation occurs in a matter of minutes [15].

Certain recent studies have focused on the role of H_2O_2 in the formation of solution species, kinetics of coating formation, and the final structure of the coating [3,6,24]. In these studies [3,23], titrations of cerium-based coating solutions with base were used to model the deposition process, *i.e.*, the addition of base, in the form of NaOH or KOH, has been used to simulate, in bulk solution, the generation of OH^- ions, via Eq.(1), at the surface of aluminum. From these studies it was concluded that the addition of H_2O_2 results in the formation of cerium (III) peroxo complexes in solution. The presence of this peroxo species has a significant influence on the solution chemistry, as first proposed by Hughes et al. [15] and elaborated by Scholes et al. [3]. The peroxo species reduces the pH at which precipitation of cerium compounds occurs [3,24,25]. In addition, Raman studies have shown that a cerium peroxo complex is incorporated into the conversion coating [3]. This is also supported by the results of thermogravimetric analysis, which showed that significant O_2 is evolved from the coating at around 100 °C [3]. Finally, increasing the H_2O_2 concentration was found to reduce the CeO_2 crystallite size in the precipitate obtained from the titrations used to model the coating process [3,24]. Similar observations have been made for the preparation of ceria in the field of catalysis [26,27]. It is assumed that this property is transferred to the coating, since similar crystallite sizes are observed in the coating and the precipitate for the same solution composition, including the H_2O_2 levels (compare crystallite sizes reported for coatings in [2] and [5] with those for precipitates [26,27]). This change in crystallite size is due to the increased incorporation of cerium peroxo complexes which are proposed to replace bridging oxygen bonds [3,24].

As observed previously the composition of the CeCC varies considerably across the surface of AA2024-T3 [3]. This variation is due to the heterogeneous electrochemical nature of the surface, leading to areas where either net anodic or cathodic reactions dominate. In the areas where there is a net anodic reaction, it can be expected that

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doi:10.1016/j.surfcoat.2009.03.022

the solution adjacent to the coating will have a higher concentration of Al^{3+} ions and probably a lower pH than the surrounding solution due to the acidic nature of $Al(H_2O)_6^{3+}$ and its oligomers. Since previous work using titrations as a model for coating have only been performed in cerium-containing solutions, it was considered important to examine the influence of aluminium ions on the precipitation process. The surface can be divided into two types of areas (i) the matrix and (ii) areas where there are localized reactions due to strong cathodes and anodes. It is anticipated that modeling of surface reactions using titrations is only applicable to the matrix. Hence the reactions over the matrix are the subject of Part I of this two part series whereas localized reactions due to the presence of strong anodes and cathodes is the subject of Part II of this series [28].

The role of Al^{3+} in coating formation is first examined through titration of coating solutions containing Al^{3+} ions. The results of the titration studies are then combined with studies of the deposition of the CeCC onto AA2024-T3 to produce a model of coating over the matrix. A number of techniques have been used to study both precipitates and the conversion coating itself. These techniques include thermogravimetric analysis-mass spectroscopy (TGA-MS), Raman spectroscopy and scanning electron microscopy (SEM). Raman and SEM were performed on the same area of the conversion coatings. In addition, the influence of ageing of the coating has been examined using Raman spectroscopy and contact angle measurements.

2. Experimental

2.1. Solution preparation

Solutions were prepared by dissolving hydrated cerium chloride ($CeCl_3.7H_2O$, 13.04 g, 35 mmol) in deionised water (~900 mL) in a 1 L volumetric flask. The solution pH was adjusted to 1.90 with concentrated HCl. After acidification freshly standardised H_2O_2 (30% w/w, ~8.5 M) added to give the desired $Ce:H_2O_2$ molar ratio. The solution was then made up to 1 L. The final solution was 0.035 M in $CeCl_3$. The standard solution, containing 0.035 M $CeCl_3$, a $Ce:H_2O_2$ ratio of 1:3, no added Al^{3+}, and a pH of 1.90 is referred to as the “coating solution”.

For solutions containing Al^{3+} ions, the same procedure was followed as above, except that sufficient $AlCl_3.6H_2O$ was also added immediately after the $CeCl_3$, to give solutions with the desired Ce:Al molar ratio.

All solutions were allowed to age for at least 30 min before titration with 1 M NaOH, to allow the formation of cerium(III) peroxo solution species to reach equilibrium [15]. Solutions which were stored before use were kept under refrigeration (~2 °C) to minimise the loss of H_2O_2.

The titrant (1.0 M NaOH) was prepared from a volumetric concentrate and stored in an airtight plastic container before use. Over a period of 18 months three different batches of solutions were prepared.

2.2. Titrations

Titrations were performed on either 50 or 100 mL aliquots of the solutions described in §2.1. Titrations were performed with an automated titration system (Radiometer Copenhagen TitraLab 90), which added 1.0 M NaOH in increments of 0.2 mL and allowed the solutions to equilibrate for 60 s prior to recording the pH. Some additional titrations were performed by hand. Titrations were performed in plastic containers with constant stirring. Any colour changes were noted and precipitates that formed were collected by filtration, rinsed with deionised H_2O, and vacuum-dried at ambient prior to subsequent analysis. Titrations were performed in duplicate on two batches of solution (*i.e.*, four titrations per solution condition).

2.3. Coating preparation

Panels of AA2024-T3 (76 mm × 25 mm × 1.5 mm) were wiped with acetone and processed through alkaline cleaning, deoxidising and conversion coating steps. After acetone wiping the panels were cleaned for 10 min in a silicated alkaline cleaner (Gibson Process 204B, 60 °C), then rinsed under flowing tap water for 1 min, immersed in a low etch rate deoxidiser (0.05 M $(NH_4)_4Ce^{IV}(SO_4)_4.2H_2O$, 0.5 M H_2SO_4) at 35 °C for 10 min and finally rinsed under flowing tap water for 1 min. The effect of this deoxidizer on the surface of AA2024-T3 has been described previously [29–31] and compared to other deoxidisers [31]. Panels were immersed in the conversion coating solution at 45 °C for either 2 or 5 min, then rinsed under flowing tap water for 1 min and dried in a compressed air stream. Experiments were performed in triplicate.

2.4. Raman spectroscopy

Raman spectra and maps of the precipitates and the conversion-coated surfaces were collected using a Renishaw inVia confocal microscope system. Specimens were illuminated through a 50× objective (NA 0.75) with 830 nm excitation from a diode laser source at an incident power of 3–150 mW and with a spot size (FWHM) of ~1.3 µm. Spectra were collected over the range 100–2000 cm^{-1}. Each spectrum resulted from two scans, corresponding to a total collection time per spectrum of ~20 s. Assessment using Raman was performed in the following manner. Three separate batches of samples were analysed. Several spectra were collected for different features at several locations on the surface. While the band intensities varied their positions were consistent.

2.5. Scanning electron microscopy/energy dispersive X-ray analysis

Scanning electron microscopy was performed on a FEI Quanta 400 field emission, environmental scanning electron microscope (ESEM) under high vacuum conditions. The coated samples were mounted on standard 25 mm scanning electron microscope (SEM) stubs using electrically-conducting, double-sided, adhesive, carbon tape. Secondary electron and backscattered electron imaging were performed using beam energies of 20 kV and probe currents of approximately 140 to 145 pA. EDS mapping was performed on at least two areas of single samples (2 and 5 min immersion). These samples had previously been assessed as typical using Raman spectroscopy.

2.6. Thermogravimetric analysis-mass spectrometry (TGA-MS)

TGA-MS of titration precipitates was performed on a Setaram Evolution Thermal Analysis system coupled with a Pfeiffer 300 amu mass spectrometer. The heat flow and mass change were monitored while the samples were heated to 1000 °C at 10 °C/min in a N_2 atmosphere. For mass spectrometry, gas evolution at 16 (O), 18 (H_2O), 32 (O_2) and 44 (CO_2) a.m.u.'s was also monitored.

2.7. Inductively coupled plasma, atomic emission spectroscopy (ICP-AES)

Duplicate samples were digested in H_2SO_4, where necessary the subsequent solutions were analysed using a Varian Liberty Series II Axial ICP-AES with a Sturman Masters spray chamber and V-groove nebuliser. A PMT voltage of 800 V and pump rate of 15 rpm were used in the analysis. The Al line at 257.51 nm and Ce line at 413.38 nm were selected for analysis. Ce standards used were 20 and 50 ppm.