

Decisive influence of colloidal suspension conductivity during electrophoretic impregnation of porous anodic film supported on 1050 aluminium substrate



B. Fori^a, P.L. Taberna^{b,*}, L. Arurault^b, J.P. Bonino^b

^a Mecaprotec Industries, 34 Boulevard Joffrery, 31605 Muret Cedex, France

^b Université de Toulouse, CIRIMAT UPS-CNRS, 118 route de Narbonne, 31062 Toulouse Cedex 9, France

ARTICLE INFO

Article history:

Received 28 May 2013

Accepted 2 August 2013

Available online 16 September 2013

Keywords:

Suspension conductivity

Aluminium alloy

Supported anodic film

Electrophoretic deposition

ABSTRACT

The present paper studies the influence of suspension conductivity on the electrophoretic deposition (EPD) of nanoparticles inside a porous anodic aluminium oxide film. It is shown that an increase in the suspension's conductivity enhances impregnation of the anodic film by the nanoparticles. Two mechanisms are seen to promote the migration of particles into the pores. Indeed an increase in the suspension conductivity leads on the one hand to a strengthening of the electric field in the anodic film and on the other hand to a thinning of the electric double layer on the pore walls. The results of our study confirm that colloidal suspension conductivity is a key parameter governing the electrophoretic impregnation depth.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Electrophoretic deposition (EPD) is a process allowing coatings to be prepared from colloidal dispersions. This method can be applied to a wide variety of materials including oxide particles [1], metallic particles [2], carbon nanotubes [3] and polymer particles [4]. It produces homogeneous deposits even on complex shaped substrates [5]. EPD has many additional advantages including its low cost, rapidity and easy implementation [6]. The quality of such electrophoretic deposits depends on many factors such as the voltage applied, the zeta potential, the concentration of solids in suspension and the conductivity of the substrate [6].

As has been previously demonstrated, suspension conductivity is also decisive in obtaining uniform EPD coating. Thus Stappers et al. [7] showed that uniform coatings were generated on flat surfaces using high-conductivity suspensions while low-conductivity suspensions resulted in non-uniform deposits. Nevertheless, a trade-off has to be found between high suspension stability when using low conductivity, and a high particle rate deposition for high conductivity [8]. Generally, finding the optimal solution depends on the surface chemical function of the particles [9], the solvent used [10] and additives such as surfactants [8].

Over the last 10 years, EPD has increasingly been used on highly porous substrates [11]. However, with the exception of Kamada et al. [12] and our team [13], EPD in anodic films still supported

on aluminium alloy has not so far been extensively studied. Indeed, all previous studies [11] focused on the preparation of oxide nanorods and nanotubes by EPD using an anodic alumina membrane (AAM) as a template, secured to a metal foil. This technique involves using EPD to fill pores in the membrane and then removing the template membrane. The resulting materials offer a significantly larger surface area than that of flat films or bulk material, and thus find varied applications in nanotechnologies (sensors, batteries, SOFCs, etc.).

Limmer et al. [14] showed that zeta potential drives the migration and deposition of nanoparticles into AAM pores. When particles have a charge with opposite sign to that of the template, deposition results, preferably on the pore walls, where the electrostatic attraction between particles and the pore walls proves stronger than the applied electric field. It also emerged that voltage levels could affect the quality of electrophoretic deposits. When the voltage is too high, the velocity of the particles in the bulk solution also increases and the surface diffusion of particles into deposit defects (e.g., kinks, steps and holes) is correspondingly impaired, leading to the formation of a highly porous deposit [14]. However, to the best of our knowledge, the influence of the suspension conductivity has not been evaluated.

The objective of the present work is to investigate the role of the suspension conductivity on the EPD of silica nanoparticles in pores of an anodic film supported on an aluminium alloy. To this purpose, current/voltage measurements were obtained during EPD and FEG-SEM characterisations were performed on the resulting composite material, i.e., the anodic film with SiO₂ particles.

* Corresponding author.

E-mail address: taberna@chimie.ups-tlse.fr (P.L. Taberna).

2. Experimental set-up

2.1. Preparation of the standard anodic film

To facilitate the penetration of particles inside the pores, the porosity of the anodic films has to exhibit low tortuosity and pore diameters larger than those of the silica nanoparticles (i.e., 15 nm) [13]. 1050A aluminium alloy (chemical composition in per cent weight: 99.5% Al, <0.40% Fe, <0.25% Si and <0.05% Cu) was used as a substrate to obtain linear pores perpendicular to the initial metal surface. Since large pores (average pore diameter >100 nm) are required, a phosphoric acid based electrolyte was chosen as the anodising bath.

Firstly, the alloy sheet (20 mm × 20 mm × 1 mm) was degreased using ethanol. Secondly, the sample was etched in an NaOH aqueous solution (0.5 g L⁻¹) at 40 °C for 5 min and then neutralised in HNO₃ (25% vol) at room temperature for 2 min; the water used to make these solutions showed resistivity of 10 kΩ cm⁻¹. Thirdly, the aluminium sheet was used as an anode and a lead plate (2 × 40 × 40 mm) as a counter-electrode (i.e., here the cathode) in the electrochemical cell. The anodising process was run for 29 min in galvanostatic mode (TDK-Lambda GEN 300-5) using a current density of 1.5 A dm². The temperature was set to 25 °C. The samples were rinsed in deionised water (10 kΩ cm⁻¹) immediately following each step. Finally, the standard anodic film typically showed a pore diameter of 130 ± 10 nm, film thickness of 10 ± 1 μm and barrier layer thickness of 130 ± 5 nm [13].

2.2. Electrophoretic impregnation

A commercial colloidal suspension of silica nanoparticles (15 nm) in isopropyl alcohol (ABCR, Germany) was used. This suspension was diluted with isopropyl alcohol (Carlo Erba, Italy) to obtain a concentration of about 15 g L⁻¹ and then vigorously stirred. Functionalisation of silica was performed in accordance with the procedure developed by Cousinié et al. [15]. 3 mL of aminopropyltrimethoxysilane (APTMS) was added dropwise to 100 mL of the diluted suspension. The mixture was then vigorously stirred for 3 days and then diluted 100 times with isopropyl alcohol, leading to a concentration of about 0.15 g L⁻¹. 1–15 mL of an I₂-acetone mixture (6 g L⁻¹) was added to the as-prepared suspension to modify its conductivity. In order to perform electrophoretic deposition, anodised aluminium was set as the cathode, while lead foil was used as the anode. A voltage of 600 V was applied (i.e., an electric field of 200 V cm⁻¹) for 5 min. The substrate was dried at ambient temperature after the experiment [13].

2.3. Characterisations

A Field Emission Gun Scanning Electron Microscope (FEG-SEM, JEOL JSM 6700F) was used to observe the microstructure of the coatings. The average impregnation depth was measured on the FEG-SEM cross-sectional views using the ImageJ software. Meanwhile, a MALVERN NANOSIZER ZS90 was used for zeta potential measurements. Conductivity was measured using a SympHony SB70D conductivity meter (VWR, France).

2.4. Current/voltage measurements

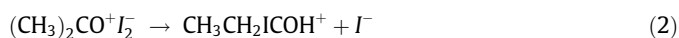
An ammeter was used to measure changes in current intensity as they occurred during EPD. Also, in order to evaluate the distribution of the electric field in the electrophoretic cell, a wire of 1050A aluminium alloy was located at 3 mm from the anodic film to act as a voltage probe. The voltage was measured with a voltmeter

connected between this probe and the cathode, with values being recorded at sampling times of 1 s.

3. Results and discussion

3.1. Relation between impregnation depth and electrolyte conductivity

To modify the suspension conductivity, an I₂/acetone mixture was used. Conductivity increases with I₂ concentration as shown in Fig. 1. This increase is probably mainly due to the formation CH₃-CH₂ICOH⁺ species that are created by reactions between I₂ and acetone [16]:



The zeta potential, which is initially negative and equal to -25 mV, first increases with the I₂ concentration and becomes positive. This phenomenon is due to CH₃CH₂ICOH⁺ species that are adsorbed onto particle surface leading to zeta potential switching from negative to positive [16]. Beyond 50 mg L⁻¹ of I₂, zeta potential then stabilises at about +25 mV. In these experimental conditions, at higher concentrations (>50 mg L⁻¹), repulsive interactions between ions are preponderant in comparison with attractive interactions between ions and particles. No more ion can go inside the double layer. Therefore, the zeta potential increases no further, remaining constant as the I₂ concentration increases.

According the Hückel equation (5), electrophoretic mobility μ (m² s⁻¹ V⁻¹) is directly proportional to the zeta potential [6]:

$$\mu = \frac{2\zeta\epsilon_0\epsilon_r}{3\pi\eta} \quad (3)$$

with ζ the zeta potential (V), ε_r relative permittivity of the fluid, ε₀ the vacuum permittivity (8.845 × 10⁻¹² F m⁻¹) and η the dynamic viscosity (Pa s). In order to minimise the influence of the zeta potential in this study, the I₂ concentration was adjusted to between 50 mg L⁻¹ and 300 mg L⁻¹ since, in this concentration range, the zeta potential can be considered to be constant. Furthermore, its positive value indicates that particles should migrate towards the cathode (i.e., the negative electrode) during electrophoretic migration. This should avoid over-oxidation of the aluminium foil, which can occur if it is used as an anode during EPD, thus leading to a change in the anodic film microstructure [17]. It is also known that the barrier layer is poorly conductive. By applying cathodic polarisation

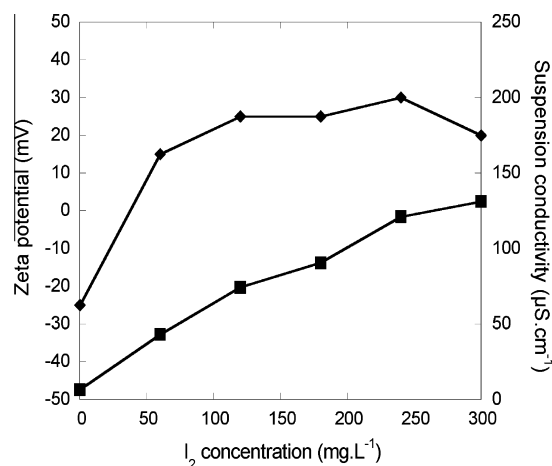


Fig. 1. Zeta potential (◆) and suspension conductivity (■) versus the I₂ concentration.

Download English Version:

<https://daneshyari.com/en/article/607489>

Download Persian Version:

<https://daneshyari.com/article/607489>

[Daneshyari.com](https://daneshyari.com)