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Electrochemical corrosion evaluation of pure, carbon-coated and anodized Al foams

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ABSTRACT

Conventional anodizing and carbon deposition coating treatment is applied to open-cell Al foams aiming to enhance the corrosion performance of the material. The Al foams used were fabricated utilizing a dissolution-sintering technique based on powder metallurgy route. X-ray computed tomography and SEM were utilized to assess the structural characteristics of the produced foams. The corrosion properties of all samples produced were assessed experimentally, employing both polarization curves and EIS measurements utilizing a 0.6 M NaCl aqueous solution. Corrosion mechanisms along with appropriate modeling circuits were deduced. Both anodizing and carbon coatings resulted in an augment of the corrosion properties of the Al foams.

1. Introduction

The unique properties of the metal foams offer promising applications in a variety of fields ranging from lightweight construction and impact-energy absorption, to various types of damping, thermal insulation, as well as filtration, separation, heat or mass exchange along with catalytic filter applications. In particular, Al foams have been used in the automobile, aerospace and railway industries [1–3]. However, the poor corrosion resistance of Al foams is an important problem that limits their wide application only to ambient-temperature applications.

One widely used approach to tailor and improve the surface properties is to employ coating technologies to obtain protective surface layers. Nevertheless due to the inherent complex inner porous structure of open-cell foams most of the coating techniques that are well suited for bulk alloys cannot be applied for metal foams. To date literature on coating methods for Al foams is limited and advancements in this area are mostly concentrated on the mechanical performance of the coated Al foam whilst little is reported for the corrosion properties [4–6]. Micro-arc deposition of ceramic coatings, plasma electrolytic oxidation (PEO) along with electrodeposition of Ni–P or Ni–W coatings on aluminum foam have been reported to increase the mechanical properties of the aluminum foams [7–10]. However the ceramic coatings produced by PEO usually present a thick porous structure which can prove detrimental to corrosion resistance. On the other hand in electroplating or electrodeposition processes, the inner struts receive less coating compared to the outer region (attributed to the foam structure inhibiting the passage of charge and altering the electric field distribution in the electrolyte penetrating the pores) thus resulting in non-uniformity of the coating layer.

To date, corrosion resistance of Al foams was reported to increase by micro-arc oxidation and electroless plating of Ni–P on open-cell aluminum foams utilizing static polarization measurements [7–9].

In the present study, we demonstrate the use of conventional anodizing and carbon deposition to coat open-cell aluminum foams, with the aim of enhancing the foam corrosion resistance. The surface-dependent corrosion behavior of the treated and untreated open-cell aluminum foams has been investigated in detail employing both static polarization measurements and electrochemical impedance spectroscopy (EIS). The Al foams were fabricated by a dissolution-sintering technique based on powder metallurgy.

2. Materials and experimental procedures

2.1. Production of Al foams

In this study, Al foams were produced using a dissolution and sintering method. Commercial crystalline raw cane sugar with mean particle sizes of 0.70 mm was applied as a leachable space-holder material. The exact procedure for producing the Al foams

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is described in detail in other works [11,12]. Briefly, the manufacturing process consists of four stages: mixing, compaction, dissolution and sintering. Initially, the metal powders (Al 99.8%, mean size 180 μm) are mixed thoroughly with the raw cane sugar at a prespecified volume or weight ratio, depending on the desired relative density of the final product. A small amount of distillated water (about 1% in weight) was added in the mixture in order to avoid segregation of dissimilar powder and particles. The mixed powders were compacted using a hydraulic press. The mixture was uniaxially pressed at 300 MPa. Complete removal of crystalline raw cane sugar powder from the green compact can be achieved by water leaching at room temperature for 3 h. The last stage is the sintering at 690 °C for 2.5 h under medium vacuum (10^{-3} Torr).

The density ρ_f of the final Al foam was calculated by dividing the mass of the foam by its volume, which was measured, based on Archimedes principle. The porosity of the as-manufactured Al foams P_f was estimated by $P_f = 1 - \rho_f/\rho_{Al}$, where ρ_f is the calculated density of the foam and ρ_{Al} is the density of aluminum ($\rho_{Al} = 2.71$ kg/m^3).

2.2. Carbon-coating process of Al foams

Production of a carbon-coated Al foam can be achieved in one step process using raw cane sugar as a pore forming and carbon deposition medium, as a result of the sugar pyrolysis, by employing the dissolution-sintering production process. In this case the sugar is partially dissolved (about 70% wt. of the sugar in the initial powder mixture is dissolved). The process is conducted under medium vacuum (10^{-3} Torr). Initially, a heat treatment is employed at 400 °C for 30 min in order to burn out all the sugar. Ensuant to the isothermal heating, the furnace chamber is evacuated and backfilled with inert gas at least one time. Any remaining crystalline raw cane sugar can be removed in a secondary heat treatment stage at a temperature of 640 °C for holding time of about 15 min. A cooling step until a temperature of around 500 °C is required in order to avoid melting of the Al foam and then to evacuate the chamber and backfill with inert gas at least one time. Finally, sintering is conducted under a partial pressure of inert gas, at 680 °C for 2 h.

The feasibility for production of carbon-coated foam in a one step-process using crystalline raw cane sugar is among the advantages of the proposed methodology, as no pre-treatment of the foam complex 3D surface is needed. The considerable control of carbon deposition process conducted at relatively low temperature (400 °C) leads to a full coverage of all internal surfaces of the foam with an external carbon layer since the carbon is first produced into the internal surfaces of the foam as a result of the pyrolysis of the remaining sugar in the compact.

2.3. Anodizing process of Al foams

The anodizing process was carried out on pure Al foam specimens at room temperature using a three-step process. Prior anodization the specimens were degreased with acetone, followed by desmutting in 10% vol. HNO_3 solution for 120 s. Degreasing as well as desmutting were concluded with a thorough rinsing of the specimens in distilled water in order to prevent a carry-over of the chemicals into the next bath. The etching step (usually conducted in 5% NaOH at 55–60 °C for 2 min) was deliberately avoided during the anodization process, since in this step a significant amount of the initial foam surface was removed, thus leading to a considerable alteration of the morphological and geometrical characteristics of the foam struts. The anodizing bath consisted of H_2SO_4 (15% vol) whilst the constant current density and anodizing time used were 1.5 A/dm^{-2} and 30 min, respectively. After anodizing the samples were sealed in distilled water at 100 °C for 30 min. It should be mentioned that the anodizing process requires several steps of pre-treatment that are imperative to be conducted cautiously. Additionally, given the inherent complex structure of the foam is quite reasonable to assume that the anodizing coating presents a certain amount of thickness non-uniformity. Nevertheless the ability to produce thin oxide layers, covering all internal foam surfaces and following the 3D geometric shape of the foam structure is crucial factor and can be accomplish by conventional anodizing process.

2.4. Production of sintered bulk Al and anodized bulk Al samples

For the purpose of comparability, samples of the same external dimensions with the foams of uncoated bulk Al and anodized bulk Al were produced using the same production techniques described in Sections 2.1 and 2.3 without the use of any space holder material. The production of sintered carbon-coated bulk Al samples is not achievable using the technique described in Section 2.2.

2.5. Electrochemical measurements

The electrochemical behaviors of the pure, anodized and carbon-coated Al foams were monitored by polarization measurements. For comparison, sintered uncoated bulk Al and anodized bulk Al specimens were also tested. All electrochemical experiments were performed in the conventional three-electrode cell containing a 0.6 M NaCl electrolyte solution following ASTM D1193 IV norm. As reference electrode a saturated calomel electrode (SCE) was used. The platinum wire was used as auxiliary (counter) electrode. The experimental setup of the electrochemical corrosion apparatus was in compliance to the ASTM G 69-97 and ASTM G71-81 norms. All electrochemical measurements were carried out using a Voltalab PGZ 402 advanced electrochemical system at room temperature (~25 °C). Before measurements of polarization curves and EIS, the working electrode was immersed in test solution at open circuit potential (OCP) for 30 min to attain a stable state. All potentiodynamic measurements were performed with a scanning rate of 0.1 mV/s. Corrosion current density values (i_{corr}) were estimated for each sample. EIS was carried out at OCP (E_{OCP}), hold potentiostatically stable, in the frequency range of 0.02 Hz–10 kHz using a 10 mV peak-to-peak voltage excitation. Bulk sintered and anodized sintered Al were used as reference specimens for the EIS measurements. The polarization and EIS parameter analysis was made via Voltamaster 4 program and EIS Spectrum Analyser 1.0 program (using Powell's algorithm), respectively.

2.6. X-ray computed tomography and microstructural characterization

An X-ray computed tomography apparatus with a 5 μm focal spot reflection target X-ray tube source operating in the absorption mode was used to acquire the 3D images of the foam samples. Generally, in such CT-systems the voxel resolution of the reconstructed samples depends on the sample size and its relative position in the tomographic facility due to the cone-shape geometry of the X-ray beam. Higher magnifications can be achieved by moving the specimens away from the detector (closer to the X-ray source). This distance is optimized to achieve the highest possible resolution, while containing the entire sample within the field of view of the detector. The specimen is rotated over a full 360° in small angular increments. The apparatus was operating at 70 kV and 115 μA while the obtained spatial resolution was 22 μm.

In order to reconstruct the 3D geometry of the Al foam the resulting series of radiographs obtained by X-ray tomography are input into a cone-beam reconstruction software which generates a series of axial slices using a standard filtered back-projection algorithm. The final three-dimensional image is reconstructed based on the two-dimensional images (tomographic images). The