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Friction stir processed Al–TiO_2 surface composites: Anodising behaviour and optical appearance

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ABSTRACT

Multiple-pass friction stir processing (FSP) was employed to impregnate TiO_2 (rutile) particles into the surface of an aluminium alloy. The surface composites of Al–TiO_2 were then anodised in a sulphuric acid electrolyte. The effect of anodising parameters on the resulting optical appearance was investigated. Microstructural and morphological characterization was performed using scanning (SEM) and transmission electron microscopy (TEM), and X-ray diffraction (XRD). The surface appearance was analysed using an integrating sphere-spectrophotometer setup which measures the diffuse and total reflectance of light from the surface. Compared to samples without TiO_2, surface appearance after anodising of samples with TiO_2 changed from dark to greyish white upon increasing the anodising voltage. This is attributed to the localized microstructural and morphological differences around the TiO_2 powder particles incorporated into the anodic alumina matrix. The TiO_2 powder particles in the FSP zone were partially or completely amorphized during the anodising process, and also electrochemically shadowed the anodising of underlying Al matrix.

1. Introduction

Aluminium and its alloys are widely used in various engineering applications due to their light weight coupled with high levels of mechanical properties. Anodising of Al enhances its corrosion and wear resistance as well as improves its aesthetic appearance for use in architectural, decorative, and automobile industries [1]. Over the years, sulphuric acid anodising (SAA) has been carried out as a preferred surface finishing technique as it provides an anodised layer with excellent decorative properties [2]. The anodised layer formed after SAA is optically transparent in visible wavelength region and the thickness of such a layer for best decorative appearance is in the range of 10–15 μm. The anodised layer contains a self-organized nano-sized porous structure (20–30 nm diameter), which can be used for colouring by impregnating with organic or inorganic dye followed by a sealing process [2] [3]. Nearly all colours including black can be produced by the dyeing process, while achieving a white anodised Al surface is difficult. This is due to the fact that the white appearance is related to optical scattering of light achieved by pigments that are too big to be impregnated into the pores of anodised Al. However, individual colours (like red, green, blue etc.) are produced by the absorption of a specific or group of wavelengths by the dye molecules that are easily impregnated as they are smaller than the pores in anodic alumina.

Previously, white anodising of Al has been studied for use in applications like aerospace, where a mixture of sulphuric acid, lactic acid, glycerol and sodium molybdate were used for obtaining anodised Al surface with improved reflectance [4,5]. Other anodising processes like plasma electrolytic oxidation (PEO) and micro arc oxidation (MAO) have also been reported to generate surfaces from grey to white appearance, but the thickness of these anodic coatings is higher than those used for the decorative anodised surfaces. Also, the surface gloss of these oxide coatings is very low owing to their very high surface roughness [6–10]. For the anodised layer to appear white and glossy, it needs to facilitate effective scattering of light along with a smooth surface to retain its gloss [11,12]. One approach for achieving this is by incorporation of high refractive index particles in the transparent anodised layer that would scatter the incident light, while the smooth anodised surface would generate the glossy appearance. Titanium dioxide (TiO_2) in rutile phase has a refractive index of 2.6–2.9 [13] and is widely used as a white pigment in many commercial applications [14,15]. Thus, the use of TiO_2 as scattering medium in anodic layer for achieving white surfaces after SAA of Al is very promising and needs understanding

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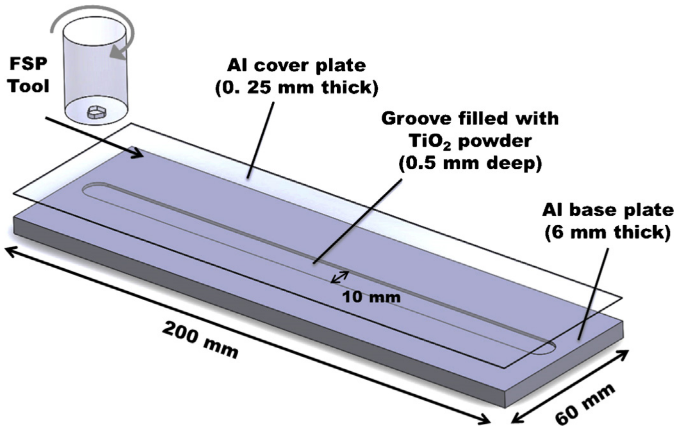

Fig. 1. Schematic of the sample geometry with groove used for FSP process.

in terms of incorporation into Al matrix, anodising behaviour, and optical appearance.

Incorporation of TiO_2 into Al matrix has been studied extensively to understand the effect on mechanical properties. Techniques like reactive hot pressing (RHP), reactive squeeze casting (RSC), and mechanical alloying have been used for dispersing the TiO_2 powders into the Al matrix [16–19]. Friction stir processing (FSP) [20] is one mechanical alloying technique which has been widely used to obtain metal matrix composites (MMCs) of various combinations [21–25]. MMCs using TiO_2 powders[26–28] and nanofibers [29] have been prepared by FSP to reinforce the Al matrix by allowing for reactive processing between Al and TiO_2 to form Al–Ti based intermetallic phases. However, the use of this technique to obtain tailored surfaces that can be further functionalized by anodising still needs to be investigated.

In this paper we evaluate the use of FSP of Al–TiO_2 to obtain surface composites which are further anodised to achieve light scattering by TiO_2 in a transparent anodised Al matrix. The effect of FSP and anodising parameters on the optical appearance of anodised layer is studied. Scanning (SEM) and transmission electron microscopy (TEM) was used to observe the microstructure of the anodised composite surfaces in terms of morphology and incorporation of TiO_2 particles. Focused ion beam milling (FIB) was used to lift out lamella in-situ from the anodised surface for TEM analysis. Grazing incidence X-ray diffraction (GI-XRD) was performed to characterize the phases in the prepared composite surfaces before and after anodising. The surface appearance was evaluated using an integrating sphere-spectrophotometer setup and the obtained data was correlated with the observed microstructure and phases to explain the appearance.

2. Experimental

2.1. Materials

Aluminium plates (Peraluman^{TM} 853, Alcan rolled products, Germany) were obtained with dimensions 200 mm × 60 mm × 6 mm for FSP. Commercial TiO_2 powder (Ti-pure R900, DuPont Titanium Technologies, Belgium) in rutile phase was used. The median diameter of the powder particles was 210 nm.

2.2. Friction stir processing

The FSP process was performed using a Hermle milling machine equipped with a steel tool having 20 mm shoulder diameter, 1.5 mm pin length with a M6 thread (see Fig. 1). The backwards tilt angle of the tool was maintained at 1°. A groove 0.5 mm deep, 10 mm wide, and 180 mm long (see Fig. 1) in the Al plates which was compactly filled with TiO_2 powder. The filled plates were then covered by the same Al sheet rolled down to a thickness of 0.25 mm to prevent loss of TiO_2 powder during the initial FSP pass. Rotational speed of the tool was 1000 rpm and the advancing speed was 200 mm/min for the first pass to insure correct closure of the groove and 1000 mm/min for the next six passes. A surface of 175 mm long × 20 mm wide was processed for each pass with a total processing time of roughly 2 min. All seven passes were performed one over the other without any shift. For comparison, reference samples without any TiO_2 powder were also produced using the same FSP parameters.

2.3. Anodising

The processed samples with and without TiO_2 powder were then mechanically polished, buffed to a mirror finish and then degreased in a mild Alficlean^{TM} solution at 60 °C. The samples were subsequently desmutted by immersing in diluted HNO_3 followed by demineralized water rinsing. Anodising was carried out in a 20 wt.% sulphuric acid bath maintained at 18 °C. Four different anodising voltages of 4.8 V, 9.6 V, 15.1 V, and 18.9 V were used. After anodising, the samples were rinsed with demineralized water. Sealing of the anodised layer was performed in water at 96 °C for 25 min followed by drying with hot air.

2.4. Spectrophotometry

Optical appearance of the FSP samples in polished condition before and after anodising was analysed using an integrating sphere-spectrophotometer setup. The samples were illuminated at 8° incidence, with light from a Deuterium-Tungsten halogen light source (DH 2000, Ocean optics). Reflected light from the samples was collected and analysed for diffuse and total reflectance using a spectrometer (QE 65000, Ocean Optics). The wavelength range analysed was 350–750 nm and was integrated over a period of 4 s. The spectrophotometer was calibrated using NIST standards.

2.5. Electron microscopy

The morphology, microstructure, and compositional analysis of the samples was performed using SEM (Model Quanta 200 ESEM FEG, FEI) equipped with EDS (Oxford Instruments 80 mm^2 X-Max). The samples were mounted in epoxy resin and mechanically polished to reveal the cross section. Transmission electron microscopy analysis was carried out on the sample cross section in the anodised as well as non-anodised regions using a TEM (Model Tecnai G2 20) operating at 200 keV. The lamellas for TEM were prepared using FIB-SEM in situ-lift out (Model Quanta 200 3D DualBeam, FEI) and further thinned for electron transparency in a FIB-SEM (Helios Nanolab DualBeam, FEI).

2.6. X-ray diffraction

Grazing incidence X-ray diffraction (Model Bruker Discover D8) analysis was performed using Cu-$K\alpha$ radiation at 40 kV and 40 mA for phase analysis of the samples after FSP and anodising. Diffraction data was recorded in the 2θ range from 20° to 70° with an incidence angle of 0.25°, step size of 0.03° and a scan step time of 4 s.

3. Results

3.1. Visual appearance

The visual appearance of the FSP samples with and without TiO_2 after SAA is shown in Fig. 2. The FSP zone without TiO_2 powder does