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Optical appearance of AC anodized Al/TiO_2 composite coatings

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Summary

AC anodization of Friction Stir Processed (FSP) surface composites of Al/TiO_2 was systematically investigated with an aim to understand the effect of the anodization parameters on the optical appearance of the anodic layer. FSP-treated Al samples were anodized at different frequencies and voltage amplitudes. The microstructure and composition of the obtained anodic films were determined by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). The optical appearance of the films was characterized by optical reflectance spectroscopy. The changes of the optical reflectance spectra were analysed and correlated to the microstructural features observed for the FSP-treated samples before and after anodization.

1 Introduction

Anodization of aluminium is widely used in different fields of industry for corrosion protection and aesthetic appearances [1]. Decorative alumina surfaces are commonly produced by direct current (DC) anodization of aluminium in a sulphuric acid bath. The resulting anodic alumina layers are usually transparent; however, their optical appearance depends on the anodization conditions as well as on the composition and surface morphology of the specimen being anodized [2-4]. Different kinds of light-grey or white appearance can be obtained by introducing metal oxide particles into the anodic film. However, it was observed [5] that DC anodization of aluminium containing metal oxide particles can result in a dark tone which is unfavourable for decorative applications. This effect appears due to the non-anodized metallic Al remaining below each embedded particle. Recently high-frequency AC anodizing of Si microparticles was reported [6]. It was observed that the microstructure of the obtained porous anodic films is very different, compared to the coatings produced by conventional DC anodizing. In particular, AC anodizing was accompanied by branching of the pores and effective oxidation of the Al right below the embedded microparticles. Applying the technique of AC anodizing for Al with embedded metal oxide particles (Al/metal oxide surface composites) is expected to improve the optical appearance of the resulting anodic coatings by completely oxidizing the Al around the oxide particles [5]. Friction stir processing (FSP) [7] is an industrial technique that has been extensively used for preparation of various composites [8-12]. However, a combination of this technique with anodizing for obtaining bright decorative coatings on Al has not been reported.The objective of the present work is to systematically study the AC anodization of FSP surface composites of Al/TiO_2 and to determine the effect of the anodizing parameters on the optical appearance of the anodic films.

2 Experimental Details

Aluminium substrates with dimensions 200 x 60 x 6 mm were obtained in rolled condition and commercial powders of TiO_2 (particle size 300 nm) were used. Friction stir processing 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 and three flats. A groove 0.5 mm deep, 10 mm wide and 180 mm long in the substrates was filled with the powders. The filled substrates were then covered by the same Al sheet rolled down to a thickness of 0.25 mm to prevent loss of powders during the initial FSP pass. The processed composite surfaces were mechanically polished to a mirror finish and subsequently degreased in a mild alkaline solution. Desmutting was performed by immersing in dilute HNO_3 followed by demineralised water rinsing. Finally the samples were cleaned by ultrasonication in acetone for 15 min. and dried in air flow.

The as-prepared FSP composites were anodized in 20% (wt.) sulphuric acid bath maintained at 10°C. The anodizing was performed by applying square voltage pulses from a function generator (33120A, Agilent). The waveforms of voltage and current during the anodizing were monitored with the help of a digital oscilloscope (TDS3034B, Tektronix). The anodized area was approximately 2 cm^2. The voltage at the cathodic cycle was -2 V; the voltage at the anodic cycle was either 10 or 20 V. The frequency was varied between 0.1 and 10 kHz. The duty cycle (i.e. the ratio between the anodic cycle duration and the time interval between two subsequent voltage pulses) was changed between 30 and 70%. The thickness of the obtained anodic layers was determined by a capacitance probe (Omniprobe, Fischer).

Surface appearance of the processed composites after anodizing was analysed using an integrating sphere-spectrometer setup. The samples were illuminated with light from a deuterium tungsten halogen light source (DH2000, Ocean Optics). Reflected light from the samples was collected and analysed for diffuse and total reflectance using a spectrometer (QE65000, Ocean Optics). The spectrometer was calibrated using NIST standards.

The microstructure and surface morphology of the obtained anodic layers were studied by SEM (Quanta 200 ESEM FEG, FEI) having EDS capability (80 mm^2 X-Max silicon drift detector, Oxford Instruments). The SEM was typically operated at the acceleration voltage of 15 kV. For cross-sectional imaging, the samples were fractured, mounted in an epoxy and polished. In order to minimize charging, the samples were coated by 2-3 nm Au layer by magnetron sputtering (Cressington 208HR sputter coater).

Transmission electron microscopy analysis was carried out on the sample cross sections in the anodized as well as non-anodized regions using a TEM (Model Tecnai G2 20). 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).

3 Results and Discussion

3.1 Rate of the anodic film growth

The growth of anodic films on FSP-treated samples was found to be strongly dependent on the AC anodizing conditions, namely the voltage amplitude and frequency. In particular, when the anodic cycle voltage increased from +10 to +20 V, the growth rate increased from 0.5 to 1.8 µm/min. Fig. 1 shows the effect of the anodizing frequency and duty cycle on the rate of the anodic film growth. It can be seen, that increasing the frequency from 0.1 to 10 kHz leads to a significant increase in the growth rate (Fig. 1a). In the case of the higher anodic cycle voltage (+20 V), this effect is much more pronounced, than in the case of the lower voltage (+10 V). On the other side, changing the duty cycle in the range between 30 and 70% does not have any notable effect on the growth rate (Fig. 1b).

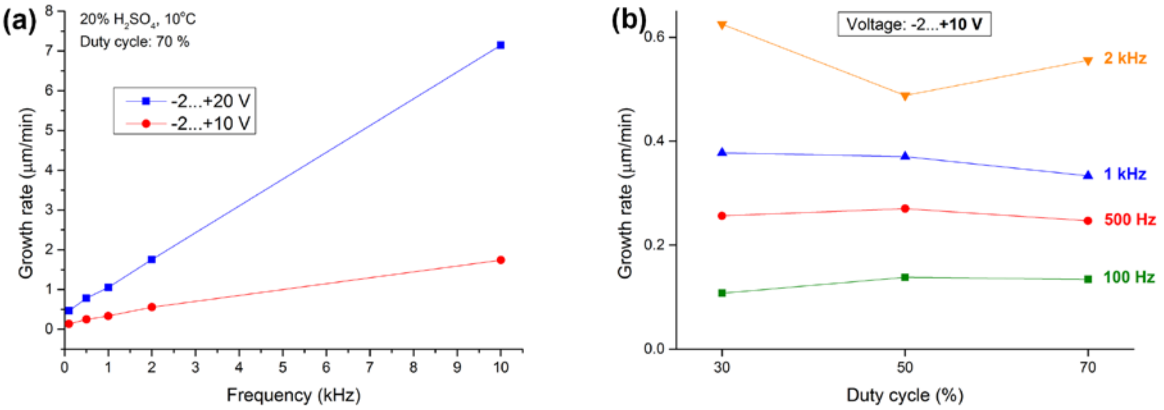

Figure 1: Rate of the anodic film growth as a function of anodizing frequency (a) and duty cycle (b).

3.2 Reflectance measurements

Optical reflectance of the AC-anodized FSP-treated samples was measured as a function of voltage amplitude, frequency and duty cycle. Fig. 2 shows the effect of the AC anodizing parameters on the optical reflectance. It can be seen, that increasing the voltage in the anodic cycle from +10 to +20 V (at 2 kHz frequency) leads to a notable increase in both the diffuse and total reflectance (Fig. 2a). The total reflectance of the samples in the visible range also increases monotonically with the increase in the anodizing frequency from 0.1 to 10 kHz (Fig. 2b). At the frequency of 2 kHz, the total reflectance is almost the same for 30% and 70% duty cycle, while being slightly lower for 50% duty cycle (Fig. 2c). However, for some other frequencies the effect of the duty cycle was different. It should be noted that the observed difference in the total reflection for different duty cycles might not be statistically significant because of the big variation of reflectance within a single sample. Such a variation is caused by non-uniform distribution of the TiO_2 particles which is typical for the FSP technique.

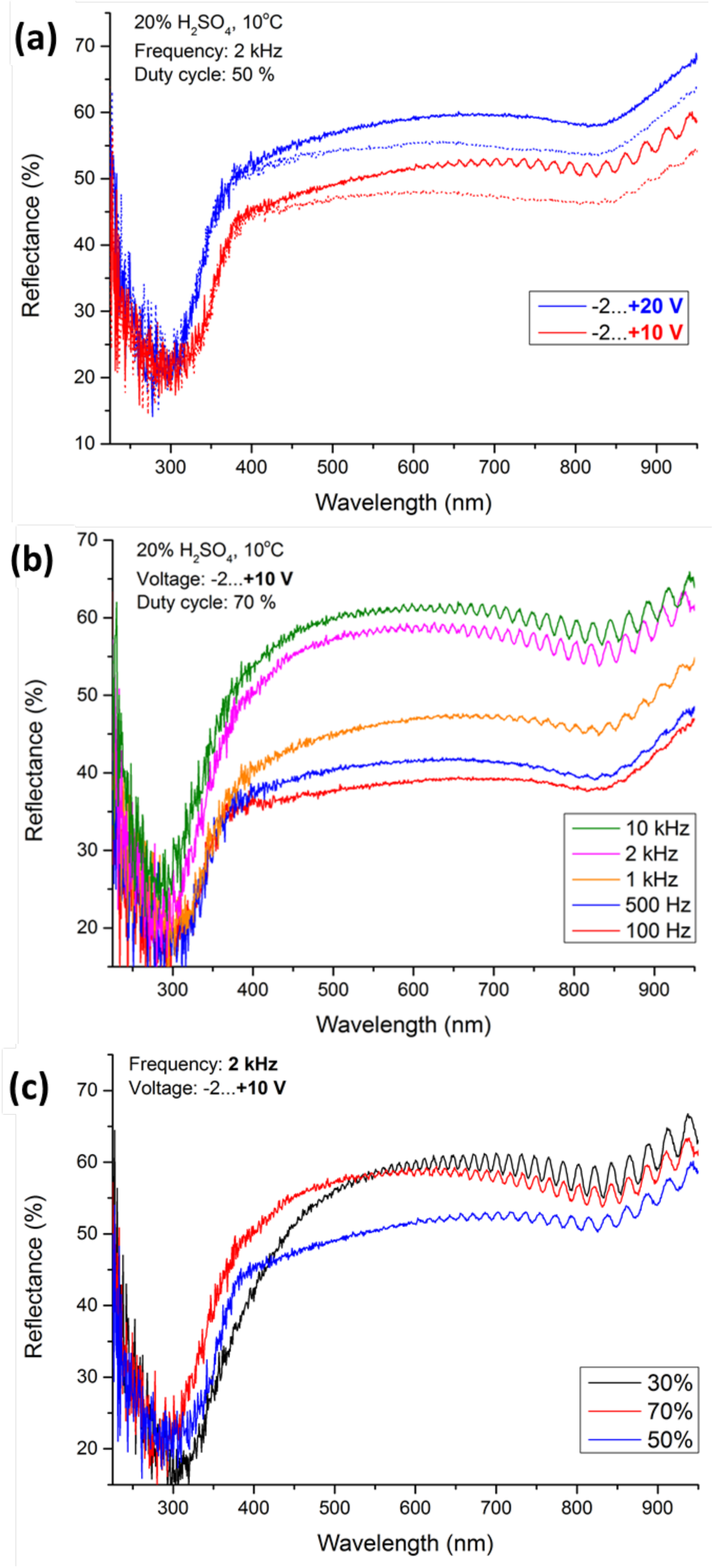

Figure 2:.Total optical reflectance of the AC-anodized FSP-treated samples as a function of the anodic cycle voltage (a), frequency (b) and duty cycle (c). In Fig. 2a the corresponding diffuse reflectance is shown by dotted lines.

3.3 Microstructure of the anodic layers

Fig. 3 shows TEM images of an FSP-processed sample anodized with voltage amplitude of -2 to +10 V and frequency of 2 kHz. As can be clearly seen from the pictures, the AC anodizing of the as-prepared samples leads to the branching of the pores. That allows complete oxidation of the Al regions right below the embedded particles, i.e. there is no metallic Al present in the anodic film. Since such non-anodized Al fragments are believed to be responsible for the darkening of the anodized layer with embedded oxide particles, AC anodizing should give coatings with brighter appearance, compared to the ones obtained by conventional DC anodizing. This point makes AC anodizing of Al with embedded particles a very promising technique for the production of decorative coatings.

As can be seen from the reflectance spectra of the AC-anodized FSP-treated samples (see Fig. 2a), increasing the voltage in the anodic cycle from +10 to +20 V leads to a significant increase in the reflectance. However, detailed SEM and EDX investigation of the sample anodized with voltage amplitude of -2 to +20 V reveals that all of the embedded TiO_2 particles have been completely disintegrated during anodizing. Therefore the observed increase in the reflectance is simply explained by the absence of scattering centers in the film. Consequently, the specific visual appearance, which is a characteristic of anodized film with a big number of incorporated metal oxide particles, was also lost. Thus further studies are required in order to obtain highly reflective anodized films which would have a sufficient concentration of embedded scattering centers.

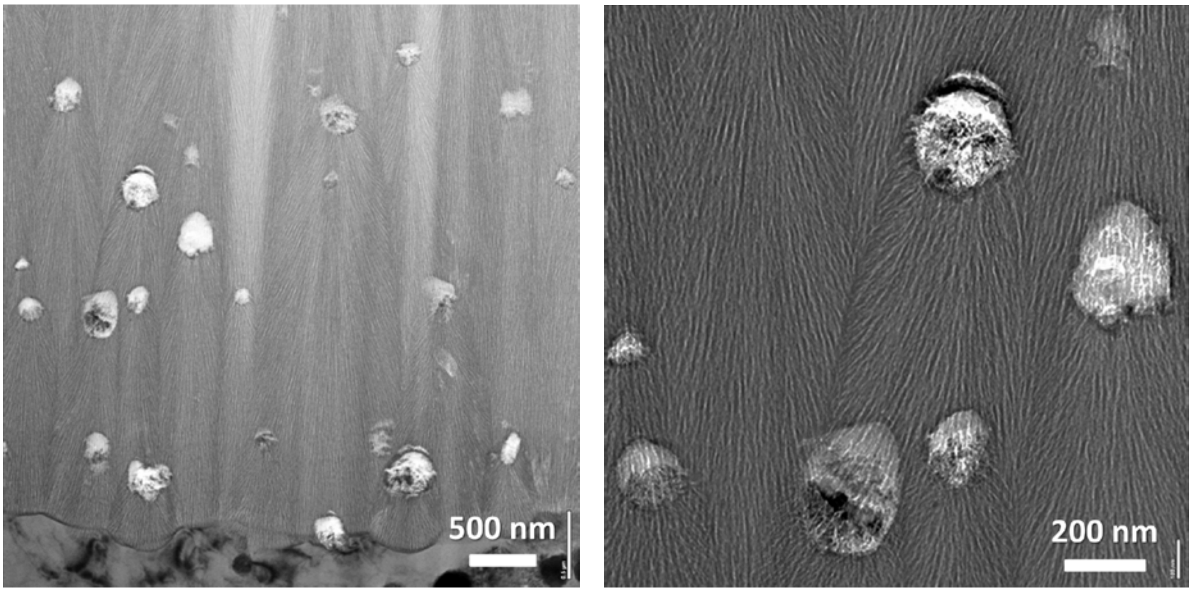

Figure 3: TEM images of an AC-anodized FSP-processed sample. Anodizing voltage amplitude: -2 to +10 V, frequency: 2 kHz.

4 Conclusions

- AC anodizing of FSP-processed Al samples was shown to be an effective technique for obtaining decorative coatings using surface composites of Al/TiO_2.
- The rate of the anodic layer growth increases with an increase in the anodic cycle voltage and frequency, but it is almost independent of the duty cycle.
- The total optical reflectance of the AC-anodized FSP-processed samples depends on the anodic cycle voltage, frequency and the duty cycle. In general, increasing the anodic cycle voltage and frequency leads to an increase in the total reflectance.
- AC-anodizing of the as-prepared samples with voltage amplitude of -2 to +10 V is accompanied by pore branching and allows complete oxidation of Al in the regions below the embedded TiO_2 nanoparticles. At the higher positive cycle voltage (+20 V), all of the embedded particles are disintegrated during the anodizing.

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