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Influence of electrolyte temperature on properties and infrared emissivity of MAO ceramic coating on 6061 aluminum alloy

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HIGHLIGHTS

- Samples of Al6061 were MAO treated in various temperatures of alkaline silicate electrolyte.
- Hotter electrolytes formed thinner and rougher layers which covered by grainy spherical hollow bulgy microstructures.
- The formed sillimanite and cristobalite phases were increased significantly in the hotter electrolytes.
- Sillimanite and cristobalite phases widened the IR opaque region and shifted the apparent peaks toward longer wavelengths.
- High LWIR emissivity of 94.4% was achieved in the electrolytes hotter than 86 °C.

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ABSTRACT

6061 aluminum alloy was treated by MAO at various temperatures of the alkali silicate electrolyte using pulsed bipolar current mode for ten minutes. The surface microstructures and properties were studied using SEM, EDX, and XRD. The infrared emissivities of the MAO ceramic coatings were measured at the 70 °C using FTIR spectrometer. The electrolyte temperature strongly affected all the surface properties. The MAO alumina ceramics prepared in cold electrolytes have volcano-like and accumulated particles microstructures, while those prepared in hot electrolytes were: rougher, thinner and contained grainy spherical hollow bulgy microstructures with more pore density and more sillimanite and cristobalite phases which enhanced the IR emissivity. Also, the increment of sillimanite and cristobalite phases moved the apparent peaks toward longer wavelengths, and broadened the opaque region of the IR spectra. As a result, the increment of electrolyte temperature from 12.3 °C to 90.5 °C increased the average of LWIR emissivity from 80.4% to 94.4%, respectively, for the MAO ceramic coatings.

1. Introduction

Applying a high voltage between the electrodes, turns the conventional electrolysis process into a micro arc oxidation process (MAO) [1,2]. During the MAO, a series of visible short-lived microdischarges occur on the work piece, which cause growing of ceramic coatings on treated surfaces of aluminum [3–7], magnesium [8,9], and titanium alloys [10,11]. The MAO coating properties depend on several parameters, such as: electrolyte compositions [12–15], treatment time [15–17], electrolyte temperature [15,18], applied voltage [19–21], current density [15,22,23], and current mode [24,25].

Few previous works have studied the effect of electrolyte temperature on the MAO treated samples. Raj et al. [15] fabricated MAO ceramic coatings over aluminum substrate in an alkaline silicate electrolyte with a temperature range of 10–40 °C. They found that the MAO electrolyte temperature had a significant impact on the growth and thickness of ceramic layer, and the best corrosion resistance was accomplished at low electrolyte temperatures. Habazaki et al. [18] reported that more alpha-alumina can be formed at low alkaline aluminate electrolyte temperature, 5 °C, which resulted in high wear resistance and low porosity.

The MAO ceramic coating has many advantages like wear resistance [26,27], corrosion resistance [5,28], hardness [22,29], strong adhesion [30,31], thermal shock resistance [11,32]. Getting high emitter MAO coatings will enhance the use of aluminum and other metallic alloys in heating and cooling applications [16].

Table 1 summarizes the previous studies of the IR emissivity of MAO coatings at elevated and low temperatures. Wang et al. [33] prepared MAO ceramic coating on 2024 Al substrate at different processing times to study the resultant IR emissivity at 500 °C,

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Table 1
Previous studies of IR emissivity of the MAO ceramics.

Alloy	Impact variable	Electrolyte components and temperature	Processing time (min)	Tested temperature (°C)	Wavelength range (μm)	Maximum emissivity avg.	Refs.
2024 Al	Processing time	Na_2SiO_3 (6 g/L) NaOH (1.2 g/L) $(NaPO_3)_6$ (35 g/L) • temp N/A	**5, 10, 15**	500	3–20	85% (8–20 μm)	[33]
Ti_6Al_4V	$Co(C_2H_3O_2)_2$ additives	Na_3PO_4 (7 g/L) $Co(C_2H_3O_2)_2$ (**0, 2, 3, 4** g/L) • temp < 30 °C	10	700	3–20	⩾94% (3–8 μm) ⩾90% (3–20 μm)	[11]
$Ti_6Al_2Zr_1Mo_1V$	Processing time	$Na_2SiO_3.9H_2O$ (9 g/L) Na_3PO_4 (3 g/L) $NaAlO_2$ (3 g/L) • temp < 50 °C	**30, 60**	700	3–20	90% (8–14 μm)	[34]
6061 Al	Processing time	$Na_2SiO_3.9H_2O$ (5.56 g/L) NaOH (1.67 g/L) • temp < 25 °C	**10, 20, .., 60**	70	4–16	91.7% (LWIR: 8–15 μm)	[16]

Bold texts to distinguish the studied changeable variables.

and illustrated that γ-Al_2O_3, silicon oxides and phosphate oxides enhanced the emissivity at wavelength range 8–20 μm, while surface roughness was responsible for increasing emissivity at the wavelength range 3–5 μm. Tang et al. [11] prepared MAO ceramic on Ti6Al4V substrate using different additives of cobalt(II) acetate; reported that more concentrations of cobalt(II) acetate increased the Co contents in the coating and consequently enhanced the emissivity of the ceramic surface at 700 °C for the wavelength range 3–20 μm. A relatively high emissivity was found by Wang et al. [34] when they studied the emissivity (3–20 μm,700 °C) of the surface of MAO ceramic coating on $Ti_6Al_2Zr_1Mo_1V$ alloy, and they pointed out the TiO_2 phases enhanced the emissivity in the range 8–14 μm. Recently, we investigated the effect of MAO processing time on the coating properties and its IR emissivity (4.0–16.0 μm, 70 °C) [16]. We found that the γ-alumina, α-alumina, sillimanite and cristobalite phases contributed on shaping the IR spectral curve. A slight enhancement of LWIR emissivity from 87.1% to 91.7% was achieved by increasing the MAO processing time from 10 to 60 min [16].

The present study has two main goals, the first is to study the effect of wide range of electrolyte temperature on the properties of the MAO coating and the resultant IR emissivity, and the second is to get the highest possible LWIR emissivity using the alkaline silicate electrolyte which is considered to be an environmentally friendly one.

2. Experimental

Rectangular pieces ($4 \times 4 \times 0.2$ cm^3) of 6061 Al alloy (Mg 1%; Si 0.65%; Fe 0.7%, Cu 0.3%; Cr 0.2%; Mn 0.15%; Ti 0.15% and Al balance) were used as substrates from one side while the other side was totally insulated using Teflon tape. For each experiment, four pieces were gathered and mounted into an Al 6061 clamp and another 243 cm^2 Al 6061 plate was connected to the other electrode. Only 6061 Al alloy contacted the electrolysis solution to avoid any contamination by wires or screws. The electrolyte was prepared using 5.56 g/L of sodium silicate and 1.67 g/L of sodium hydroxide; the PH was 12.8. The cooling and stirring bath has stainless steel walls capable to contain up to 22 Lof solution. We used the pulse controller SPIK 2000A (Shen Chang Electric Co. Ltd., Taiwan) to generate an asymmetric bipolar pulsing mode with 360 μs for anodic period (a_{on}), and 200 μs for: anodic neutral period (a_{off}), cathodic period (c_{on}) and cathodic neutral period (c_{off}). Two electrical power supplies (PR Series, 650V, 7.7A, Matsusada) were connected to the pulse controller to supply the sample by an anodic pulse of 500 V, 7.0 A, and a cathodic pulse of 100 V, 3.5 A. More details about the experimental arrangement, in addition to the polarity of alternating electrodes can be found in our previous work [16]. To avoid the effect of chemical reactions with the plate surface, we renewed the plate for each MAO experiment, despite it was in a good situation. Both electrodes (sample and plate) were alternating between cathode and anode according to the output bipolar pulse, and the MAO treatment was conducted for 10 min for each sample. The initial temperatures for the electrolyte were: 5, 10. . .85 °C. Despite using of stirring and cooling system to control the electrolyte temperature but the temperature was not constant, so the average was taken. After completing each treatment, the samples were immediately immersed and cleaned with distilled water, followed by a cleaning process using an ultrasonic bath of distilled water, propanol, acetone, and again distilled water; 10 min for each, and then the samples were drying in the fume hood, and stored in sealed bags.

Around 21 randomly selected places were captured by the SEM (S4160, Hitachi) to get the micrographs for each sample. For pores larger than 0.1 μm^2 we performed the image analysis using Image Pro Plus 7.0 software (Media Cybernetics, Inc.) to estimate: the porosity as the percentage of total pore surface area to the total area of the SEM micrograph frames (for each individual sample); the pore density as the percentage of the total pores number to the total area of the SEM micrograph frames; and the pore diameter average. Another 10 cross-section positions were captured for each sample to estimate the layer thickness average.

Hitachi EDX S4800 was used to investigate the elemental composition of coating surface. Low angle X-ray diffraction (Cu Kα; XRD, X'Pert PRO MPD, PANalytical, Netherlands) was used to estimate the phases and compositions of as-deposited ceramic coatings. We performed a semi-quantitative analysis of the XRD spectra using the so-called "Reference Intensity Ratio method" (RiR-method, de Wolff and Visser (1964), [35]) by MATCH! software (V.1.11f, Crystal Impact GbR) and selected the best fit phases and compositions, in addition to estimate the weight percentage of phases and compositions.

For each sample, at least 16 different locations were studied to determine the average of surface roughness using a surface roughness tester (Mitutoyo, SJ310).

We analyzed the IR emissivity of samples at 70 °C using a modified Fourier transform infrared spectroscopy (FTLA2000 Series Spectrometer, ABB); by comparing with a reference blackbody radiation in the wavelength range 4–16 μm.