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Analyses of reinforcement phases during plasma electrolytic oxidation on magnesium matrix composites

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ABSTRACT

A plasma electrolytic oxidation (PEO) process on SiC_P/AZ31 and Al_2O_3–$SiO_{2(sf)}$/AZ91 magnesium metal matrix composites (MMCs) in phosphate electrolyte was carried out to reveal the evolution of SiC_P and Al_2O_3–$SiO_{2(sf)}$ reinforcement phases in relation to coating growth. Optical emission spectroscopy (OES) was used to identify the elements presented in the plasma discharge process and evaluate the plasma electron temperature. XRD, SEM, EDS and ICP-AES were employed to characterize the microstructure, composition and phase constituents of the PEO coatings and the dissolved quantity of MMC in the electrolyte. The results show that the elements from the reinforcement phases can be found in the OES spectrum, which indicates that the reinforcement phases are involved in the plasma discharge, and the average electron temperature is about 5000 K–7000 K during the plasma discharge. The microstructure and composition suggest that $MgSiO_3$, Mg_2SiO_4 and $MgAl_2O_4$ oxide layers are formed at the reinforcement/coating interface due to the local high temperature of the plasma discharge. It is believed that most of the reinforcement phases are molten firstly and then react with oxygen and magnesium oxide to form other oxides. However a few reinforcement phases still remain in the coating close to the MMC/coating interface.

1. Introduction

Plasma electrolytic oxidation (PEO), also called microarc oxidation (MAO), which evolved from the conventional anodizing process, is an effective surface modification technique to fabricate ceramic oxide coatings on light metals, such as Al, Mg and Ti, which improve their wear and corrosion performance [1–5]. At present, some papers about the microstructure, properties and growth mechanism of PEO coatings on metal matrix composites (MMCs) have been reported [3–5]. These researches were devoted to investigating the PEO process on SiC_P/2024 and SiC_P/A356 aluminum matrix composites [6,7] and SiC_P/AZ31, ZC71/SiC/12p-T6 and SiC_P/AZ91 magnesium matrix composites [8–12].

As the reinforcements hinder the growth of the oxide coating and disrupt the coating film continuity, it is interesting to determine the effects of reinforcement phases on the growth mechanism of PEO coatings. Xue [3] proposed a growth model of PEO coating on Al/SiC_P composite to describe the evolution of SiC reinforcement particles as a tracer. He suggested that most of the SiC reinforcement particles in the coating were molten and then oxidized to become silicon oxide, though a few small SiC particles still remained in the coating, especially close to the composite/coating interface. However, Arrabal et al. [9] analyzed the growth of a PEO coating on ZC71/SiC/12p-T6 magnesium MMC, and revealed that the SiC particles were incorporated largely unchanged into the coatings, although a thin silicon-rich layer was also formed at the particle/coating interface. These SiC particles may undergo oxidation below its melting point of 3003 K rather than the complete melting due to the insufficient temperature in the micro-discharge zone. So these reports result in a divergence about the characteristics of reinforcement phases during plasma electrolytic oxidation on metal matrix composites. This divergence actually focuses on whether the temperature in the plasma discharge zone is high enough to make the partial reinforcement phases molten in the oxide coating, and whether the reinforcement phases are obviously consumed during the growth of PEO coating.

Plasma spectroscopy is a sensitive diagnostic tool of plasma characteristics to establish a more complete and reliable arsenal of atomic parameters [13]. Optical emission spectroscopy (OES) has been utilized to investigate the complex plasma discharge phenomena during the growth of PEO ceramic coatings [14–17]. The elements involved in the plasma discharge can be identified by the OES spectrum, and the plasma electron temperature in the discharge zone can be calculated from the

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OES spectral lines. It is interesting to analyze whether the reinforcements in MMC take part in the optical emission during plasma electrolytic oxidation. However, such work has not been reported.

In our paper, the growth of PEO coatings on SiC_P/AZ31 and Al_2O_3–$SiO_{2(sf)}$/AZ91 magnesium metal matrix composites (MMCs) is investigated. Optical emission spectroscopy (OES) was used to examine the elements involved in the plasma discharge and evaluate the local discharge temperature. In addition, the microstructure, composition and phase composition of the coatings were analyzed. The evolution of reinforcement phases during the coating growth was discussed.

2. Experimental procedure

The as-received 6 vol.% SiC_P/AZ31 (2.5–3.5 wt.% Al, 0.6–1.4 wt.% Zn, 0.2–1.0 wt.% Mn and Mg balance) magnesium matrix composite was prepared by a stir casting method. The average size of the SiC particle is about 10 μm. The 33 vol.% Al_2O_3–$SiO_{2(sf)}$/AZ91 (8.3–9.7 wt.% Al, 0.35–1.0 wt.% Zn, 0.15–0.50 wt.% Mn and Mg balance) composite was fabricated by a squeeze infiltration method. The sizes of the fiber are 1–3 μm in diameter and 50–100 μm in length. Rectangular specimens (40 mm × 15 mm × 2 mm) of composites were used as anode materials. The composite sample and a stainless steel cathode were connected to a bipolar pulsed power supply with a frequency of 75 Hz. The electrolyte was an aqueous solution of Na_3PO_4 (4 g/L), KOH (4 g/L) and KF (4 g/L). The PEO treatment was carried out under constant voltages of +520 V/−110 V. The electrolyte solution was maintained at a stable temperature (26 ± 2 °C) during PEO process. The oxidation time for the two composites was 15 min.

The optical emission spectra can provide some information about the active species in the plasma discharge zones on the MMC samples. The OES spectra were collected by an optical emission spectrometer (AvaSpec-2048) with a resolution of about 0.08 nm. This spectrometer had eight channel slots with a spectral region of 200 nm–750 nm. This scope is available for a dual or multiple channel instrument, where all spectra are taken simultaneously. The spectrometer with a slit size of 10 μm consists of a 2048 pixel CCD detector array with gratings of 2400 lines/mm in the spectral region of 200 nm–565 nm, and 1800 lines/mm in the spectral region of 565 nm–750 nm. The spectrometer collected the light from an optical fiber, which was placed at a distance of 2 cm away from the MMC sample through a glass window. Then the spectral data were analyzed by the software of Plasus Specline 2.1 and the NIST database [18].

The morphology, microstructure and composition of the coatings were examined using an S-4800 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS). An X' PERT PRO MPD X-ray diffractometer (XRD) was used to examine the phase constituents of coatings. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique, also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), is used to measure the dissolved quantity of MMC in the electrolyte after PEO treatment. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

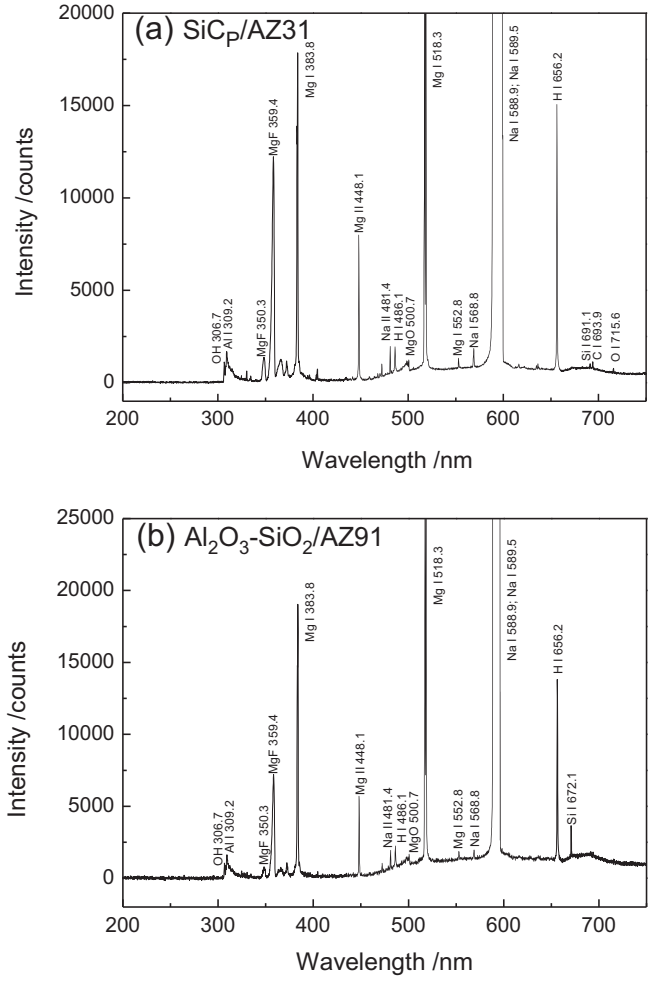

Fig. 1. Typical PEO emission spectra of (a) SiC_P/AZ31 MMC and (b) Al_2O_3–$SiO_{2(sf)}$/AZ91 MMC in the phosphate electrolyte.

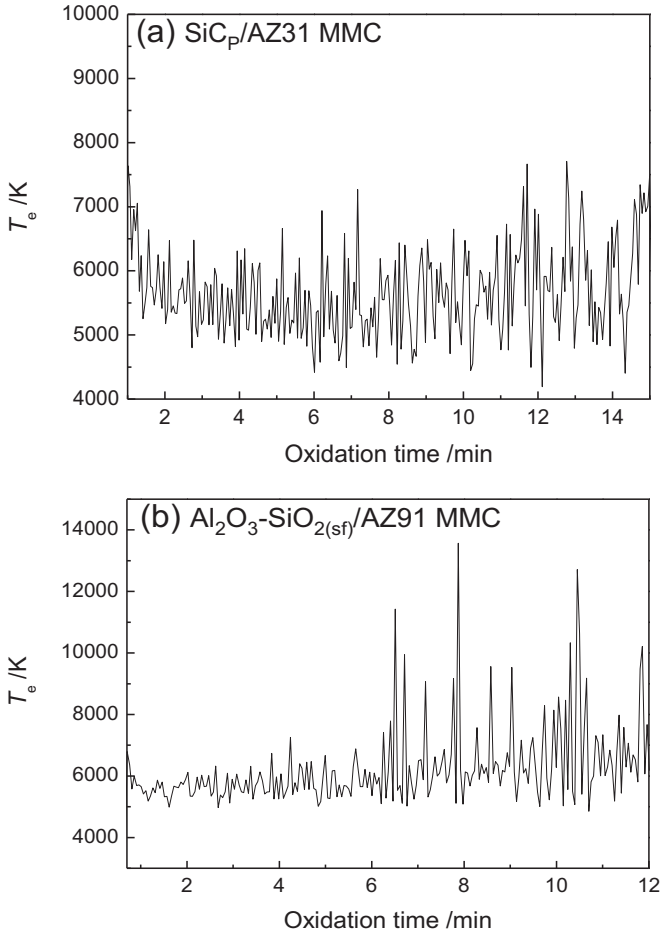

Fig. 2. Plasma electron temperature (T_e) as a function of oxidation time. (a) SiC_P/AZ31 MMC and (b) Al_2O_3–$SiO_{2(sf)}$/AZ91 MMC.