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Preparation of self-lubricating composite coatings through a micro-arc plasma oxidation with graphite in electrolyte solution

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ABSTRACT

In this study, low friction and wear resistant composite coatings were produced through the micro-arc oxidation (MAO) on 6061 aluminum alloy with graphite particles in alkali sodium silicate electrolyte solution. The ball-on-disk wear tests were performed in humid environment to investigate the friction and wear properties. The Al_2O_3, Al_2OC, Al_4C_3, Al_4O_4C, and graphite phases were observed in a grown layer with graphite additives in electrolyte solution. The volcano-like microstructures were decreased in population and widened significantly in the sample prepared with the additive of graphite particles. For the sample prepared without graphite additives, the coating failure occurred after 1200 cycles, while the additive of graphite maintained the average of friction coefficient around 0.1, and reached a maximum of 0.12 after 15000 cycles of wear test. The graphite and carbon containing lubricating phases trapped in the alumina matrix or crevices acted as micro/nano-reservoirs to maintain low friction and favor high endurance of the coating.

1. Introduction

According to the tribological principles, a soft or lubricant coating deposited on top of a hard base coating can provide low friction and wear resistance [1,2]. These arise because of a reduction in both the contact area and shear strength. The soft/hard duplex coatings can be obtained by various surface engineering processes that have been reviewed by several researchers [3–8]. Recently, several studies have indicated that nanocomposite coatings with nanoparticle lubricants embedded in hard coatings can provide a superior self-lubrication effect without interface problems. These so called self-lubrication films include CrN–Ag [9], CrSiN–Ag [10], VN–Ag [11], TiN–Ag [12], YSZ (yttria-stabilized zirconia)–Ag–Mo [13], TiO_2–Au [14], MoS_2–Au [15], and Mo_2N–MoS_2–Ag [16]. These nanocomposite coatings are able to automatically and reversibly adjust their surface composition and morphology through multiple mechanisms, which is promising for the reduction of friction and wear over broad ranges of ambient conditions [17,18]. However, most nanocomposite coatings were unable to sustain a heavy load on a soft substrate because of limited layer thickness that was produced through a physical vapor deposition process [19,20]. It was essential to develop a low cost process to obtain a thick self-lubricating coating for practical applications.

Micro-arc oxidation (MAO) or plasma electrolytic oxidation (PEO) has been widely used to produce thick protective coatings on light metals to provide high wear resistance and adhesive strength to substrate materials [21,22]. Expectations are that low friction and wear resistant carbon containing composite coatings can be obtained through the micro-arc plasma oxidation on 6061 aluminum alloy with graphite in electrolyte solution. Recently, a duplex coating of MAO combined with a graphite spraying process on titanium alloy was developed by Wang et al. [23]. The results indicated that duplex coatings exhibited efficient antifriction properties. Skoneczny and Bara [24] created a thick composite ceramic–graphite surface layer by using duplex technology that included the electrochemical oxidation of the surface alloy and thermo-chemical carburization treatment. Lv et al. [25] attempted to add graphite grains to electrolyte to prepare ceramic coatings on aluminum through the micro-arc plasma oxidation. The results demonstrated that the coatings were less porous and more compact. Thus, the corrosion resistance of the coatings with embedded graphite grains was greatly improved. However, the tribological properties were not demonstrated in their studies.

Nie et al. [26] reported a duplex coating consisting of an oxide underlayer and oxide/graphite lubricant composite top layer to reduce the friction coefficient of the coatings. The duplex coating exhibited effective compatibility with the steel counterface during dry tribological tests. These duplex coating methods are inconvenient because they require a two-step coating process. Recently, Wu et al. [27] demonstrated that graphite incorporated Al_2O_3 ceramic coatings were obtained on an Al 2024 alloy substrate through the one-step micro-arc plasma

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oxidation in an aluminate–graphite electrolytic solution. No graphite phase was observed in the X-ray diffraction pattern. However, the C peak markedly increased in the energy disperse spectrum. Therefore, it could be concluded that carbon was presented in the coatings. The tribological test results indicated that the graphite incorporated MAO coatings exhibited a friction coefficient of 0.09 after a 500 s duration test. A long duration test of wear life has not been reported.

In the present study, a production of self-lubricating alumina–graphite composite coatings was attempted through one-step MAO on 6061 aluminum alloy. A long duration wear test was conducted to investigate the wear life and wear mechanisms.

2. Experimental

Rectangular pieces ($4 \times 4 \times 0.2$ cm^3) of aluminum alloy 6061 (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 the substrate. The surface roughness, R_a, was 0.2 μm as provided by the manufacturer. All samples were cleaned by DI water prior to the experiments. The electrolyte solution consisted of 5.56 g/L sodium silicate, 1.67 g/L sodium hydroxide, and (0, 4 g/L) of graphite particles with an average size of 1 μm (ranged from 0.5 μm to 6 μm, as provided by Homy Tech. Ltd., Taiwan). An SPIK 2000A pulse controller (Shen Chang Electric Co. LTD., Taiwan) was used to generate an asymmetric bipolar pulse with parameters of 200, 200, 360, and 200 μs for t^+_{off}, t^+_{on}, t^-_{on}, and t^-_{off}, respectively. Two electrical power supplies (PR Series, 650 V, 7.7 A, Matsusada) were connected to the pulse controller, with 100 V, 3.5 A for the cathodic biasing, and 500 V, 7.0 A for the anodic biasing.

The MAO treatments were conducted for 30 min, and the electrolyte temperature was controlled to lower than 25 °C, using a stirring and cooling bath system. The samples were cleaned with distilled water immediately after the MAO treatment, and then dried in the air.

The surface roughness, R_a, was measured using a stylus type surface profilometer (Mitutoyo, SJ310). The coatings' phase structure was investigated using X-ray diffraction (CuKα; XRD, X'Pert PRO MPD, PANalytical, Netherlands) with scans from 10 to 80°. The microstructural and chemical compositions of the coatings were investigated using a high resolution Scanning Microscope and Energy Dispersive X-ray (Hitachi SEM/EDX S4800). We performed the image analysis using Image Pro Plus 7.0 software (Media Cybernetics, Inc.) to estimate the total occupied surface area of the volcano-like (VL) microstructures of more than 10 different locations for each sample, while the volcano-like average number was estimated visually from the SEM top-view micrographs. The mean area of a volcano-like microstructure was evaluated from dividing the total area over the total number. The average of layer thickness was estimated from the SEM micrographs for 10 positions at the cross section. The hardness of the coating was determined using the micro-hardness tester with Vickers hardness at an applied load of 100 g at five different positions after a slight polishing of the surface. Friction and wear were measured using a pin-on-disk machine with a 5 mm diameter tungsten carbide/cobalt (3 wt.%) ball as the pin with a hardness of Hv 1800. The normal load was 5 N, the initial maximum Hertz contact stress was 1.7 GPa, the sliding speed was 100 rpm (13 cm·s^{-1}), and the friction force was monitored using a force transducer. The wear rate was obtained from estimation of the average depth of three different positions over the wear track. All the tests (except hardness test) were conducted over the ceramic coating as formed by the MAO treatment without post-treatment in air at approximately 30 °C, and the relative humidity was approximately 62%–75%.

3. Results

3.1. Microstructural characterization

Fig. 1 displays the surface microstructure of the MAO coating on Al alloy without and with graphite particles. Most of the surface area of the MAO coating was covered by volcano-like microstructures, which formed during discrete localized micro-discharge events. The rapid solidification of the molten alumina formed micro-cracks and accumulated particles on and around the discharge channels. The accumulated particles were denser and smaller in the sample prepared without graphite additives. By analyzing the SEM micrographs, the volcano-like (VL) microstructure occupied an average of 66% of the surface and the population was around 3200 mm^{-2} with an average area of 3.3×10^{-4} mm^2/VL for the volcano-like microstructure of the MAO coating without graphite additives. With the additive of graphite, the volcano-like microstructure was widened (average area 5.7×10^{-4} mm^2/VL) and the population was decreased to 1255 mm^{-2}, while the average of occupied area was 68%. Fig. 2 shows the elemental compositions of EDX study points over samples prepared by MAO without and with graphite additives in the electrolyte solution, while Fig. 3 shows the EDX surface mapping for the sample prepared with the additive of graphite particles. The elemental distributions were not uniform on the MAO coating. For both samples, the aluminum was dominant near to the craters, while its concentrations decreased as the study point moved away from the craters. More silicon was found in the accumulated particles. For the graphite additive sample, the carbon concentration gradually increased when it moved away from the craters.

The cross-sectional microstructure of the MAO coatings on Al alloy is demonstrated in Fig. 4. The thicknesses of the MAO coatings for 30 min were approximately 15 μm for both samples.

The surface roughness, R_a, was 1.16 and 1.40 μm for the sample treated without graphite and with graphite particles, respectively.

The elemental distributions of Al, C, and O are indicated in Fig. 5 for the sample treated with graphite particles. The cross-sectional elemental analysis revealed that the carbon concentration was not uniform in the MAO layers. Certain Al and O depleted regions were corresponded

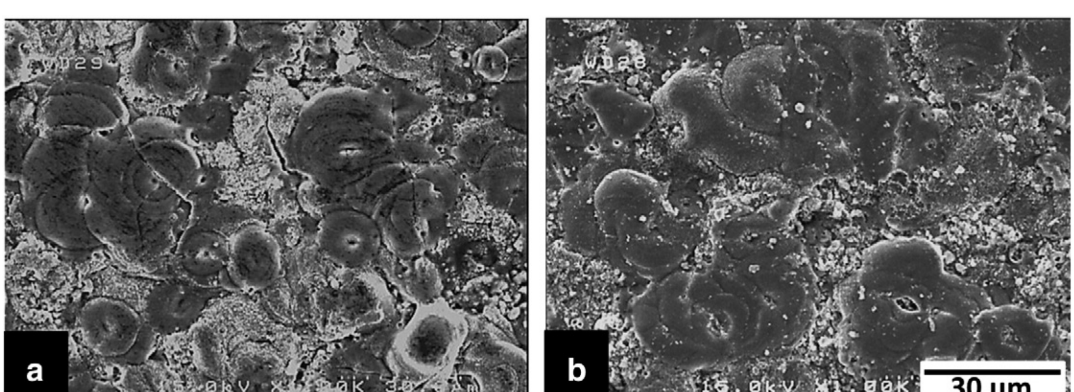

Fig. 1. SEM micrographs for MAO samples prepared (a) without and (b) with graphite additives in electrolyte solution.