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Structural properties of the oxide coatings prepared by electrolyte plasma process on the Al 2021 alloy in various nitrogen solutions

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Abstract

AlON–Al_2O_3 coatings on Al alloy 2021 were prepared in the eco-friendly electrolytes in various nitrogen inducing agents by the electrolytic plasma process (EPP) method. The ceramic coatings formed on 2021 Al alloy was carried out by EPP-treated at room temperature for 15 min. The coatings were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), ball-on-disc friction test and Vickers hardness test. It is found that coatings surface produced in $NaNO_2$, NH_4NO_3 and $NaNO_3$ additions have a homogeneous morphology of discharge channels. These coatings can protect the Al 2021 alloy substrate from the abrasion well.

Keywords: A. Films; Electrolytic plasma processing; AlON; Electrolyte

1. Introduction

The Al alloys are one of the most widely used materials in engineering for its favorable properties of light weight, corrosion resistance, thermal conductivity, nonmagnetic ability and low cost [1]. But Al alloys are vulnerable to such mechanical property as hardness and wear that limited its application in many fields. Surface treatment of Al alloys has become one of the most active fields for increasing hardness property. There are many surface treatment methods to prepare ceramic coatings on Al alloys for protection purposes such as arc-discharge plasma, gas-flame, spray and vacuum deposition. However, these techniques require a high temperature rise on substrates which seriously decrease their mechanics performance [2]. It is well known that electrolytic plasma process (EPP) method is a consistent researching for surface engineering. In this surface technique, some aqueous solutions are utilized as electrolytes for producing a gaseous medium which can be converted into plasma. Consequently, if a nitrating-rich electrolyte is used, Al alloy oxidation is possible [3]. Aluminum oxynitride (AlON) is a polycrystalline ceramic material with potential in applications requiring high strength [3]. Owing to its cubic spinel structure, polycrystalline AlON has thermal properties and favorable combination of good mechanism. The mechanical and tribological properties of the coatings were primarily studied [4,5].

2. Experimental

A column sample (D 20 mm × H 30 mm) of Al alloy 2021 (Cu, 5.8–6.8 wt.%; Mg, 1.2–1.8 wt.%; Si, 0.5 wt.%; Fe, 0.5 wt.%, Zn, 0.1 wt.%; Mn, 0.2–0.4 wt.%; Ti, 0.15 wt.% and Al, balance) was used as the substrate in the present study. The surface of the sample was polished by diamond paste to a uniform roughness of 0.1 ± 0.05 μm. It was degreased with acetone and alcohol in ultrasonic cleaner, and then immersed in the electrolyte for EPP treatment. The EPP treatment was carried out by a power supply of AC voltage at 50-Hz frequency (200 V) with constant 260 V DC power. The electrolysis environment was an aqueous electrolyte containing 10 g/l $NaAlO_2$, 2 g/l NaOH, and 0.3–1.1 g/l $NaNO_2$, NH_4NO_3 and $NaNO_3$. The temperature of the electrolyte was kept at 28 °C using the chiller and the reaction time is 15 min. The different phases present in the coatings were investigated by a Philips-X'Pert X-ray diffractometer (XRD) (Cu Kα radiation) and the scans were performed with 0.02° θ step size in the 2θ range of 20–90°. The microstructures of the polished cross-sections mounted in epoxy resin were studied by a JSM 5610 scanning

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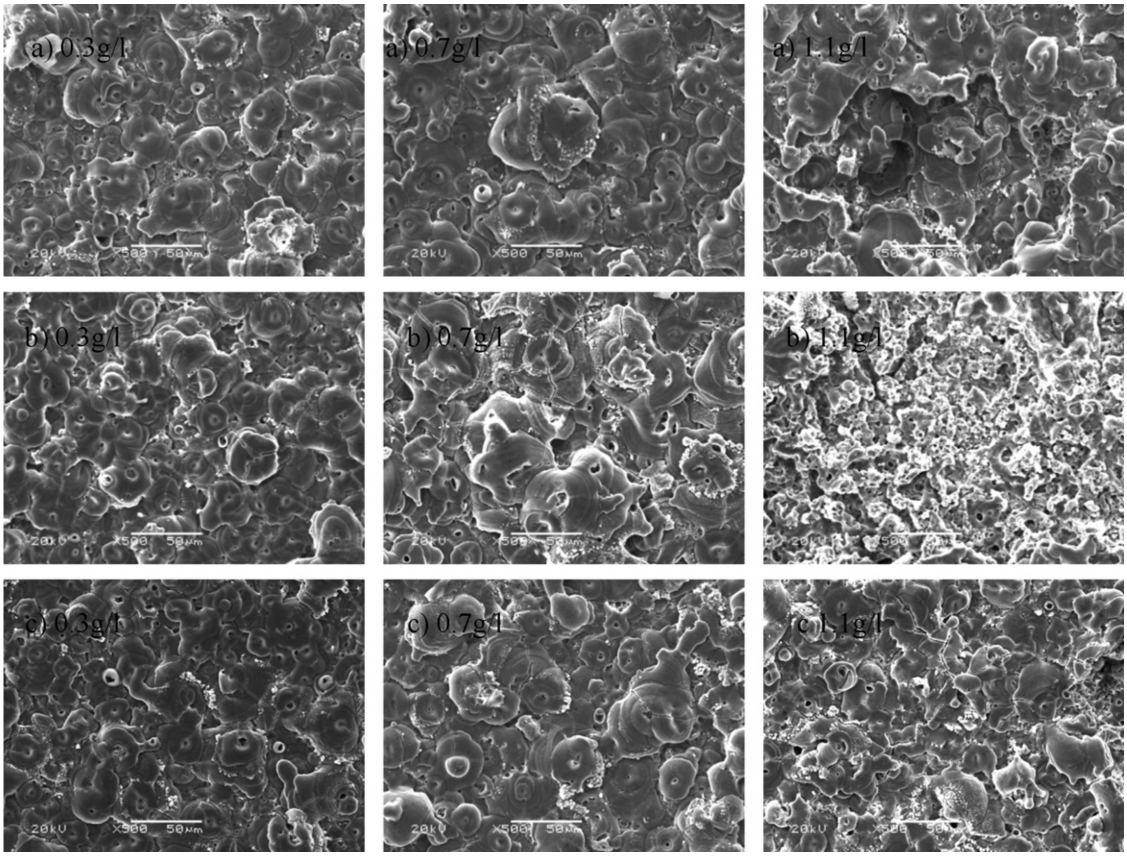

Fig. 1. The surface morphology of oxide coatings on Al alloy 2021 substrate by EPP treatment in different concentrations of (a) $NaNO_2$, (b) NH_4NO_3 and (c) $NaNO_3$.

electron microscopy (SEM). The microhardness of the coating layers was measured in 10 different places by a VLPAK2000 Mitutoyo hardness test machine using 0.01 N loads. In order to investigate the anti-abrasion properties of the oxide coatings, dry ball on disc wear tests were carried out by a PD-102 wear test machine.

3. Results and discussion

Fig. 1 shows the surface morphology of the coatings on Al alloy 2021 substrate treated by EPP method in different concentrations of NH_4NO_3 (0.3 g/l, 0.7 g/l, 1.1 g/l), $NaNO_2$ (0.3 g/l, 0.7 g/l, 1.1 g/l) and $NaNO_3$ (0.3 g/l, 0.7 g/l, 1.1 g/l) in 15 min. Pan-cake like microstructures were observed, as the center holes are the discharge channels. With increasing the concentrations of NH_4NO_3, $NaNO_2$ and $NaNO_3$, the uniformity and compactness of the surface increase at first from 0.3 g/l to 0.7 g/l. When the concentrations increased to 1.1 g/l, big pores appeared in $NaNO_2$ contained solution, many tiny pores in NH_4NO_3 contained solutions and the surface of $NaNO_3$ contained solution also became porous. With increasing the concentrations of nitrogen inducing agents, micro cracks on surfaces of these oxide coatings also increased. It is due to the high temperature gradients between the cool electrolytes and the discharge channels. Therefore, these cracks are formed by the molten oxide and gas bubbles through micro-arc discharge channels and rapid solidification of molten oxide in the cool electrolyte [6]. Due to the intensive thermal stress and great temperature gradients, the micro cracks initially appear at the sites of the center holes, and then spread to the borders [3]. Compared the coatings in different concentrations of nitrogen electrolytes, the sample in NH_4NO_3 contained electrolytes has more micro cracks.

Fig. 2 shows the XRD patterns of the oxide coatings on Al alloy 2021 prepared in various concentrations of $NaNO_2$, NH_4NO_3 and $NaNO_3$. It can be seen that all of the XRD patterns

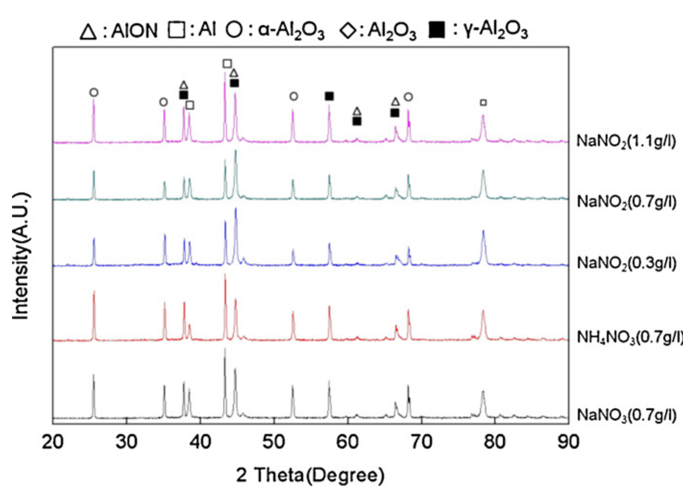

Fig. 2. XRD spectrum of the oxide coatings processed in various concentrations nitrogen inducing agents.

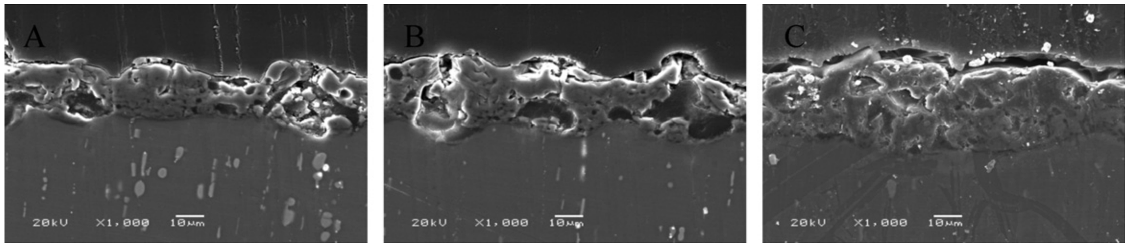

Fig. 3. Cross-section SEM micrograph of the coatings processed in (A) 0.7 g/l $NaNO_2$, (B) 0.7 g/l NH_4NO_3 and (C) 0.7 g/l $NaNO_3$ contained electrolytes, respectively.

revealed the presence peaks of Al, α-Al_2O_3, γ-Al_2O_3 and AlON phases. All the XRD patterns of the Al_2O_3 and AlON phases are at the same degrees. The AlON peaks remain same when all the concentrations of $NaNO_2$, NH_4NO_3 and $NaNO_3$ increased. It means that all those nitrogen concentration would results in the growth of AlON phase. To confirm this situation, we carried out the XPS tests for different samples in various nitrogen induced agents.

XPS tests were carried out to analysis the element types and contents in the coatings. Fig. 3 shows XPS spectrum of the samples treated by EPP in 0.7 g/l $NaNO_2$, 0.7 g/l NH_4NO_3 and 0.7 g/l $NaNO_3$ contained electrolytes, respectively, including none nitrogen induced electrolyte. The result indicates that the coating mainly consists of Al, C, Na, N, and O elements. It can be explained that Al and Cu elements are derived from the Al alloy substrate, while N, Na and O elements come from the electrolytes. It was conducted to analyze the existence of N which participated in the EPP reaction to form the AlON phase to increase the hardness and anti-abrasion properties of the oxide coatings. Nitrogen in electrolyte was incorporated successfully into the oxide film during the EPP process at 0.92% ($NaNO_2$ 0.7 g/l), 1.46% (NH_4NO_3 0.7 g/l) and 2.81% ($NaNO_3$ 0.7 g/l). It indicates that nitrogen would participate more actively in the EPP reactions for coatings treated in the $NaNO_3$ contained electrolyte.

The cross-section morphologies of the coatings treated in the electrolytes contained of $NaNO_2$, NH_4NO_3 and $NaNO_3$ with the concentrations of 0.7 g/l were observed by SEM (shown in

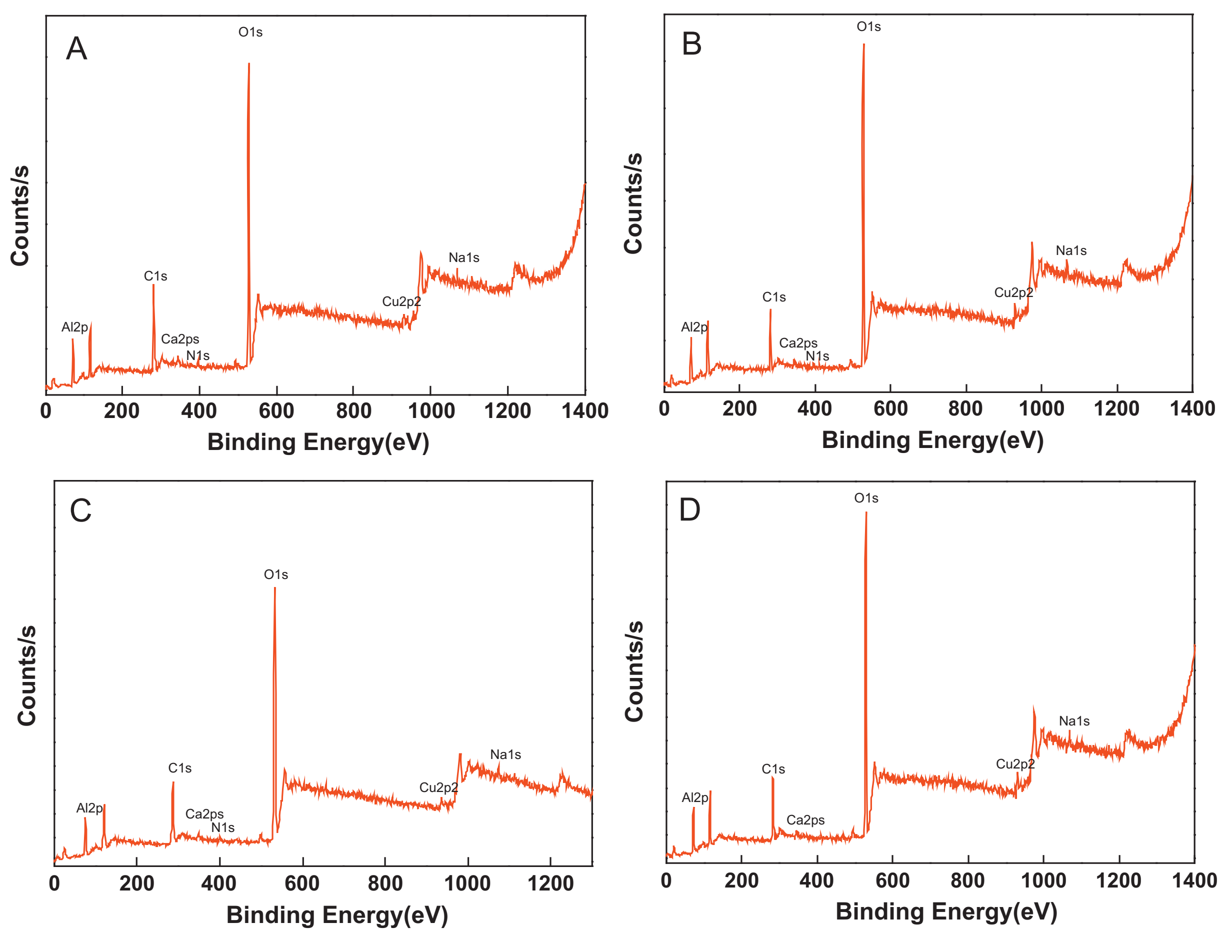

Fig. 4. XPS spectrum of the oxide coatings processed in (A) $NaNO_3$ (0.7 g/l), (B) NH_4NO_3 (0.7 g/l), (C) $NaNO_2$ (0.7 g/l) and (D) none.

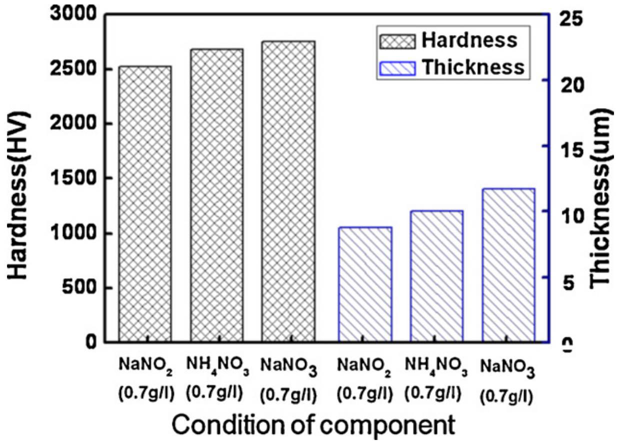

Fig. 5. Microhardness and thickness of the coatings processed in various concentrations nitrogen inducing agents.

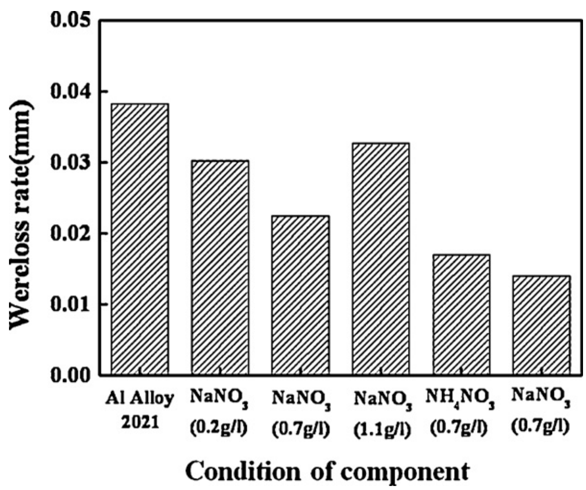

Fig. 6. Wears loss ratio of the coatings processed in uncoated Al substrate and the coated samples in various concentrations nitrogen inducing agents.

Fig. 4). The oxide coatings formed upon the substrates can provide a considerable strengthening effect on aluminum substrates [3]. It is seen that with increasing the content of nitrogen in the coatings, the coating increased accordingly. It is due to the formation of AlON phase could accelerate the growth of the coating. Also, the coating density increases due to the content increasing of nitrogen in the coatings.

Fig. 5 shows the microhardness and thickness of the coatings processed in the electrolytes contained of $NaNO_2$, NH_4NO_3 and $NaNO_3$ with the concentrations of 0.7 g/l. The results confirmed that the hardness and thickness of coatings dependent upon the nitrogen ratio and coatings thickness [3]. In $NaNO_2$ contained electrolyte, the hardness of coatings is about 2580 Hv, whereas the coating treated in NH_4NO_3 contained electrolyte can reach to 2700 Hv, and it can reach to 2750 Hv in $NaNO_3$ contained electrolyte. It is concluded that nitrogen amounts in the coatings have a positive effect to both the thickness and the hardness of the coatings.

Wear tests were carried out for the uncoated Al substrate (for purposes of comparison) and the coated samples in various concentrations of $NaNO_2$ (0.3, 0.7 and 1.1 g/l), NH_4NO_3 (0.7 g/l) and $NaNO_3$ (0.7 g/l) electrolytes. The results obtained from each concentration as cumulative weight loss are shown in Fig. 6. The EPP-coated aluminum alloy samples exhibited higher abrasive wear resistance properties than the uncoated aluminum alloy. The coating in 0.7 g/l $NaNO_3$ contained electrolyte, which is smooth, thick and hard, shows the lowest wear loss (seen in Figs. 1, 4 and 5). It can be explained by that the nitrogen content is helpful to form a clear and hard surface, which is advantage in the wear resistance properties of the coatings.

4. Conclusions

The coatings were formed on Al 2021 alloy in the electrolytes containing various concentrations of $NaNO_2$ (0.3, 0.7 and 1.1 g/l) and NH_4NO_3 (0.3, 0.7 and 1.1 g/l) under a hybrid voltage (260 V DC and 200 V AC) for 15 min. The coatings are mainly composed of γ-Al_2O_3, α-Al_2O_3 and AlON compounds which can provide hard and anti-abrasive properties. Electrolyte with proper concentration of nitrogen, especially $NaNO_3$, could result in a high-performance coating combined of a uniform surface.

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