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Investigation of Hybrid Composite Coating on ZA-27 Alloy Produced by MAO

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Abstract – In this paper, the steps in the production process of forming hybrid composite coatings on surface of the ZA-27 alloy known as a sliding bearing material, and analysis of surface morphology of the coated samples were investigated. The process includes forming an electrolytic solution with solid lubricant particles content in a stainless steel tank and coating procedures that called micro arc oxidation (MAO). The substrate materials used in this study are commercial ZA-27 alloy that produced by using die-casting method. Two different electrolytic solutions were used for the surface coating process. Electrolytic solutions include solid lubricant particles (graphite and hexagonal boron nitride (h-BN)). The results showed that both graphite/Al_2O_3 and h-BN/Al_2O_3 hybrid composite coating were successfully grown on surface of the ZA-27 alloy. The structural and chemical compositions of the both coated samples were analyzed using scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS) and X-ray diffraction (XRD). In the meantime, coating thickness were also determined.

Keywords – MAO coating, ZA-27 alloy, Solid lubricants, hexagonal boron nitride, graphite

I. Introduction

Zinc aluminum alloys (ZA alloys) exhibit unique of combination of properties such as high strength and hardness, high resistance to wear and corrosion, good cast ability and machinability, together with low production costs [1]–[6]. Due to these versatile properties, ZA alloys have increasingly became popular materials for engineering components (such as thrust washers, wear-plates, journal bearings, bushings, and so on) in machinery and automotive industry [7]–[14].

Commercially available ZA alloys are classified as ZA-8, ZA-12 and ZA-27 alloys according to their approximately aluminum content in the alloys [15]. Among these alloys, ZA-27 is the lightest alloy and offers better bearing performance and wear resistance properties [16]. However one of its major limitations has been property deterioration at temperatures above 100 °C. This is seriously limited its applications in industry [17], [18].

Numerous attempts have been made to reduce elevated temperature sensitivity of the ZA-27 alloy [19]–[24]. Difficulties and long processing period in used current techniques have led us tend to simpler and cheaper production techniques like surface treatment. One of them is called micro arc oxidation method (MAO). This coating technique is a low-costed and effective technique that modifies and enhances the surface properties of materials for increase service life in demanding contact condition or various environment such as at high-temperature applications [25]. This method has been extensively applied on light materials such as aluminum, titanium, magnesium and their alloys. But, investigations of the application of MAO on ZA alloys are still restricted with rare exceptions.

In this study, hybrid composite coatings, including solid lubricant particles, were grown on surface of the ZA-27 alloy using MAO method. The microstructure and composition analyses of the coatings were performed with scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), and X-ray diffraction (XRD).

II. Materials and Method

Die-cast ZA-27 alloy were used as the substrate materials that produced by a company. The chemical composition of the alloy, taken from producer company catalog, (in wt. %) was 25.5-28 % Al, 2-2.5 % Cu, 0.012-0.02% Mg, ≤0.07% other elements, Zn balance. Prior to MAO process, the samples with a dimension of 30 mm diameter and thickness of 2.5 mm were successively polished with SiC abrasive papers up to 1200 grits (Ra≈0.1). Then, samples were cleaned with acetone, ethanol, and pure water and dried, respectively.

The MAO process of ZA-27 alloy were carried out in the coating system produced by Faraday Electronic, Ltd. Two different electrolytes were prepared in this study. (a) Na_2HPO_4 (8 g/lt), Na_2SiO_3 (6g/Lt), KOH (2g/lt) and graphite (≈800-900nm size (6 gr/lt)), (b) Na_2HPO_4 (8 g/lt), Na_2SiO_3 (6g/Lt), KOH (2g/lt) and h-BN (≈20-30μm size (6 g/lt)).

An AC power source, in the bipolar mode operating at 450/−100 V, was used to perform the process at a constant frequency of 250 Hz. The MAO process was run for 15 min. In both experiments, the ZA-27 samples were used as the anode and the stainless steel tank walls were used as the cathode. The electrolyte temperature was controlled at low than 30 °C. After the MAO process, the samples were washed with pure water, then cleaned with ethanol, and subsequently dried.

Scanning electron microscopy (SEM) was used to observe the surface morphology and coating thickness. X-ray diffraction (XRD) was performed using with a Cu-Kα

radiation source. The measurements were conducted over a scan range between 20° and 80° at a scan speed of 2°/min.

III. RESULTS AND DISCUSSION

Two MAO coatings were formed on ZA-27 substrates in different electrolytic solutions at a constant current density of 1 A/dm^2 after micro arc oxidation treated for 15 min.

During the coating processes of all samples the applied voltage was slowly increased, within 20s, up to the 450/-100 V and then kept constant for 160 s. Within the initial instants, increase of the voltage led to a severe linear increase in the current and then by reaching to breakdown (spark) voltage of the samples a little increase in the current was seen. When the applied voltage reached 450/-100 V and was fixed, the current decreased sharply during 20-50s and finally reached to a constant amount. From 400 s, micro arc oxidation occurred with numerous sparks on each sample surface [26], [27].

The arc starting time and arc starting voltage during the MAO process is different in different electrolytes. The addition of graphite or h-BN into the base electrolyte (Na_2HPO_4, Na_2SiO_3 and KOH mixed) caused the variations of arc starting time and arc starting voltage. Compared with each other, the arc starting time changed obviously long and the arc starting voltage increased in the electrolyte with h-BN additives (electrolyte-(b)). However, the arc starting time largely decreased and the arc starting voltage slightly decreased in graphite additives (electrolyte-(a)), indicating that the hybrid composite coating film could be quickly formed in this composite electrolyte. Figure 1 shows the surface SEM microstructure of the coatings formed in electrolyte-(a) and (b). Most of the surface area of the MAO coating formed in both electrolyte were covered by volcano-like micro-structures as shown in Figure 1 (a) and (c). Figure 1 (b) and (d) show the agglomeration of particles on the surfaces (randomly selected) of both coatings.

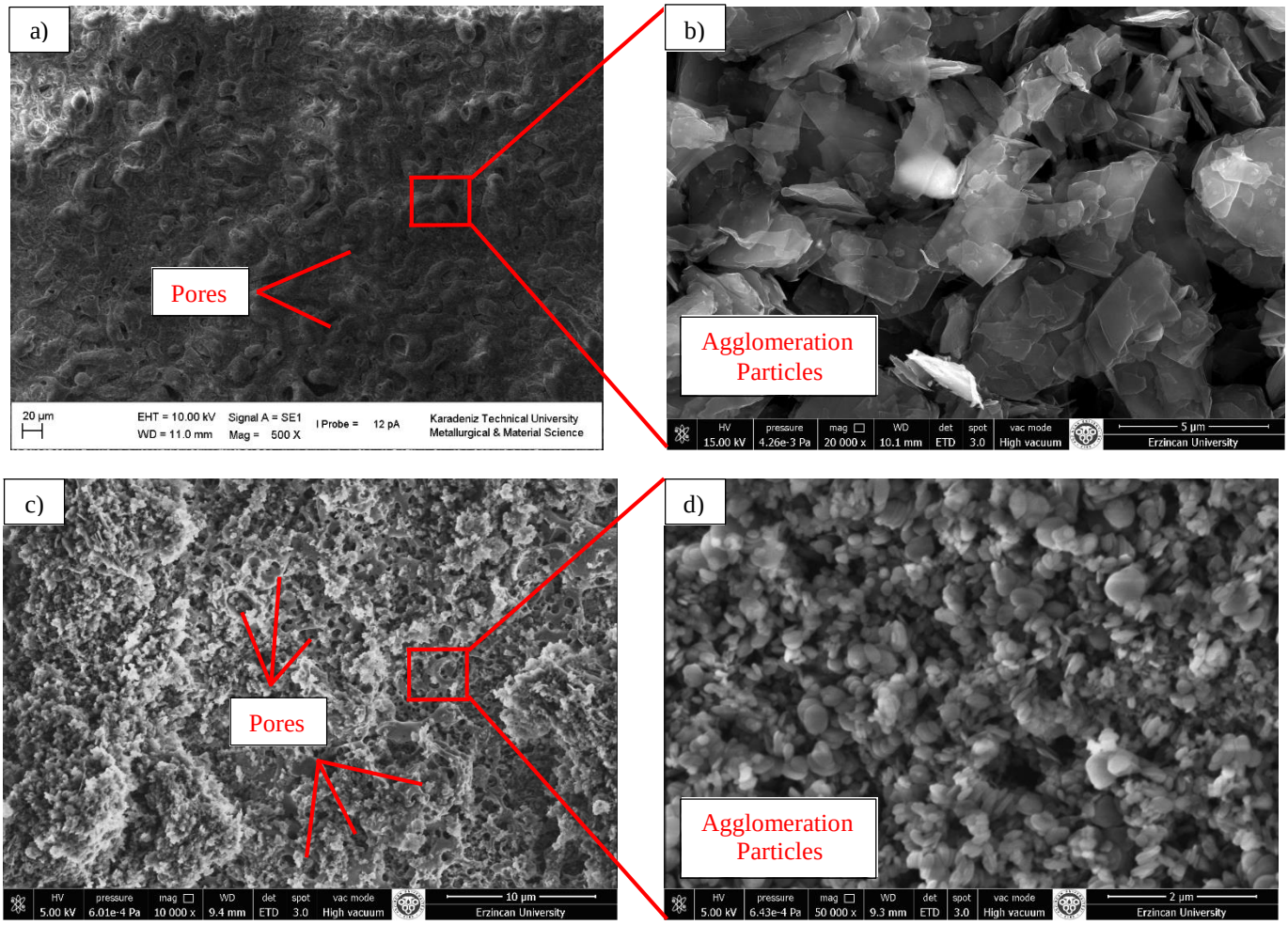


Fig. 1 Surface SEM microstructure of the coatings formed in electrolyte with a, b) graphite additives (electrolyte-(a)) and c, d) h-BN additives (electrolyte-(b))

The surface morphology of the coatings had significant changes compare to each other. The pores on the coatings formed in electrolyte-(a) became smaller as shown in Figure 1 (a), exhibiting a relatively uniform. So it could be seen that the additional particles were denser and smaller in the sample prepared with electrolyte-(a). There is significantly limited literature on this subject. However, the results are in parallel with the literature [28]. With the addition of particle, the volcano-like microstructure was full of them. Because of the rapid solidification of the molten oxide formed micro cracks and additional particles on and around the discharge channels [29]. It is clearly seen at the Figure 1. The particle size of the graphite was smaller than h-BN. So the surface that coated in electrolyte-(a) is more uniform than the other (Figure 1).

The discharge of the electrolytes added with h-BN had higher discharge voltage than that of the electrolyte with graphite additives. This result may be attributed to the fact that the added h-BN changed the electrical conductivity of the electrolyte. In this study, the presence of graphite particles increased the electrical conductivity of the electrolyte and then accelerated the production of a gas medium layer on the

sample surfaces [30]. Because of this phenomenon the coating thickness was increased (Figure 2).

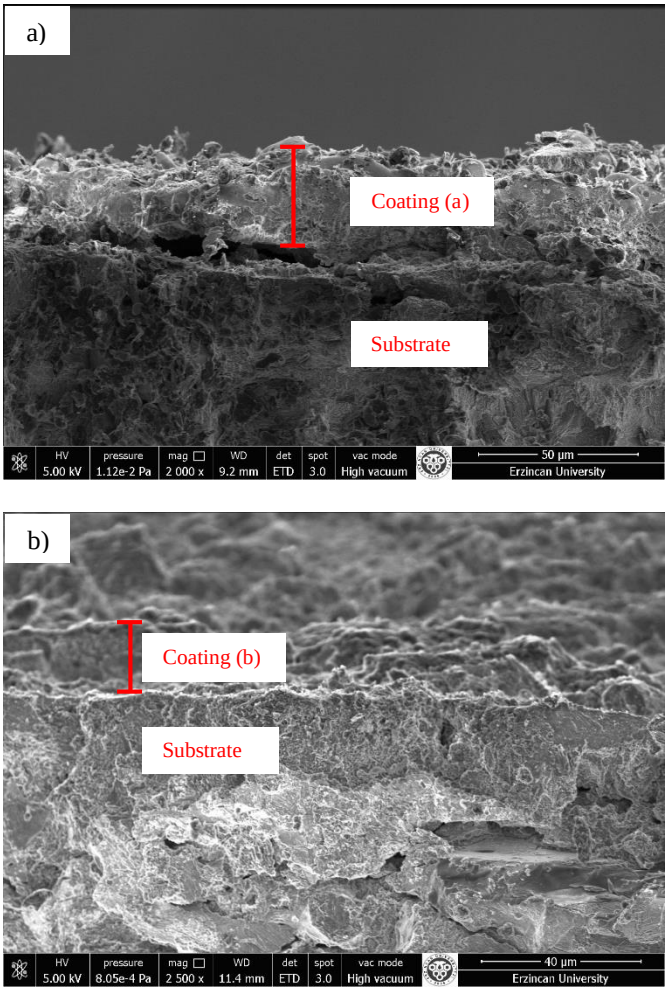


Fig. 2 Cross section of the MAO hybrid composite coating layers a) graphite/Al_2O_3 and b) h-BN/Al_2O_3

As a result, a hybrid composite coating with a maximum thickness of 25 µm was obtained in the electrolyte-(a) which contained graphite additives. And also it could be seen that the thickness of samples that coated in electrolyte-(b) was 15µm.

The XRD results of the coated and uncoated samples were shown at Figure 3. The figure shows that all the hybrid composite coatings were mainly composed of Al_2O_3 and $ZnAl_2O_4$. Other researchers also obtained the same conclusion [31]. No diffraction peaks of graphite were observed in the XRD patterns [29], [30]. But the variation of uncoated ZA-27 peak intensity in both coated samples might be caused by the different orientations of ZA-27 substrate. When graphite particles were added to the electrolyte solution, some phases were observed such as η-Al_2O_3, Al_4C_3, Al_2OC and Al_4O_4C phases, Figure 3 [29]. XRD results also support the h-BN particles peaks. When peaks were compared with literature, the presence of h-BN peaks was determined [32].

The elemental compositions of the coatings are detected by EDS and are listed and shown at Figure 4. The coatings formed in the two different electrolytes were mainly composed of Na, K O and Si. Na, K, Si and O were from the electrolyte, while the Al and Zn were believed to be from the ZA-27 substrate. The MAO coating formed in the electrolyte with graphite additives contained in electrolyte-(a). It should be noted that, adding graphite and h-BN into the base solution, the Al and Zn concentration in coatings obviously decreased and the C, B and N concentration in coatings strongly increased compared with the uncoated ZA-27 substrate. The high temperature and high pressure conditions caused by micro arc discharges led to h-BN and C doping into the ceramic coatings.

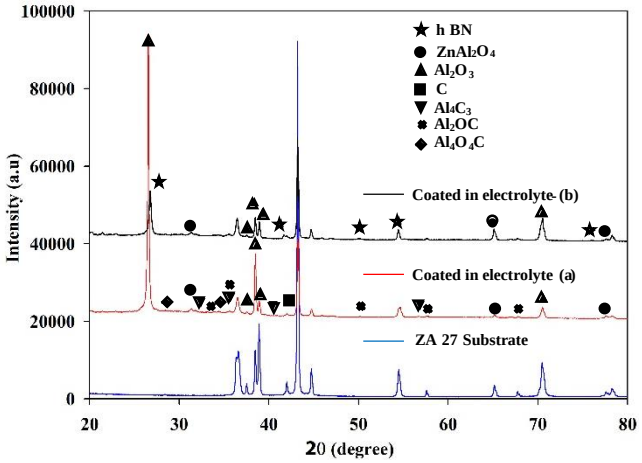


Fig. 3 XRD patterns of substrate, MAO coatings formed in electrolyte with graphite additives (electrolyte-(a)), and h-BN additives (electrolyte-(b))

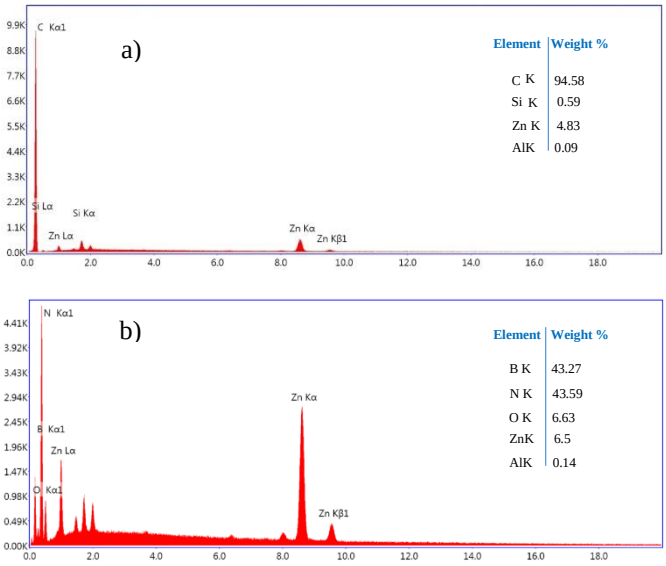


Fig. 4 EDS analyses of MAO coatings formed in electrolyte with a) graphite additives (electrolyte-(a)), and b) h-BN additives (electrolyte-(b))

IV. CONCLUSION

In the present study, hybrid composite coatings containing graphite and h-BN particles were coated on ZA-27 alloy by MAO process in two different electrolytes and the results can be summarized as follows:

- The arc starting time changed obviously long and the arc starting voltage increased in the electrolyte with h-BN additives (electrolyte-(b)).
- The arc starting time largely decreased and the arc starting voltage slightly decreased in graphite additives (electrolyte-(a)), indicating that the hybrid composite coating film could be quickly formed in this composite electrolyte.
- Electrolyte composition significantly influenced thickness, roughness and chemical composition of coatings.

- The presence of graphite particles increased the electrical conductivity of the electrolyte.
- The high temperature and high pressure conditions caused by micro arc discharges led to h-BN and C doping into the ceramic coatings.

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