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Formation of aluminum phosphate coating on graphite by cathodic electrochemical treatment

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ABSTRACT

Electrochemical treatment is a new method for accelerating the phosphating processes at low temperatures that can be performed as cathodic and anodic treatments. In this study, aluminum phosphate coating was deposited on graphite by cathodic electrochemical treatment, and, then heat treatment was performed on it. Microstructure, chemical composition, phase structure and adhesion of the coating produced in current densities of 35, 45, and, 55 mA/cm^2, temperatures of 55, 70, and, 85 °C, and, treatment types of a three-layer coating at 120 min and a single-layer coating at 360 min were characterized using a scanning electron microscope, energy dispersive X-ray analysis, X-ray diffraction, and, scribe-grid test. The results revealed that the three-layer aluminum electrophosphate coating deposited in the current density of 35 mA/cm^2, temperature of 70 °C, and, treatment time of 120 min was favorable due to a dense microstructure, suitable thickness, and, good adhesion. Furthermore, the phase that was formed in this coating was characterized as $Al(PO_3)_3$.

1. Introduction

Phosphates are widely used in various industries such as in refractories industry and in high-temperature applications. Aluminum phosphate is one of the phosphates used as sealing in refractories or as coating for protecting materials (especially carbon materials) against oxidation at high temperatures [1–4]. Good strength, high-temperature stability and abrasion resistance are other desirable properties of aluminum phosphate [1, 5]. Aluminum phosphate is synthesized by dissolution of aluminum hydroxide in orthophosphoric acid in specific molar ratios. The produced gel is heat treated again to produce a coating layer of aluminum phosphate [6, 7]. Heat-treatment is performed in order to achieve an amorphous solid or crystalline phases depending on heating temperature and interaction between the aluminum phosphate and the base material [8]. The physicochemical properties of aluminum phosphate depend on the molar ratio of phosphorus and aluminum in its composition that depends on the intended applications. If the amount of phosphorous is too high in the aluminum phosphate composition, pore-filling and hydrophobic capability will be improved. However, by increasing the amount of aluminum in the aluminum phosphate composition, the refractoriness capability and high thermal stability are achieved [9, 10].

Aluminum phosphate has been used as an oxidation resistant coating on graphite. However, there are very few published researches with a focus on formation of aluminum phosphate on graphite as an anti-oxidant coating. Lu et al. [3] utilized a chemical method for deposition of aluminum phosphate on carbon material that required high temperature and time for completion. Energy demand, as a major crisis in the present-day scenario, is the main drawback associated with the necessity of high temperature and time of operation in the mentioned technique. The second issue is the overheating of the bath solution, which causes an early conversion of the primary phosphate to tertiary phosphate before metal which results in an increase in the free acidity of the bath and consequently delays the precipitation of the phosphate coating. With respect to the recent advancements, it is possible to use an electrochemical method for phosphating process in which current density acts as an accelerator to obtain a thick phosphate layer at a lower temperature and time operation [11–14].

The electrochemical methods can be carried out using cathodic and anodic treatments. Both cathodic and anodic treatments can affect the deposition mechanism, porosity, and, other properties of the formed coating. According to the studies, in the cathodic electrochemical treatment, dissolution rate of the substrate is low and the coating is thicker and denser compared to the anodic electrochemical treatment [13, 15].

Formation of aluminum phosphate coating on graphite by cathodic electrochemical treatment has never been studied ever. Hence, in the present paper, we report the formation of the aluminum phosphate coating on graphite by cathodic electrochemical treatment in which the effect of current density, temperature, and, treatment type on

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Table 1
The basic properties of graphite substrate.

Carbon content	98%
Density	1.55 g/cm^3
Flexural strength	30 MPa
Electrical resistivity	7×10^{-4} Ω·cm

Table 2
Chemical composition of the bath.

Composition	Amount (gr/lit)
Phosphoric acid (85%)	1013
Aluminum hydroxide	137
Ethanol	7.5
Distilled water	167
Tween 80	0.1

aluminum phosphate coating properties such as microstructure, chemical composition, phase contents, and, adhesion have been investigated.

2. Experimental

The basic properties of the graphite substrates, which were utilized in this study, were given in Table 1. In order to prepare the substrate, first of all, the graphite cylindrical samples were cut in diameter and height of 2 cm; afterwards, samples were wet-polished with emery papers SiC grades #600 to #1200 grits. The oil and the greasy matter present on the samples were removed by electrolysis in a 10% NaOH (with a purity higher than 98%) solution for 30 min. The electrolysis was carried out by a direct voltage of 5 to 6 V, and, a current density of 0.05 to 0.1 A/cm^2, between graphite (anode) and copper (cathode). Next, to pickling, the samples were immersed in 10% HNO_3 (65%) for 10 min. They were rinsed twice with distilled water in order to remove acid residues present on them. The prepared samples were subject to deposition of aluminum phosphate with cathodic electrochemical treatment. The chemical composition of the bath used for the cathodic electrochemical treatment has been presented in Table 2. Ethanol was added to the bath to make a viscous slurry with a controlled vigorous evolution of gas [16, 17]. Also, Tween 80 as a wetting agent causes better adhesion of the coating to the graphite substrate during cathodic electrochemical treatment and plays a role in improving the penetration and retention of the metal phosphate and phosphoric acid [18, 19]. Platinum plate was used as anode and graphite cylindrical substrate was used as cathode. In order to the coating to be uniformly distributed throughout the graphite cylindrical substrate, it was rotated by the motor inside the electrolyte. Deposition of the aluminum phosphate coating was carried out under galvanostatic conditions at current densities of 35, 45, and, 55 mA/cm^2, temperatures of 55, 70, and 85 °C and deposition times of 120 min (in three-layer coating) and 360 min (in single-layer coating). After deposition, a gel coating was formed on the surface of the samples. The samples were then dried in air at 200 °C for 1 h to remove water present in the coating. This was followed by heating the samples to 800 °C at a rate of 10 °C/min under nitrogen atmosphere and holding them for 20 min at this temperature. The obtained coating has very little thickness and cannot completely fill all

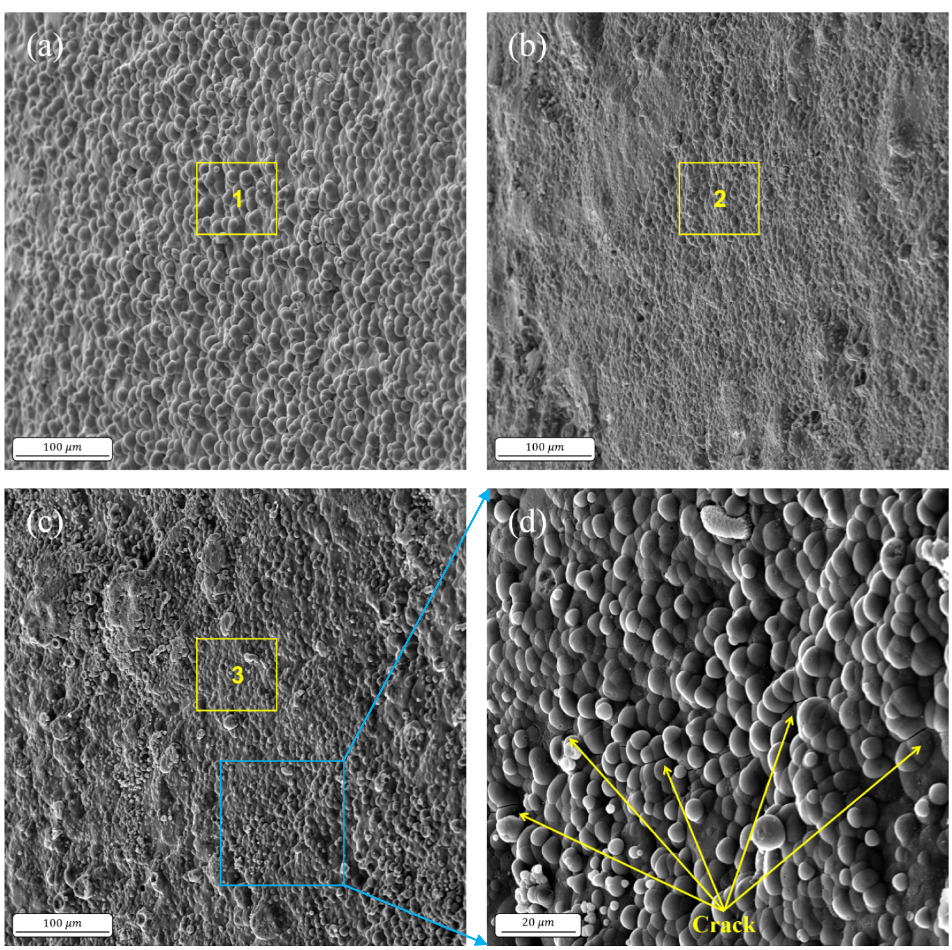

Fig. 1. SEM micrographs from the surface of three-layer aluminum electrophosphate coating at different current densities. (a) 35 mA/cm^2, (b) 45 mA/cm^2, (c) 55 mA/cm^2, (d) A higher magnification from the specified rectangular area.