Morphological evaluation of graphite substrates coated with alumina nanoparticles deposited by electrophoresis

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Abstract. Due to its high electrical conductivity and unique refractory properties, graphite has been widely used in several industrial applications. However, one of the major disadvantages associated with its use lies in its low mechanical resistance to shear stress. Therefore, for engineering applications that involve frictional stress, the surface mechanical properties of graphite need to be improved. Alumina (Al₂O₃) is a ceramic material that shows stability at high temperatures, as well as mechanical and corrosion resistance. The present study focused on the morphological evaluation of Al₂O₃ nanoparticle coatings produced via electrophoretic deposition (EPD), as a first step towards developing graphite-based materials with enhanced resistance to shear stress. The deposition of alumina on graphite samples was evaluated, and the influence of the following process parameters was studied: colloid stability and charge, EPD applied voltage and substrate characteristics. Colloidal stability was measured by Z potential and the morphology and rugosity of the obtained coatings was evaluated by confocal microscopy. A stable, regular, and homogeneous alumina coating was successfully obtained on graphite substrates, using EPD. The characteristics of the coating were strongly related to the Z potential of the precursor colloid, the substrate roughness, the applied voltage and the sintering process.

1. Introduction

The development of composite materials allows for the combination of different individual qualities in order to give rise to materials with enhanced properties [1]. Alumina is widely used in industry due to its remarkable mechanical properties [2]. Moreover, carbon in the form of graphite has a high range of applications, although it exhibits relatively low tribological properties. An electrophoretic process allows for the fabrication of coatings, based on a colloidal suspension containing the particles to be deposited, which are subjected to an electric field that forces them to migrate to a target substrate. In the present study, alumina nanoparticle coatings were prepared on graphite rods by electrophoresis, followed by a subsequent sintering process in order to enhance the mechanical properties of the resulting ceramic coating [3]. The influence of several synthesis parameters on the morphology and coverage of alumina coatings was analysed. To ensure proper preparation of the nanoparticle suspension precursor, zeta potential tests were carried out [4], whereas coating morphology was evaluated by confocal microscopy.
2. Experimental Procedure

2.1. Substrate preparation
Graphite samples of cylindrical (2mm x 150mm) and parallelepipedal (10mm x 7mm x 4mm) shape (see figure 1(a)), were used as substrates for all the experiments reported in this study. Prior to coating deposition, substrates were polished using SiC paper of three different grit sizes: 120, 320 and 600. After this, samples were cleaned by rinsing with water followed by sonication (10 min) using ethanol.

2.2. Preparation of nanoparticle colloidal suspensions
Al₂O₃ nanoparticle suspensions were prepared in a 90:10 ethanol: water (vol:vol) solution. In order to evaluate colloidal stability, the zeta potential of the suspended Al₂O₃ nanoparticles (5 nm, US Research Nanomaterials, Inc.) was measured at different pH conditions, employing a Zetasizer Nano S90 system (Malvern). The pH of the nanoparticle suspensions was adjusted using either HNO₃ or NH₄OH. The media that provided favorable suspension stability was selected for use in the electrophoretic deposition (EPD) process.

2.3. Electrophoretic deposition of Al₂O₃ nanoparticle coatings
The EPD cell used in this study consisted of five stainless-steel (316L) slabs welded together to form a cubic cell (2.5 cm x 2.5 cm x 2.5 cm), which worked as the anode, as shown in figure 1(b). A plastic cell lid was also machined and the graphite substrate, which served as the cathode, was positioned at the center of the cell, parallel to the cell walls. The volume of the deposition bath was 10 ml, and both electrodes were connected to a high voltage power supply that applied a fixed voltage (20, 40, 60 and 80 V) for 5 min.

2.4. Al₂O₃ coating sintering and characterization
Once deposited on the graphite substrates, the Al₂O₃ nanoparticle coatings were subjected to heat treatment at 1200 °C for 1h, under inert atmosphere. A heating ramp of 5 °C/min was used, whereas the cooling rate after dwell time was 7 °C/min. The morphology of the sintered Al₂O₃ coatings was characterized by confocal microscopy using a Hirox 3D digital microscope.

3. Results and Discussion
The results from zeta potential measurements are presented in figure 2, which shows the variation of the zeta potential of the nanoparticles as a function of the solution pH. It can be noted that for strongly acidic suspensions (pH < 4) the Z potential values exceeded 30 mV, whereas stabilization (~ 20 mV) occurred at pH values between 4 and 8. The isoelectric point (iep) of the solution was reached at pH = 9.8, while the Al₂O₃ nanoparticles were negatively charged in strong alkaline solutions. These results are in agreement with previous reports that indicate that Z potential variation depends on the adsorption of H⁺ and OH⁻ ions on the particle surface and that these two types of adsorption are equal at the isoelectric
point of the colloidal suspension [5]. The stability of the colloid depends on the electrical permissiveness of the medium and the magnitude of the zeta potential, being unstable as these values approach the isoelectric point, which could possibly cause coagulation of the suspension.

![Zeta-potential vs pH](image)

**Figure 2.** Variation of the Z potential of Al₂O₃ nanoparticles as a function of solution pH.

The chronoamperometric response of the alumina nanoparticles EPD on cylindrical graphite electrodes is show in figure 3(a). It is observed that the magnitude of the current increases proportionally as a function of the applied potential, which is in agreement with what would be theoretically expected. According to Ohm’s Law, the conductivity of a substrate varies as a function of coating thickness, and stability is due to the stable resistance and the very low levels of hydrolysis of the alcohol in the electrolyte [6]. Figures 3(b)-3(e) show the Al₂O₃ nanoparticle coatings obtained by EPD at different voltage conditions. Using 80 V resulted in a layer with pores and agglomerates, whereas the coating fabricated at 60 V presented some imperfections as well. On the other hand, improved coating homogeneity was found when using 40 V and 20 V (figures 3(d)-3(e)). These results indicated that using a fixed voltage of 20 V or 40 V provided favorable conditions for the Al₂O₃ nanoparticle EPD process.

![Chronoamperometric response](image)

**Figure 3.** (a) Chronoamperometric response of alumina EPD varying the voltage (suspension pH = 2, particle concentration = 13 mg/L), Coatings obtained at: (b) 80 V, (c) 60 V, (d) 40 V, and (e) 20 V.

Figure 4 shows the chronoamperometric response of alumina EPD performed with varying electrode roughness. All curves present the expected behavior, with a sharp reduction of the current during the
first seconds followed by a stabilization zone [7]. The difference across the three evaluated rugosities is the magnitude of the stabilized current, showing a significant increase as the surface rugosity of the electrode increased (see insert). This variation could be related to the electrochemically active area that is available, since it becomes greater as the rugosity of the surface increases as well.

The alumina coatings obtained varying the surface rugosity of the graphite substrates were thermally treated at 1200°C during one hour to promote the sintering of the nanoparticles. During this treatment, two important processes occur simultaneously: the first one is the nanofusion of the particles surface that promotes the neck formation and the cohesion between the nanoparticles through superficial interdiffusion; the second process is the thermomechanical expansion that depends on the expansion coefficient and generates internal stress. If the substrate and the coating show a large difference in the expansion coefficient, the interfacial forces could generate decohesion of the coating and subsequent crack formation [8]. The surface of the treated samples was evaluated by confocal microscopy, and surface roughness was calculated based on the obtained images.

**Figure 4.** Chronoamperometric response of alumina nanoparticle EPD using different electrode rugosities: Abrasive Paper (A.P.) of grit sizes 120, 320 and 600. (E = 40 V, pH = 2, particle concentration: 13 mg/L).

Figure 5(a) shows the variation of coating roughness relative to the initial electrode (substrate) roughness. For all the evaluated samples, the difference in roughness between the coating and the bare substrate appears to be similar [9]. This change in surface topography is related to crack formation during thermal expansion (figures 5(b)-5(g)). From the 3D images, it can be seen that the cracks formed preferentially on the valley location and not over the peaks; this phenomenon is related to the tension accumulation in the valleys. Finally, comparison of crack depth and distribution across samples indicated that cracks were randomly distributed and weakly related to the bare substrate roughness for coatings prepared on substrates with the lowest roughness [10].
Figure 5. (a) Effect of abrasive paper grit size on the surface roughness of the uncoated substrate and the deposited coating. (b) and (c) Confocal image (280X magnification) and 3D reconstruction of EPD coating with highest roughness; (d) and (e) medium roughness; (f) and (g) lowest roughness.

4. Conclusions
Stable, regular and homogeneous alumina coatings were successfully deposited on graphite substrates by EPD. The characteristics of the coatings were strongly related to the Z potential of the colloids, the rugosity of the substrate, the voltage applied, as well as the sintering process. This process could be useful to modify the surface of graphite elements in order to improve their tribological properties.

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