Influence of process parameters on the electrophoretic deposition of zirconia nanoparticle coatings

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Abstract. Ceramic coatings have been widely used to enhance material surface properties, such as corrosion and wear resistance. Towards this goal, several coating fabrication techniques, including plasma spray, sol-gel, physical/chemical vapor deposition, as well as electrophoretic deposition (EPD) have been studied. EPD offers the advantage of a relatively simple and economic method that requires low deposition times. In this context, the purpose of the present work was to study the effect of EPD process parameters on the morphology of zirconia (ZrO₂) nanoparticle coatings fabricated onto a graphite substrate. To achieve this, the stability of the colloidal precursor was first evaluated using zeta potential measurements of nanoparticle suspensions of different pH values. Moreover, EPD parameters such as applied voltage and nanoparticle concentration in the precursor solution were varied in order to gain insight into the chronoaamperometric response of the prepared coatings. A clear effect of both, voltage and nanoparticle concentration in the precursor was observed. Furthermore, the influence of substrate preparation conditions on the morphology of the resulting coatings was also analyzed. Surface treatment prior to coating deposition appeared to impact the roughness of the final ZrO₂ coating.

1. Introduction
Electrophoretic deposition (EPD) is an electrokinetic phenomenon in which a colloidal suspension is exposed to an electric field [1] in order to promote particle migration and eventual deposition onto a substrate, resulting in the formation of a coating. Due to its high versatility and relative low cost, EPD has been widely studied for the fabrication of thin ceramic and metallic films [2]. Besides requiring a simple apparatus, EPD allows to control coating morphology by varying the deposition process parameters [3]. This represents a remarkable advantage in the context of the development of coatings with defined structures at both, the micro and nano scales [2]. The effectiveness and reproducibility of the EPD method relies primarily on the properties of the colloidal suspension that contains the particles to be deposited, which should exhibit a zeta potential that ensures adequate particle dispersion in the precursor solution. Otherwise, low levels of particle dispersion lead to the formation of agglomerates, which in turn result in poor coating adhesion and irregular morphologies after sintering [4]. In this context, the aim of the present work was to carry out preliminary studies into the influence of several process parameters on the EPD of ZrO₂ nanoparticle (20 nm) coatings, using graphite as the substrate. Given the remarkable mechanical strength and thermal properties of zirconia films, the development of approaches for the cost-effective fabrication of ZrO₂ coatings will remain a topic of great interest in areas such as the creation of thermal barrier coatings, as well as hard coatings for anticorrosive applications.
2. Experimental Procedure

2.1. Substrate and colloidal suspension preparation
Graphite samples (10 mm x 7 mm x 4 mm) were used as substrates. Prior to coating deposition, sample surfaces were polished using SiC paper of different grit sizes: 120, 320 and 600. In order to evaluate the stability of zirconia nanoparticle suspensions, and thus select a medium that favored particle dispersion, ZrO$_2$ nanoparticles (20 nm, US Research Nanomaterials, Inc.) were added to ethanol: water (90:10, vol.) solutions of varying pH values. A 90:10 ethanol:water mixture was used in order to increase the stability of the electrolyte and decrease the evaporation rate of the solution. The zeta potential of these colloidal suspensions was measured on a Zetasizer Nano S90 (Malvern). The pH of the suspensions was adjusted by adding either HNO$_3$ or NH$_4$OH

2.2. ZrO$_2$ nanoparticle coating fabrication
For ZrO$_2$ coating fabrication, each colloidal suspension was vortexed for 3 min, followed by sonication for another 10 min. Immediately after this, the suspension was transferred to the EPD cell (see figure 1(a)), which was made from stainless steel and acted as the anode, whereas the graphite substrate served as the cathode. A fixed voltage (40 and 60 V) was applied for 5 min. Figure 1(b) shows the appearance of the coated graphite sample. Once deposited, the green coatings were sintered at 1200 °C for 1 h under inert atmosphere. After sintering, coating morphology was characterized using confocal microscopy on a Hirox 3D digital microscope.

![Figure 1. (a) Diagram of the EPD cell used for the fabrication of ZrO$_2$ nanoparticle coatings; (b) coated graphite sample.](image)

3. Results and Discussion

3.1. Zeta potential measurements
The Z potential is a function of the surface charge of the suspended particles and the ionic strength of the medium that contains them [5]. Figure 2 shows the relationship between the Z potential of the zirconia colloids and the solution pH. To vary this pH, the original solution (ethanol:water, 90:10 vol, pH: 5.9) was modified with either HNO$_3$ or NH$_4$OH to generate H$^+$ or OH$^-$ ions, which were further adsorbed on the surface of the ZrO$_2$ nanoparticles. It can be noted that the maximum Z potential values that were measured (35-40 mV, approximately) were obtained for suspensions whose pH values fell below 4, point at which H$^+$ adsorption appeared to be maximized and the colloidal system was stable. The DLVO theory (named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodor Overbeek) describes the relationship between surface forces present in a colloidal system, including the electrostatic repulsion and the London Van der Waals attraction. The Z potential values that were obtained for colloidal suspensions at pH below 4 indicated that the electrostatic repulsion forces among particles were greater than the London-Van der Waals attraction forces, which in turn resulted in favorable particle dispersion that prevented subsequent sedimentation [6]. The electric field established during the
EPD process exerted an additional force on the ions located on the diffuse layer, a force that was directed opposite to the surface charge and was further transmitted to the nanoparticles through viscous tensions, promoting their movement towards the electrode surface. The mass of the deposited nanoparticles is proportional to their electrophoretic mobility, and is also a function of the colloid Z potential as well as the applied field.

Figure 2. Variation of the Z Potential (ζ) of ZrO$_2$ nanoparticles as a function of the pH of the medium.

Figure 3 shows the chronoamperometric response of ZrO$_2$ nanoparticles deposited by EPD applying 40 and 60 V, using two different nanoparticle concentrations: (a) 13 g/L and (b) 10 g/L. For both particle concentrations, the curves present the expected dependence with the applied potential, showing an increment in the current with an increase in the applied potential. The abrupt reduction of the current magnitude that is observed during the first 50 seconds is related to the change in the surface resistance produced by the deposited nanoparticles, since the ceramic deposit is less conductive than the graphite substrate.

Figure 3. Chronoamperometric response of ZrO$_2$ nanoparticles deposited from colloidal suspensions with different nanoparticle concentrations: (a) 13g/L, and (b) 10g/L.

Furthermore, the subsequent reduction of the current is related to the thickening of the coating. In terms of the chronoamperometric response, the main difference between the two ZrO$_2$ colloids that were used (10 and 13 g/L) was the variation of the current in the second stage. For the 13 g/L colloidal system, the current reduction took place at a faster rate, reaching a value close to zero at the end of the experiment. On the other hand, the current response for the 10 g/L suspension shows a plateau at 0.0018 mA, approximately. Altogether, these results indicate that the thickness of the coating and its associated resistance were larger when EPD was performed using a 13 g/L nanoparticle suspension, which is in agreement with theoretical models previously proposed [7]. Finally, comparison of both curves in figure
3(a) indicates that the current obtained by applying 60 V is larger than the current obtained when using 40 V, although it shows some perturbation that could be related to water decomposition on the electrode surface, a phenomenon that most likely affected coating homogeneity and coverage. Based on this, further analyses were performed using a 13 g/L nanoparticle suspension and a voltage of 40 V. After coating deposition and sintering, the roughness of the uncoated and ZrO$_2$ coated graphite substrates was measured using confocal microscopy. Figure 4(a) shows the variation of sample surface roughness as a function of the grit size of the abrasive paper that was used for sample preparation. It can be noticed that substrate roughness for both, the coated and uncoated samples, appears to consistently decrease as the grit size of the abrasive paper increases. Moreover, figures 4(b)-4(d) are three-dimensional reconstructions that display the 3D superficial texture of plain graphite substrates that were polished using different types of sandpaper. It has been previously suggested that surfaces with higher roughness have a larger proportion of broken bonds, which in turn results in greater levels of surface energy (also called “dispersive energy”) available for interactions with other substances on the surface [8]. Therefore, the bonds created between the substrate surface and the deposited coating should be expected to be stronger for a sample prepared with SiC paper of grit size 120, relative to a sample treated with SiC paper of grit size 320.

![Figure 4](image_url)

**Figure 4.** (a) Effect of abrasive paper grit size on the roughness of uncoated and ZrO$_2$ coated graphite substrates, (b, c, d) 3D reconstructions of graphite surfaces before and (e, f, g) after nanoparticle EPD, (b, e) which were prepared using abrasive paper of grit sizes 120, (c, f) 320 and (d, g) 600.
Figures 4(e)-4(g) show 3D reconstructions of the coated graphite substrates, which reveal the cracking that occurred upon sintering. This phenomenon could be explained by the difference between the thermal expansion coefficients of graphite and ZrO$_2$ (1.4x10^{-6} °C$^{-1}$ and 5.5x10^{-6} °C$^{-1}$, respectively) [9,10], since such difference produces residual stresses between the substrate surface and the ceramic coating during thermal treatment, especially during the cooling stage.

4. Conclusions
Several process parameters of the EPD of zirconia nanoparticle coatings were studied using ethanol-based media and graphite as the substrate. Given the importance of colloidal stability in EPD, the zeta potential of ZrO$_2$ colloidal suspensions was evaluated at different pH conditions, being the acidic media the most favorable for suspension stability. The chronoamperometric response of the ZrO$_2$ precursor suspension appeared to depend on the initial concentration of nanoparticles in the solution, as well as on the fixed voltage that was applied during EPD. Moreover, the preparation of the substrate prior to coating also appeared to have an effect on the surface properties of the ceramic coatings, as roughness of the coated substrate seemed to increase with decreasing size of the grit of the SiC paper used for polishing. Cumulatively, this data allows to enhance our understanding of the EPD process for the fabrication of cost-effective ZrO$_2$ ceramic coatings that could be employed in the development of thermal barrier coatings and anticorrosive films. Further studies will look into the surface mechanical reinforcement effect of the proposed ceramic coatings on graphite substrates.

Acknowledgements
The authors would like to thank Vicerrectoría de Investigación y Extensión (VIE) at Universidad Industrial de Santander for the financial support provided through project code 2442. The authors are also grateful to Ambrosio P. Carrillo from the Corrosion Lab at Universidad Industrial de Santander for his technical support.

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