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Surface reactivity and electrophoretic deposition of ZrO_2–MgO mechanical mixture

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Abstract Electrophoretic deposition (EPD) is a precision technique useful for obtaining high quality ceramic bodies with controlled dimensions and smooth coatings. The electrophoretic deposition rate is highly dependent on the surface chemistry of the powders, especially when dealing with multi-component systems. The objective of this work is to study the surface reactivity of both ZrO_2 and MgO in ethanol suspension to provide experimental benchmarks to control EPD of a ZrO_2–3 wt% MgO mechanical mixture (Z3M) in ethanol. Infrared spectroscopy (FTIR) showed that ZrO_2 surface spontaneously reacts with ethanol, generating negative electrophoretic mobility of the particles (-0.07×10^{-8} V^{-1} s^{-1}) measured by Electroacoustic Sonic Amplitude (ESA). MgO surface also spontaneously reacted with ethanol, but a positive electrophoretic mobility was observed in this case (0.26×10^{-8} V^{-1} s^{-1}). Scanning Electron Microscopy of Z3M dried from ethanol suspension showed that MgO particles were located around the ZrO_2 particles, forming composite agglomerates, probably due to the electrostatic attraction between MgO and ZrO_2 particles. Homogeneous deposits could be obtained from EPD of Z3M ethanol suspensions. Mercury intrusion porosimetry showed that the ZrO_2–MgO green deposited bodies using different voltages had similar pores diameters distributions, indicating that the ZrO_2–MgO agglomerates are not affected by the increasing deposition rates.

Introduction

Surface chemistry is of major importance in controlling and optimizing colloidal processing of multi-component systems [1–3]. This is because the surface reactions are intimately related to the interparticle forces in suspensions, which are responsible for their homogeneity and rheological properties [3, 4]. However, since in multi-component systems there can be a large number of different surfaces, the control of these surface related properties in a suspension may be a very complex task. A common solution for this problem is to obtain a single homogeneous powder synthesized by a chemical route containing all the components needed for the application. This alternative route creates the advantage of a unique surface, but ignores the important economical benefits of a direct mixture of the powders in the suspension to be processed. In electrophoretic deposition (EPD) [5, 6], a fast and precision technique for obtaining reliable ceramic bodies, the benefits of a homogeneous multi-component suspension certainly offset the multi-surface challenge.

Several works have been published on suspensions and EPD of multi-component ZrO_2 based powders [7–10]. These works are usually carried out on ZrO_2 powders doped with magnesium [9], yttrium [8], or other phase stabilizers [11, 12], prepared by chemical routes or on commercial chemical mixtures. In the present work we explore the benefits of a direct mechanical mixture of ZrO_2 with 3 wt% MgO [13] in ethanol suspension, exploring the

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applicability of this suspension to a EPD process. The surface chemistry of both MgO and ZrO_2 particles is independently studied by infrared spectroscopy, specially considering the reactivity with the solvent (ethanol). Electrophoretic mobility measurements were carried out in both MgO and ZrO_2 suspensions to evaluate the stability of the suspension and the electrostatic interactions between the particles in the mixture. Scanning Electron Microscopy (SEM) was applied to study the spatial distribution of the particles in the mixture caused by the electrostatic interactions. Since high homogeneity and high mobilities were obtained in the powder mixture, EPD was successfully applied and a homogeneous ceramic body could be obtained.

Experimental procedure

Electrophoretic mobility measurements were performed for suspensions prepared to a solid loading of 2-vol% using ESA-8000 equipment (Matec Applied Sciences, USA). The suspensions were prepared using ZrO_2 (99%—IPEN—Brazil), with specific surface area of 50.9 m^2/g (measured by N_2 adsorption); and MgO (98%—Synth), with specific surface area of 63 m^2/g. Solvent was ethanol (purity higher than 99.5%—Synth; H_2O content < 0.2%; methanol content < 0.1%). ZrO_2 containing 3 wt% MgO (8.6 mol%), named Z3M in this work, was prepared by mechanical mixing of the components. All suspensions were ball-milled for 4 h before the analysis.

The studied powders (ZrO_2, MgO, and Z3M) were analyzed before and after exposition to ethanol by infrared spectroscopy with Diffuse Reflectance Infrared Fourier Transform (DRIFT) using Magna 560 Nicolet equipment. Powders were treated for 4 h at 70 °C before the FT-IR measurements.

The particles morphology and spatial distribution in the suspensions were analyzed by Scanning Electron Microscopy (SEM) using LEO Stereoscan 440 with high vacuum (2.5×10^{-6} Torr), secondary electron detectors for images (10.00 kV), and scattered electrons for Energy Dispersive Spectroscopy—EDS (12.00 kV—Ge detector and INCA v.16 Software, Oxford). The SEM samples were prepared by dropping dilute ethanol suspensions on Al substrates, drying at 70 °C for 4 h, and applying pure conductive Pt coating.

Electrophoretic deposition was carried out under constant applied voltage using cylindrical graphite electrode (0.5 mm thick) and cylindrical stainless steel counter-electrode. A specially designed set-up was used to measure the deposited mass as a function of time and applied voltage using suspension containing 10-vol% of solid. Polyvinyl butyral (PVB) was used as a binder to assure green body strength of the depositions. The applied voltage was varied between 7.5 V and 50 V. A series of electrodeposited green bodies was submitted to mercury intrusion porosimetry using Micromeritics AutoPore III 9410 to evaluate the effect of the applied voltage in the pore size distribution.

Results and discussion

Table 1 shows the electrophoretic mobility (μ_B) and pH of ZrO_2, MgO, and Z3M ethanol suspensions milled for 4 h to assure homogeneity and equilibrium of any possible surface reaction (without any additives). A negative μ_B is observed for ZrO_2 powder in suspension with a spontaneous pH of 4.9, while a positive mobility is observed for MgO suspension with pH 13.4, consistent with the literature available data [14].

The spontaneous charging and pH modification for both suspensions may be explained based on the small amount of H_2O (<0.2%) available in the solvent [15]. Hydroxyl groups from ZrO_2 surface have characteristic acid behavior, and in contact with H_2O may cause H^+ dissociation, with a consequent negative surface charging and pH decreasing. On the other hand, the inherent basicity of OH groups from MgO may explain the positive charges and increased OH^- concentration in solution observed for MgO suspensions [3].

Interestingly, despite the relatively low concentration of MgO in Z3M (3 wt% MgO), μ_B of the mixture is positive and the observed spontaneous pH is 9.0. At pH 9.0, one observes (Table 1) that the surface of ZrO_2 becomes more negative with relation to initial pH 4.9, with an electrophoretic mobility of -0.11×10^{-8} m^2 V^{-1} s^{-1}. At this same pH, MgO particles in suspension have μ_B equal $+0.06 \times 10^{-8}$ m^2 V^{-1} s^{-1}. If one considers a homogeneous distribution of the particles in the mixture, without interactions between ZrO_2 and MgO particles, combining the contributions of the mobilities of the individuals ZrO_2 and MgO suspensions at pH 9.0, a μ_B of about -0.05×10^{-8} m^2 V^{-1} s^{-1} can be

Table 1 Electrophoretic mobility and pH measurements in ZrO_2, MgO, and ZrO_2–3 wt% MgO (Z3M) ethanol suspensions

Sample	pH	Electrophoretic Mobility (10^{-8} m^2 V^{-1} s^{-1})
ZrO_2	4.9	–0.07
MgO	13.4	0.26
ZrO_2	9.0	–0.11
MgO	9.0	0.06
Z3M (measured)	9.0	0.03
Z3M (calculated)*	9.0	–0.05

* Multi-component prediction by Bruinsma et al. [16]

calculated using volume fraction basis [16]. Since the measured mobility of the mixture is positive (+0.03 × 10^{-8} m^2 V^{-1} s^{-1}), the data suggest an electrostatic interaction due to the opposite measured electrophoretic mobilities. A possible explanation for the positive surface charges of Z3M can be based on the distribution of the particles. Hirata et al. [4] showed that a surface coverage of one particle by another is feasible when opposite charged particles are present in a multi-component suspension. This suggests that MgO particles may be located around ZrO_2 particles and, therefore, may be compensating the negative ZrO_2 surface charges. This hypothesis can be tested by studying the surface composition of Z3M and comparing with those of ZrO_2 and MgO. The surface study was carried out by means of FT-IR using diffuse reflectance technique (DRIFT).

Figure 1 shows portions (from 900 cm^{-1} to 3,900 cm^{-1}) of the infrared spectra of the samples before and after exposition (reaction) to ethanol. In the ZrO_2 spectra (Fig. 1a), the pronounced band at 3,695 cm^{-1} observed in the powder before exposition to ethanol can be attributed to a surface hydroxyl vibration. After the washing with ethanol, the hydroxyl band is not observed, but C–H bands around 3,000–2,900 cm^{-1} and C–O stretching at 1,050 cm^{-1} and 1,090 cm^{-1} could be detected, indicating a surface reaction with the formation of an ethoxide [17, 18]. One may also observe a noticeable decrease of hydroxyl related bands at 1,550 cm^{-1} and 1,250 cm^{-1} in ZrO_2 after reaction with ethanol.

Once the surface chemistry is affected by the formation of ethoxide, one could argue that this influences the surface charging. However, the presence of H_2O and inherent ZrO_2 acidity give rise to a more reasonable explanation, suggesting that, despite the reaction of some types of hydroxyl groups from the surface with ethanol, there are still available OH groups for the interaction with H_2O, as shown by the unaffected OH stretching bands (~1,500 cm^{-1}) in the spectrum of ZrO_2 exposed to ethanol (Fig. 1a). The effect of the ethoxide group would be restricted to a possible hindrance effect of the hydrogen from the ethoxide on others from S–O–H, facilitating H^+ dissociation; or to a modification in the surface electron density.

Figure 1b shows infrared spectra of MgO and MgO washed with ethanol. Characteristic MgO hydroxyl stretching vibrations bands are observed at 3,750–3,640 cm^{-1} [19]. After the reaction of the surface with ethanol, the more intense bands located at 3,712 cm^{-1} and 3,700 cm^{-1} are unaffected. This indicates that, despite being the most pronounced hydroxyl site, these hydroxyl groups do not interact directly with the solvent. A considerable adsorption decrease can be observed in the broad bands at 3,269, 3,650 and 3,735 cm^{-1}, also attributed to hydroxyl groups, while ethoxy bands at 1,132–1,062 cm^{-1} and C–H stretching bands at 3,000–2,800 emerge after the exposition to the solvent [18]. Similarly to ZrO_2 surface, even after exposition to ethanol, Fig. 1b shows that there are still OH groups on MgO surface. These groups would be responsible for the positive surface charging, due to the intrinsic basicity of MgO surface.

Figure 1c shows the infrared spectra for Z3M before and after exposition to ethanol. The spectra are more similar to those of MgO. The pronounced peaks at ~3,700 cm^{-1} are also observed in Z3M and suggest that the surface may be composed mainly by MgO. The hydroxyl bands at around 1,500 cm^{-1} also supports this hypothesis. The exposition to

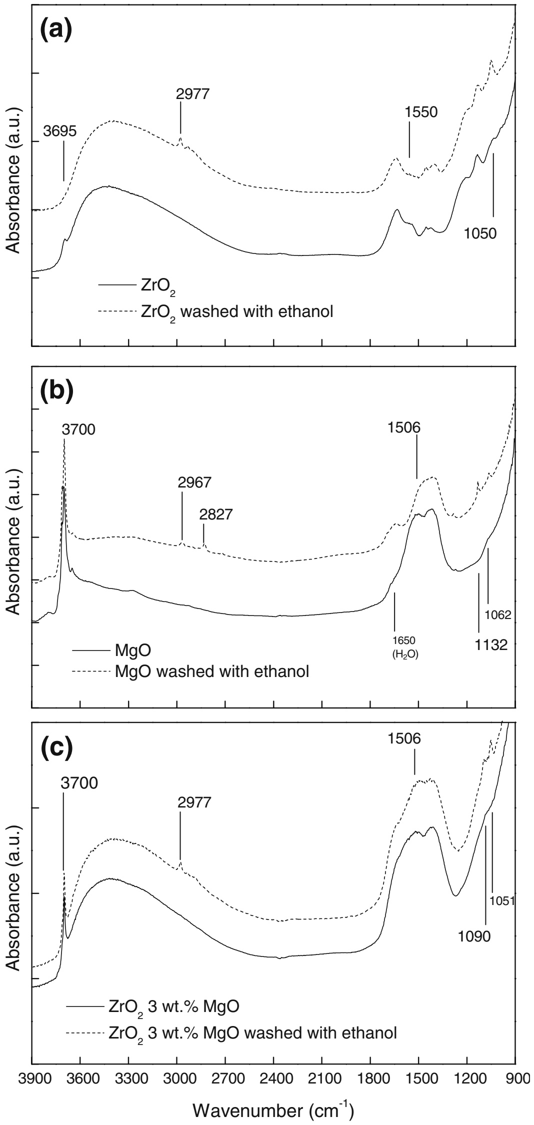

Fig. 1 Infrared spectra of (**a**) ZrO_2 and ZrO_2 washed with ethanol; (**b**) MgO and MgO washed with ethanol; and (**c**) ZrO_2–3 wt% MgO before and after washing with ethanol

ethanol affected the same bands as in MgO, supporting the positive electrophoretic mobility of the mixture.

The coverage of ZrO_2 particles by MgO can be observed by SEM. Figure 2 shows the micrographs of ZrO_2, MgO, and Z3M powders dried from ethanol suspensions. Figure 2a shows an isolated typical ZrO_2 particle obtained from a ZrO_2 ethanol suspension. Figure 2b shows a typical MgO particle from a dried MgO ethanol suspension. One may observe a porous morphology of MgO particle when compared to ZrO_2. Figure 2c shows Z3M particles dried from ethanol suspension. When comparing this micrograph to those of ZrO_2 and MgO, one may suggest, by observing the particles morphologies, that Fig. 2c shows a ZrO_2 particle with small MgO ones located around it. The MgO particles are tightly attached since an electrostatic interaction between ZrO_2 and MgO is expected due to the opposite μ_B. Figure 2d reinforces this hypothesis showing a micrograph using lower magnitude to observe a larger number of particles. Note that the surface of the observed particles is rough (and not smooth as ZrO_2 particles in Fig. 2a), probably due to the adhesion of the smaller porous MgO particles on the surface of ZrO_2. Qualitative EDS of the particles shown in Fig. 2d detected a pronounced Mg peak in addition to that of Zr, supporting the hypothesis of the surface coverage.

The coupling of the particles turns Z3M into a special candidate to electrophoretic deposition. If the observed particles distribution remains under an applied voltage in the suspension and after deposition, homogeneous Z3M bodies could be shaped and sintered to obtain partially stabilized zirconia. A 2-vol% solid loading Z3M suspension was submitted to EPD under constant voltage. Figure 3 shows deposited mass as a function of time for different applied voltages. The curves are consistent with a constant-voltage but decreasing suspension concentration EPD [6]. An important observation is that no particles were deposited on the counter-electrode. This would occur if the particle coupling were broken by the applied voltage and electrophoretic motion, since ZrO_2 and MgO would be separated and have opposite charge signals. The deposition rate increases with increasing applied voltage, but the deposition trends remains the same for all voltages, supporting that the Z3M agglomerates are not affected by the electrophoresis process.

Figure 4 shows the pore size distribution of the green bodies deposited by EPD. Three pore diameter families, at 200 µm, 0.10 mm, and 0.01 µm are observed. The high-pressure pore families at 0.10 µm and 0.01 µm are attributed to intra and interparticles voids. Note that these pores do not change with increasing applied voltage. This indicates that the deposited particles have always the same surroundings, supporting the hypothesis that the EPD process does not affect the ZrO_2–MgO agglomerates even after deposition. The pore family at 200 µm can be attributed to macro pores related to the compaction of the deposited body. The volume of these pores decrease with increasing applied voltage, which is consistent with an increasing compaction of the particles with the voltage.

Conclusion

The results reported here show the formation of an organized ZrO_2–MgO agglomerate in a mechanically mixed ZrO_2–3 wt% MgO ethanol suspension. The agglomerate was generated by electrostatic interaction between the

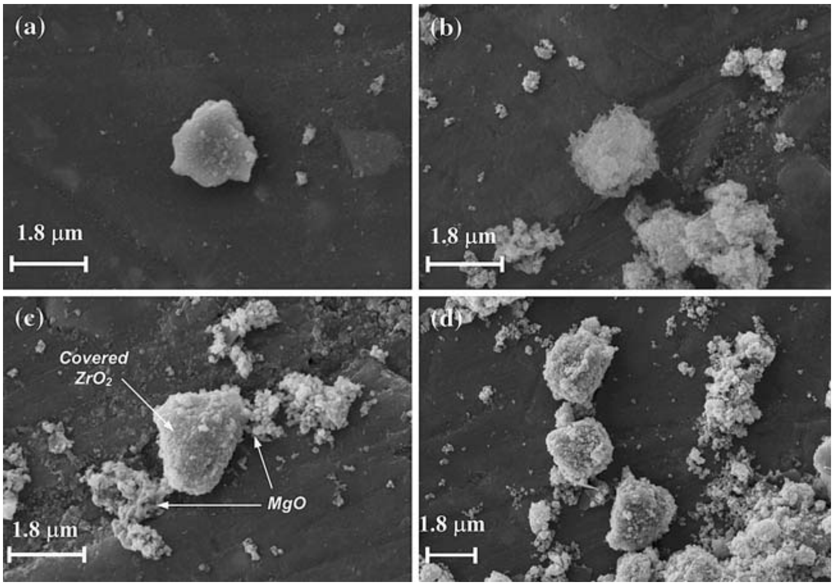

Fig. 2 Scanning electron micrographs of (**a**) ZrO_2; (**b**) MgO; and (**c**) and (**d**) ZrO_2–3 wt% MgO (8.6 mol%), dried from ethanol suspensions

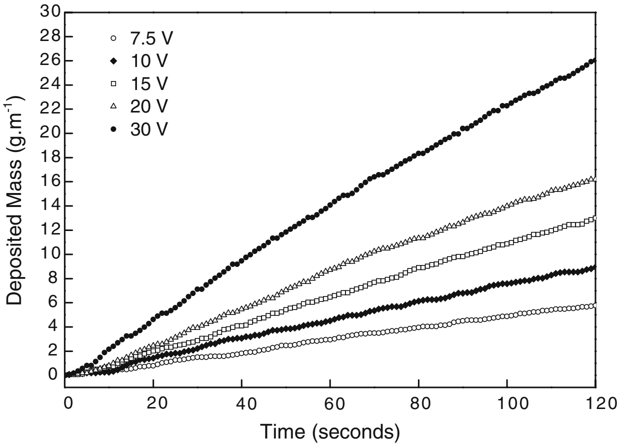

Fig. 3 Deposited mass during EPD of ZrO_2–3 wt% MgO mechanical mixtures as a function of time and applied voltage

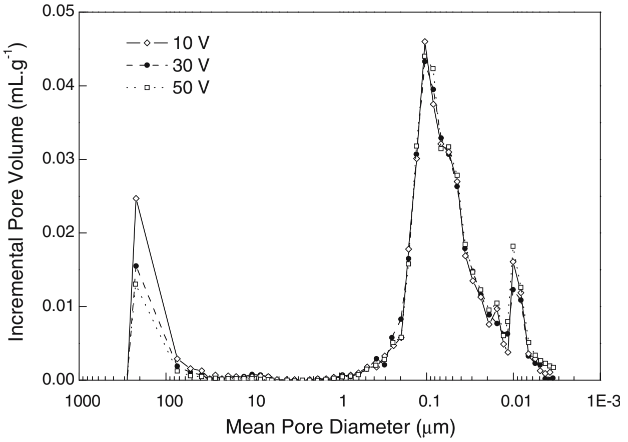

Fig. 4 Pore size distribution of ZrO_2–3 wt% MgO green bodies deposited by EPD as a function of applied voltage

particles due to the opposite charges of MgO and ZrO_2 resulted from the surface reactions with ethanol, as showed by FT-IR and electrophoretic mobility measurements. SEM showed that MgO surrounds ZrO_2 particles, and, therefore, the final electrophoretic mobility of the mixture is more similarly to MgO than ZrO_2. EPD experiments were carried out with the mixture and porosity measurements of the deposited green bodies indicated that the agglomerate is not affected by electrophoresis or deposition even under high voltages. This confirms that a simple mechanically mixed ZrO_2–MgO ethanol suspension may be a suitable option to obtain homogeneous EPD shaped bodies.

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