Silica-Zirconia Coatings Produced by Dipping and EPD from Colloidal Sol-Gel Suspensions

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Abstract. SiO₂-ZrO₂ sols have been prepared via acid catalysis using a commercial colloidal suspension of zirconia and two silica alkoxides; tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES). Suspensions with 10, 15 and 25-mol% of ZrO₂ were prepared. The stability of the suspensions was followed by rheological measurements showing that the amount of water incorporated with the colloidal suspension is the factor that limits the maximum ZrO₂ content. Coatings have been prepared by dipping using the suspensions up to 25-mol% ZrO₂ onto glass-slides at different withdrawal rates. EPD process has been used to prepare coatings onto stainless steel AISI 304 using the suspension with 25-mol% ZrO₂ at different pHs. The parameters associated with the EPD process (current density, electric field, potential and deposition time) have been evaluated. The critical thickness for a ZrO₂ addition of 25-mol% was 0.8 μm and it increased for diminishing ZrO₂ content.

Keywords: SiO₂-ZrO₂ coatings electrophoretic deposition, suspension

1. Introduction

The sol-gel process is considered a suitable method to produce protective functional coatings onto different metallic substrates. The low processing temperature needed to densify the coatings is one of the most important advantages of this process since some metals present structural changes with temperature that degrade the mechanical properties of the substrate and promote corrosion.

A wide range of compositions has been prepared by sol-gel. However, the preparation of silica-zirconia coatings have aroused a particular interest due to their superior chemical resistance to alkaline attack [1, 2] and fracture toughness [3]. The main problem of preparing coatings of this composition is related to the amount of ZrO₂ that can be incorporated, the difficulty to obtain homogeneous materials without phase separation [4] and the low critical thickness that can be achieved. There are several works

that report the preparation of silica-zirconia films and the difficulty to obtain crack-free coatings thicker than 0.5 μm [5–8] in a single layer. This fact restricts the use of these coatings with protective purposes.

Some works have been developed using EPD process to obtain thick silica coatings onto stainless steel using either acid-catalysed sols containing colloidal particles, or basic-catalysed particulate sols. These works have demonstrated that the use of EPD process can increase the critical thickness of the coatings over that reached by dipping [9, 10].

The present work examines the preparation of SiO₂-ZrO₂ sols via acid catalysis containing up to 40% mol of colloidal ZrO₂ to produce hybrid glass-like coatings onto steel substrates by EPD and dipping. The stability of the sols and the processing parameters involved in the preparation of sols and coatings by dipping and EPD have been studied.

2. Experimental

Four compositions in the system $\text{SiO}_2\text{-ZrO}_2$ with 10, 15, 25 and 40-mol% ZrO_2 were prepared via acid catalysis. Tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) were used as precursors of SiO_2 and a commercial colloidal suspension of ZrO_2 (Nyacol(ac), PQ-Corporation, $\text{pH} = 3.5$) as precursor of ZrO_2 . The suspensions were prepared by mixing TEOS and MTES with the corresponding amount of colloidal suspension of ZrO_2 and adding concentrated HCl up to reach a $\text{pH} 4$. Table 1 summarises the molar ratios fixed for the synthesis and the total concentration obtained for each composition.

The suspensions were diluted adding absolute ethanol between 120 to 200 g/l. In the following the compositions will be named as $\text{XZr } n(\text{m})$ g/l, where X is the ZrO_2 content, n the total concentration of oxides and (m) the particle concentration.

The pH of the 25Zr suspension was modified toward acidity and basicity adding HCl and tetramethylammonium hydroxide (TMAH), respectively.

The rheological characterisation of the suspensions was performed by measuring the viscosity with composition, concentration, and storage time, using a rotational rheometer (Haake, RS550, Germany) under controlled rate conditions at 25°C . The shear rate was increased from 0 to 1000 s^{-1} in 5 min, with 1 min at the maximum rate and decreasing again to 0 in 5 min.

Coatings were deposited by dipping on glass substrates and stainless steel AISI 304 varying the withdrawal rates from 9 to 65 cm/min. Glass substrates were cleaned in ultrasonic bath with ethanol and the stainless steel with an alkaline solution (P3Emalan5668:P3Emalan0469, Miele, Germany).

EPD tests were carried out at current densities from 0.2 to 1.8 mA/cm^2 and deposition times up to 60 min by using a potentiostat/galvanostat (AMEL 551, UK) under galvanostatic conditions in order to maintain a constant electric field. Polished stainless steel AISI 304 was used as working electrode and graphite as counter-electrode. A low withdrawal rate was used to minimise the dipping contribution to the total thickness.

Coatings produced by either dipping or EPD were dried at room conditions and sintered at 525°C for 30 min in air.

The thickness of the coatings obtained on glass substrates was determined by profilometry (Talystep, Taylor Hobson, UK) while that of coatings onto stainless steel was calculated by gravimetry. Optical mi-

croscopy (Zeiss, HP1, Germany) was used to evaluate defects and cracks in the coatings.

3. Results and Discussion

Homogeneous and translucent suspensions with a maximum amount of 25% mol ZrO_2 were prepared via acid catalysis. The suspension of 40% mol ZrO_2 gelled quickly due to the excess of water added with colloidal ZrO_2 that produces the unstabilisation of the suspension. Therefore, the amount of water is the factor limiting the ZrO_2 particles content, which can be incorporated to the suspension.

The evolution of the suspensions was followed through viscosity measurements as a function of concentration, composition and time. Figure 1 shows the evolution of viscosity with shear rate of 25Zr suspension with concentration 210(110)g/l as prepared and after 268 h at 25°C . The fresh suspension shows a Newtonian behaviour with a viscosity of 5 mPa.s. After 268 h, the viscosity increases and the suspension becomes thixotropic. The increment of viscosity is related to the evolution of the condensation reactions that increase the cross-linking and the agglomeration of the particles. A similar behaviour was observed for compositions 10Zr and 15Zr.

In order to increase the stability of the suspensions they were diluted with absolute ethanol up to 120 g/l. Figure 2 plots the evolution of viscosity with time for compositions 10Zr, 15Zr and 25Zr showing that the stability decreases for increasing amounts of ZrO_2 due

Figure 1. Evolution of the viscosity with the shear rate for the composition 75Zr.

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Figure 2. Stability of the $\text{SiO}_2\text{:ZrO}_2$ sols for concentration of 120(40) g/l at 25°C .

Figure 3. Structure of the $\text{SiO}_2\text{:ZrO}_2$ sols.

to the larger amount of water incorporated. The concentrated suspension 25Zr maintains stable for 100 h, while the diluted one maintains stable over 190 h.

A structure similar to that described by Mennig [11] is expected for these sols (Fig. 3), where ZrO_2 particles are either linked by hydrolysed molecules of MTES and TEOS or covered by OH group or hydrolysed species.

Dipping tests were performed onto glass substrates using the suspensions 10Zr, 15Zr and 25Zr with concentrations of 282(53), 280(74) and 270(110) g/l, respectively, and varying the withdrawal rates up to 65 cm/min. Homogeneous and transparent coatings were obtained indicating a good dispersion of the particles. However, all the coatings cracked during drying. In order to determine the critical thickness (e_c) of the coatings after sintering at 525°C the suspensions were diluted. Table 2 summarises the final concentration used to measure the dry and critical thickness (e_c) for each suspension.

Figure 4. Deposited mass as a function of current density for the 75Zr sols with concentrations of 270(109) and 120(40) g/l.

The critical thickness decreases for increasing ZrO_2 particles content. This behaviour is usually observed in systems of two oxides ($\text{SiO}_2\text{-B}_2\text{O}_3$ [12,13], $\text{SiO}_2\text{-TiO}_2$ [14], $\text{SiO}_2\text{-ZrO}_2$ [2], etc.) and is related with the appearing of high stresses, that generates cracks. In the studied system $\text{SiO}_2\text{:ZrO}_2$ the internal stresses can be more important due to the dense particles embedded in the SiO_2 network with very different expansion coefficient.

The suspension 25Zr was selected to obtain EPD coatings, since it has the highest content of ZrO_2 with adequate stability. A withdrawal rate of 3 cm/min was used to extract the substrate, in order to distinguish the contribution of EPD respect to dipping. Figure 4 shows the evolution of weight per unit area with the current density for suspensions 270(110) g/l and 120(40) g/l for a constant deposition time of 5 min. A change of slope is observed for both suspensions, as in other sol-gel systems [15, 16]. The deposition mass varies slowly up to current densities of 1.2 and 0.8 mA/cm^2 for suspensions 270(110) g/l and 120(40) g/l, respectively. Above these values the deposition rate increases.

Homogeneous coatings were obtained using the concentrated suspension within a wide current density range. In the case of diluted suspension (120(40) g/l), homogeneous coatings were only obtained for current densities lower than 0.8 mA/cm^2 ; for higher values, preferential deposition of the particles was detected, leading to heterogeneous coatings. Maximum dry thickness of 1 μm and critical thickness of 0.8 μm were reached with both suspensions. All the coatings present a good adhesion to the substrate.

In order to increase the thickness and the homogeneity of the coatings two aspects were considered.

First, the pH of the suspension 120(40) g/l was modified adding TMAH and HCl in order to increase the mobility of the particles. Second, the deposition kinetics was studied applying low current densities and long deposition times.

The modification of pH toward more basic region adding TMAH decreases the mobility of the particles because pH approaches to the isoelectric point of ZrO_2 . For this reason, the pH of the suspension was further modified by adding HCl up to values of 3.5 and 3. In this case, the ZrO_2 particles are positively charged and migrate toward the cathode under an electric field. Under this condition, no degradation of the substrate is expected. EPD tests were performed using the modified suspensions varying the current density between 0.38 and 1.4 mA/cm^2 for a constant deposition time of 5 min. Figure 5 shows the evolution of the deposition mass versus the current density for suspensions of 120(40) g/l with pH3, 3.5 and 4. The diminution of pH below 3.5 involves the increment of the viscosity and leads to a deviation from behaviour. The modification of pH seems to improve the dispersion of the particles, allowing to obtain homogeneous coatings from diluted suspensions, even at high current densities. However, the critical thickness maintains around 0.8 μm after sintering.

The conductivity (σ) of the suspensions has been calculated from the slope of the plot of electric field as a function of current density (Fig. 6). The conductivity increases for decreasing pH. If the Hamaker's equation is considered (Eq. (1)), the increment of σ should decrease the deposited mass, since $E = I/\sigma$ (where I is the current intensity).

$$m = CtA\mu_e E \quad (1)$$

Figure 5. Weight per unit area vs. current density for 75Zr sols at different pHs.

Figure 6. Evolution of the electric field with the current density for 75Zr sols at different pHs.

(m = deposition mass, C = concentration, t = deposition time, A = area, μ_e = electrophoretic mobility and E = electric field).

However, Fig. 5 shows an increase of mass with decreasing pH. This could be explained through a significant increase of the electrophoretic mobility, μ_e , for lowering pH.

The deposition kinetics of the suspension 120(40) g/l at pH3 was studied at two current densities (Fig. 7). For a current density of 0.55 mA/cm^2 the deposition mass maintains constant for 2 min of deposition. Over this time, the deposition rate increases quickly. In the case of 0.77 mA/cm^2 an increment in the deposition mass is observed from the beginning of the test. In both cases, homogeneous coatings have been obtained. However, neither the maximum dry thickness nor the critical thickness was increased.

Figure 7. EPD kinetics at current densities of 0.55 and 0.77 mA/cm^2 for 25Zr sol at pH3.

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239 The modification of pH has allowed to improve the
240 dispersion of the particles, although the viscosity of the
241 suspensions is increased. On the other hand, the con-
242 trol of EPD parameters permitted to obtain homoge-
243 neous coatings using low deposition times. However,
244 the problem of cracking during drying has not been
245 solved; the maximum thickness of dry coatings was
246 1 μm and it became 0.8 μm after sintering at 525°C.

247 Further work is in progress to study the increment of
248 the thickness of $\text{SiO}_2\text{-ZrO}_2$ coatings by adding drying
249 control chemical additives (DCCAs) such formamide,
250 or binder/plasticizer, such polyethylenglicol (PEG),
251 Polyvinylbutyral (PVB), etc.

252 4. Conclusion

253 Homogeneous and translucent $\text{SiO}_2\text{-ZrO}_2$ sols with a
254 maximum amount of 25-mol% ZrO_2 were prepared
255 via acid catalysis. The water content in the colloidal
256 suspension limits the amount of ZrO_2 which can be
257 incorporated.

258 The dilution of the sols with ethanol improves their
259 stability reducing the initial values of viscosity and
260 avoiding the agglomeration of particles.

261 Homogeneous and transparent coatings with good
262 adherence to glass and stainless steel have been pre-
263 pared by dipping. Maximum dry coatings of 2 μm and
264 1 μm and critical thickness of 1.5 and 0.8 μm have
265 been obtained for 10Zr and 25Zr sols, respectively.

266 The modification of pH enhances the dispersion of
267 the particles and allows to obtain homogeneous EPD
268 coatings in short times using the diluted sols. EPD dry
269 and critical thickness were similar to those obtained by
270 dipping process.

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