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Correlation between sol–gel reactivity and wettability of silica films deposited on stainless steel

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ABSTRACT

Sol–gel silica films were deposited on 316L and 409 stainless steel substrates in order to investigate their wettability properties. These films were deposited by dip-coating varying some parameters of the sol–gel process, including the acid used in the synthesis, its concentration, and the heat treatment temperature. Water and oil contact angles were measured on the surfaces and discussed regarding the physico-chemical and morphological properties of the prepared films. The findings shown in this work allow correlating the wettability behavior of silica coatings with the sol–gel reactivity of sols prepared using various amounts of nitric acid. It was observed that the more reactive the silica sol, the more hydrophilic and oleophilic the prepared coating. The presence in the films of alkoxy residues due to an incomplete condensation reaction could decrease both the polar and dispersive components of the coating surface energy, respectively responsible for water and oil wetting.

1. Introduction

The sol–gel process has received much attention over the past years since it presents advantages such as low processing temperature, high homogeneity of the final product, and ability to produce materials with tailored surface properties [1,2]. Several works deal with the modification of the surface properties of stainless steel by using the sol–gel technique. Among these properties, it is worth mentioning the corrosion resistance [3–5], biocompatibility [6–8], photocatalytic activity [9–11], antibacterial behavior [12–14], and surface cleanability [15–17].

The wettability behavior of the prepared coatings plays a key role in tailoring the aforementioned properties. It is well established that the processing of hydrophobic films can lead to materials with enhanced corrosion resistance and antibacterial behavior [18]. This observation is related to the difficult penetration of water molecules into the open pores present on the stainless steel surface. On the other hand, hydrophilic films can lead to materials with enhanced cleanability properties, which could improve the efficiency of removing dirt particles by using water [19,20]. The oleophilicity of the prepared coatings is also an important factor that must be taken into consideration when tailoring the cleanability of steel samples. Thus, it is clear that the control of the wettability behavior of the stainless steel surface is an issue of great importance.

This work aims to investigate the influence of sol–gel parameters on the wettability behavior of silica coatings deposited on stainless steel substrates. Sol–gel syntheses were performed using different acids and various molar ratios of nitric acid. The as-prepared solutions were deposited by dip-coating on AISI 316L and AISI 409 stainless steel substrates, followed by heat treatment at either 200 or 400 °C. The reactivity of the silica sol was studied as a function of its gelation time. The obtained materials were examined by Fourier transform infrared spectroscopy (FTIR) and nitrogen adsorption tests. Contact angle measurements were carried out using deionized water and mineral oil. Thus, the films prepared in this work were studied with respect to the formulation and reactivity of the sol. Then, the physico-chemical and morphological properties of these films were discussed regarding their hydrophilicity and oleophilicity.

2. Experimental

2.1. Sol–gel synthesis

Silica sols were prepared by the hydrolysis and condensation of tetraethyl orthosilicate (TEOS/Aldrich/98%) in the

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presence of absolute ethanol (EtOH/Synth/≥99.5%) and deionized water. Hydrochloric (HCl/Sigma–Aldrich/37%), nitric (HNO_3/Quimex/65%), hydrofluoric (HF/Sigma–Aldrich/≥ 48%), and acetic (HOAc – Sigma–Aldrich/≥ 99.7%) acids were used as catalysts. The molar ratio of TEOS/EtOH/H_2O/catalyst was kept at 1/4/4/*x*. *x* varied from 0 to 1 when HNO_3 was used in the syntheses, whereas it was kept at 0.1 for experiments using HCl, HF or HOAc. The as-prepared sols were vigorously stirred for 5 min. The dip-coating step was performed with a withdrawal speed of 0.5 mm/s, using 316L and 409 stainless steel substrates. Prior to the coating step the substrates were polished with a 600 grit SiC paper, washed with detergent, deionized water, and degreased with acetone. Finally, they were placed in an ultrasonic bath with acetone and dried under hot air. The coated samples were placed in furnaces at either 200 °C or 400 °C for 30 min. After the deposition step, the residual solutions were kept closed at room temperature until their complete gelation. The gelation times were estimated by daily inspection of the solutions. After complete gelation, the obtained monoliths were heat treated in similar conditions as the coated samples and crushed to be used in nitrogen adsorption tests.

2.2. Characterization

Nitrogen adsorption tests were carried out in a Quantachrome Autosorb 1 C apparatus, using samples previously degassed at 100 °C for 24 h under vacuum. The specific surface area (S_P), specific pore volume (V_P), and mean pore size (d_P) were assessed using the BET multipoint and BJH models. d_P was estimated by Eq. (1):

$$d_P = \frac{4V_P}{S_P} \tag{1}$$

FTIR was performed using a PerkinElmer Spectrum 1000 spectrometer. The spectra were taken in the spectral range from 4000 cm^{-1} to 300 cm^{-1}, with a resolution of 2 cm^{-1} and 64 scans. The mineral oil (Nujol, Schering-Plough) used in the oleophilicity tests was examined with an attenuated total reflectance (ATR) accessory and using a zinc selenide (ZnSe) crystal as reflection element. The coated samples were examined using the variable angle specular reflectance (VASR) technique. Their spectra were taken considering an incidence angle of 30°.

The hydrophilicity and oleophilicity of the sol–gel films were evaluated by measuring the water and oil contact angles, respectively. These tests were performed at room temperature, approximately 30 min after the heat treatment step. The droplets formed on the films surface were photographed with a Digital Camera (Sony MVC-500). The contact angles were evaluated with the ImageJ software, using a contact angle plugin [21–23]. Deionized water (pH 5.65) and mineral oil droplets of about 1 μL in volume were placed on the samples surface. The contact angles were measured at different positions in each sample for statistical purposes. Images were taken immediately after the droplets were placed on the surfaces to avoid water evaporation. Since the software cannot assess contact angles smaller than 5°, all angles inferior to 5° were fixed at this value.

3. Results and discussion

3.1. ATR-FTIR characterization of the mineral oil

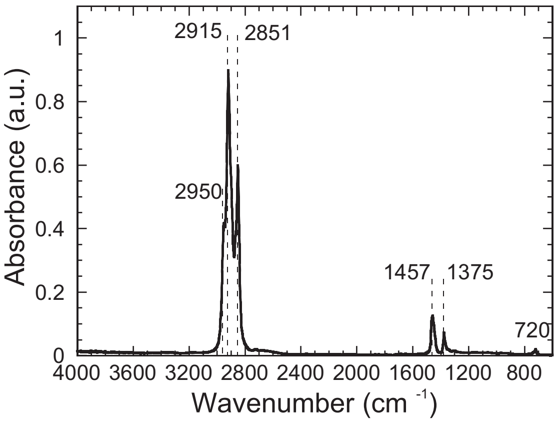

Fig. 1. ATR-FTIR spectrum of the mineral oil used in oleophilicity tests.

Fig. 1 shows the ATR-FTIR spectrum of the mineral oil used in this work. The bands in the spectral range from 2950 cm^{-1} to 2850 cm^{-1} are related to CH asymmetric and symmetric stretching modes [21]. The features at 1457 cm^{-1} and 1375 cm^{-1} are ascribed to CH bending modes [22]. The peak at 720 cm^{-1} has been related to the asymmetric angular deformation of CH_2 groups [23]. The absence of bands at 3500–3300 cm^{-1}, 2700–2600 cm^{-1}, 1800–1700 cm^{-1}, and 1200–1100 cm^{-1} reveal the lack of oxygen bonds in this oil. Based on these results, one notices that the mineral oil used in the oleophilicity tests basically shows hydrocarbon components. As a result, the water and oil contact angles measurements performed in this work reveal, respectively, the affinity of the silica coatings to liquids containing either O–H or C–H bonds, i.e. polar or apolar bonds. Therefore, the wetting properties evaluated with these two liquids will be related, respectively, to the polar and dispersive components of the surface energy of the studied coatings.

3.2. Effect of the acid type

During the deposition at room temperature of silica films, the solvent vaporizes and the silicium precursor reacts to form the silica network following the reactions 1 and 2 [24]. In the presence of water, ethoxy groups of the TEOS precursor are hydrolyzed according to the simplified reaction:

$$\text{Si–(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{(OR)}_3\text{–Si–OH} + \text{ROH} \tag{1}$$

where R, OR, and ROH represent ethyl, ethoxy, and ethanol groups, respectively. This reaction describes an equilibrium between the hydrolysis of ethoxy groups and the reverse reaction (reesterification). Then, the hydrolyzed groups can react by condensation, leading to Si–O–Si bridging bonds according to reactions (2) and (3).

$$\text{(OR)}_3\text{–Si–OH} + \text{OH–Si–(OR)}_3 \rightarrow \text{(OR)}_3\text{–Si–O–Si–(OR)}_3 + \text{H}_2\text{O} \tag{2}$$

$$\text{(OR)}_3\text{–Si–OH} + \text{OR–Si–(OR)}_3 \rightarrow \text{(OR)}_3\text{–Si–O–Si–(OR)}_3 + \text{ROH} \tag{3}$$

Reaction (2) prevails for sols with high water contents (molar ratio of water to silica precursor (R_W) superior or equal to 2) while reaction (3) is predominant for sols with a low water content (R_W smaller than 2). Since we used in this work an $R_W = 4$, Eq. (2) should be predominant. In both cases, it is the content of Si–OH silanol groups formed in reaction (1) which induces the polycondensation reactions. This reaction is commonly catalyzed using different acids to control the reactions [24]. The gelation times measured in this work are representative of the polycondensation kinetics, which leads to the formation of silica coatings and monoliths.

Fig. 2 exhibits the gelation time of silica sols prepared using different acids and keeping the molar ratio of TEOS/EtOH/H_2O/acid at 1/4/4/0.1. The theoretical pH of the solutions was estimated considering HNO_3 and HCl as strong acids, and HF and HOAc as weak acids. It was observed that the gelation time of the sols depends on the acid used in the synthesis. Several works reported that the gelation time of the silica sol tends to be longer when the solution pH is about 2 (silica isoelectric point), making more difficult the contact