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The influence of an acid catalyst on the morphology, wettabillity, adhesion and chemical structure properties of TiO_2 and ZrO_2 sol–gel thin films

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ABSTRACT

The proper selection of synthesis parameters and the way of preparing materials is of crucial importance in successful sol–gel synthesis, hence high quality of coatings is essential. The pH value of the sol–gel reaction mixture, which is dependent on the used catalyst, influences the hydrolysis and condensation reaction and also affects the form and structure of the received materials. Acids contribute to protonate alkoxide groups and intensify the hydrolysis reaction kinetics. Moreover, during condensation the pH affects the structure of the produced polymeric chains. Acid-catalyzed reaction is preferentially directed to the end of chains and leads to the achievement of less branched and more extended structures. The studies presented in this paper, focused on the influence of a catalyst type used in the acid catalysis for the preparation of thin films.

TiO_2 and ZrO_2 thin films have been investigated due to the ability to form crystalline structure at relatively low temperatures. The influence of the used acid catalyst (HCl, HNO_3, H_2SO_4, H_3PO_4) on physicochemical properties was considered. SEM examination of the obtained materials was carried out to check the influence of different catalysts on the surface morphology and topography. The impact of the type of the used catalyst on the chemical structure of material has been investigated by Raman and Infrared Spectroscopy. Wettability measurements were conducted to verify the catalyst and materials structure effect on surface properties of the obtained materials. All described results have proved that sol–gel process of zirconia materials is much more sensitive to the pH value of a reaction in comparison with titania materials.

1. Introduction

Sol–gel is a method of preparing highly advanced materials which can find application, e.g. in forming thin layers for a variety of purposes. In each case of potential application of considered coatings, synthesis parameters influence the physicochemical and morphological structure, and thus the properties of obtained materials. So investigations of process parameters are of crucial importance [1,2]. The concentration of particular components of the sol [1,3], the presence or type of a catalyst and stabilizing agents [4], pH [5], and annealing process [6] are examples of these parameters.

The proper selection of synthesis parameters and the way of preparing materials is significant in successful sol–gel synthesis. The most undesirable, but also very commonly reported, effects of improper conduction of the synthesis are: in the case of powders – agglomeration [7,8], in the case of thin films and monoliths – material shrinkage and cracking [9,10,11,12]. Such defects exclude them from efficient use.

The suitable, herein considered sol–gel coatings are widely investigated in the area of optics [13,14], biomaterials [15,16,17], nanobiocomposites [18], protective coatings [19], self-cleaning materials [20] and others [21]. Sol–gel materials are also often modified because of oxide matrix passivity [22,23].

The sol–gel method is based on hydrolysis and condensation reactions [24]. Most of the literature data refer to the sol–gel reactions for preparing silica. Typically used catalysts increase the rate of hydrolysis. The type of catalyst determines the pH of sols and affects the form of sol–gel materials, obtaining the films, powders or monoliths. Fig. 1 shows the relative condensation and kinetics of hydrolysis reactions of silica sol–gel materials and their dependence on reaction environment pH. Although Fig. 1 presents relationships for silica materials, it is well known that the pH of environment has influence on hydrolysis and condensation kinetics of all metal alkoxides, e.g. titanium and zirconium alkoxides considered herein.

The pH value of the reaction mixture, which is dependent on the used catalyst, influences the hydrolysis and condensation reaction and affects the form and structure of the received materials. Acids contribute to protonate alkoxide groups and intensify the hydrolysis reaction kinetics. In the case of bases, the influence on hydrolysis rate is strongly

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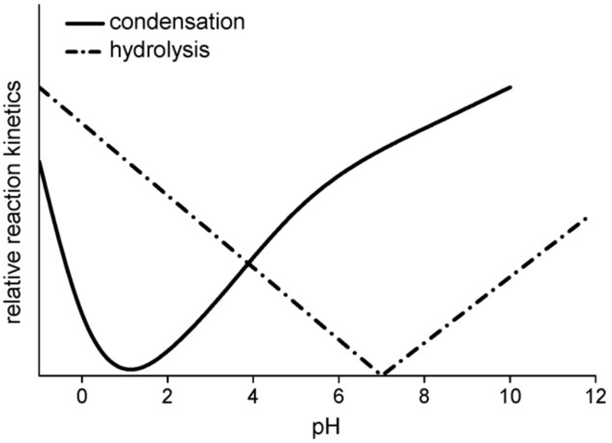

Fig. 1. Relative hydrolysis and condensation kinetics of alkoxysilanes as a function of reaction mixture pH [9].

dependent on the type of alkoxide. For example the hydrolysis rate in basic conditions is promoted for siloxanes but is reduced for $Ti(OBu)_4$ [24]. Moreover, during condensation the pH affects the structure of the produced polymeric chains. An acid-catalyzed reaction is preferentially directed to the end of chains and leads to achieving less branched and more extended structures. Whereas, base-catalyzed condensation is more directed to the middles of chains and results in highly branched and more compact frameworks [24]. The pH impact on material structure has a corresponding effect on properties and it is the subject of research of [8,25,26,27,28].

The most frequently used catalysts are aqueous solutions of NH_3 or HCl for powders and films respectively. The studies presented in this paper focus on the influence of a catalyst type used in the acid catalysis for the preparation of thin films.

Studies of the impact of a catalyst on the properties of materials obtained by the sol–gel method are not frequently encountered but the reported results reveal clear influence of the used catalyst. Asomoza et al. [29] showed that in the case of sol–gel silica monoliths the material is more ordered and regular when the catalyst was used than when it was absent. In his work, three analogous sols were prepared — one without a catalyst and the remaining two with HCl or NH_4OH used as catalysts. Moreover, it was found that NH_4OH catalyzed materials did not dehydroxylate in contrast to other materials. Nawaz et al. [30] presented the significant effect of the used catalyst on the microstructure of aerogels obtained by the sol–gel method. According to the used catalyst the density of materials and size or density of pores varied. It was observed that materials made using an acid catalyst were characterized by a smaller pore size and more dense structure than the ones made using a basic catalyst, which caused changes in the mass diffusivity of materials. The diffusion coefficients decreased with the increase of the pore diameter [30].

Interesting impact of the catalyst is observed in the case of materials which can occur in different crystalline forms, e.g. TiO_2. Alzamani et al. [4,31] investigated the influence of catalysts on the properties of TiO_2 sol–gel films and they noticed the catalyst influence on the phases and particle size present in samples. Researchers compared materials obtained with use of DEA (diethylamine) as a basic catalyst (not as a stabilizer) and with the use of different acid catalysts (HCl, HNO_3, H_2SO_4). The results indicated that materials prepared with the use of an acid catalyst demonstrated better photocatalytic activity and contained the largest share of the anatase structure. The best photocatalytic activity was revealed in samples using H_2SO_4 as a catalyst, characterized by the smallest grain size. Syrrokostas et al. [32] prepared TiO_2 films for dye-sensitized solar cells using one of the following: two strong acids (hydrochloric, HCl and nitric, HNO_3), a weak one (acetic acid, CH_3COOH) and a ketone (acetylacetone, $C_5H_8O_2$). It was shown that the properties of the obtained films are dependent on the concentration and the kind of the acid. The effect of acidic peptization on the formation of highly photoactive TiO_2 films was presented by Vinogradov et al. [33]. The authors used the nitric acid, sulfuric acid, hydrochloric acid or glacial acetic acid as peptizing mediators and they showed that the size of colloids in an aqueous solution was proportional to the protonation degree of the surface of particles — it is observed under weakly acidic conditions formation of dense rod-like aggregates, whereas in the case of strong acids the ultradisperse spherical nanoparticles were formed. Colleoni et al. [34] presented the results of the use of acid catalysts (nitric, hydrochloric and acetic acids) during the sol–gel synthesis of the TiO_2 thin films. They showed that photocatalytic activity of materials coated by TiO_2 was moving from acetic to nitric and finally to chloride acid. Additionally, it was presented that acetic acid apart from its catalyst function acts as a chelating ligand changing the whole hydrolysis condensation process. Zirconia and titania sol–gel derived coatings might find application as coatings for metallic implants because of their biocompatibility, high mechanical strength and good corrosion resistance [35,36,37].

In this paper the influence of the type of used acidic catalysts on the structure and properties of the obtained sol–gel layers are examined. Similar studies have been carried out by Houmard et al. [38] for SiO_2 layers and no specific relationship between the type of the used acid catalyst and the wettability properties of the obtained materials were observed. This can be due to the fact that SiO_2 obtained by sol–gel method occurs usually in an amorphous form. Because of this, in the present study the TiO_2 and ZrO_2 thin films have been investigated according to their ability to take the crystalline form. The influence of the used acid catalyst (HCl, HNO_3, H_2SO_4, H_3PO_4) on physicochemical properties was considered. In order to do this, several TiO_2 and ZrO_2 thin films were obtained using particular acids as a catalyst respectively. The SEM examination of the obtained materials was carried out to determine the impact of different catalysts on the surface morphology and topography. The impact of the type of the used catalyst on the chemical structure of material has been investigated by Raman and Infrared Spectroscopy. Wettability measurements were conducted to verify the catalyst and material structure effect on surface properties of obtained materials. In this paper alternative names were used for the obtained materials: films, thin films, layers or coatings.

2. Materials and methods

2.1. Materials preparation

Disks made of austenitic steel SS316L (15 mm of diameter and 1 mm of thickness) were used as substrates. Fig. 2 present the general schema of the obtained final product. In order to promote adhesion between the

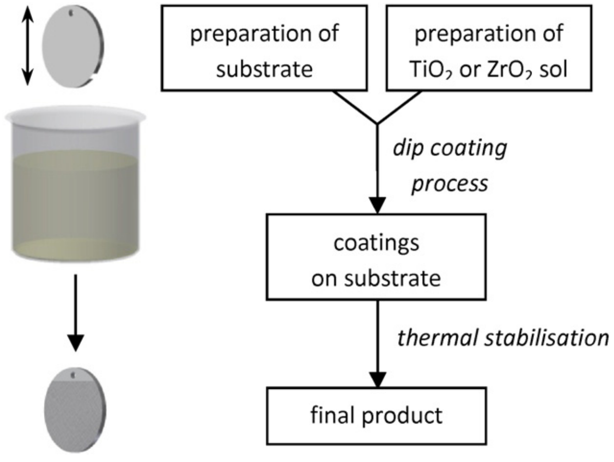

Fig. 2. The general procedure of sample preparation with sol–gel layers.