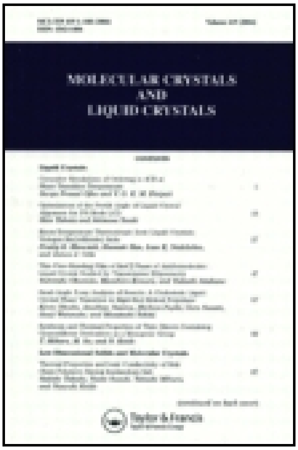

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Improvement in Quality of Sol-Gel Derived Zirconia Multilayer Coatings by Polymeric Additive

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An improved method of preparing thick, multi-layer coatings of zirconia on glass is described and the results have been discussed. Basic sol-gel solutions which comprise zirconium propoxide, n-propanol, acetylacetone and a few drops of nitric acid were stable for several months. However, coating prepared on the base of these solutions has numerous defects such as crazing, cracking and pin-holing.

It was found that the quality of thick films can be improved by adding polymeric additive PEG 200 to the sol-gel solution. The best ratio of zirconium propoxide to PEG 200 was established. Prepared films have been characterized by Thermal Analysis (TA), x-ray Diffraction (XRD) and Rutheford Backscattering Spectroscopy (RBS).

Keywords: zirconia coating; sol-gel coating; organic additives

INTRODUCTION

The formation of high quality thick oxide coatings by sol-gel technique has still remained a far from perfect performance.

The structure of such thick layers can be altered during all steps of the coating process, therefore it is very difficult to control. The main disadvantages caused by these circumstances are: non-uniform composition through the film's layer and defects such as cracking, crazing and pin holing.

A significant way to reduce and remove above-mentioned defects is the addition of suitable organic or polymeric compounds to the precursor sol-gel solution. The main purpose of this paper is to describe the improvement in quality of zirconia coatings by two additives: acetylacetone (Acac) [1-4] and polyethylene glycol (PEG-200). The fact that some polymeric materials can control supramolecular structure of coatings during drying and syntering processes was taken as a basis for using polyethylene glycol as the polymeric additive [5-7].

EXPERIMENTAL

All used chemicals were commercial (Aldrich). Water was purified by the Millipore System.

Preparation and Coating Formation

Basic sol-gel precursor solution

The basic sol-gel precursor solution was prepared under nitrogen at the room temperature as follows: (1) a suitable volume of distilled Acac was mixed with n-propanol, (2) zirconium propoxide was dissolved in n-propanol, (3) the required amount of PEG 200 was dissolved in the mixture of water and n-propanol. The solution (2) was mixed with the desired volume of solution (1) then, after approximately 12h, solution (3) was added to the resulting mixture, giving the final solution . Chemicals were transferred and added by using a syringe and a cannula.

Dip-coating Process

The process was carried out in a dip-coating tube in the nitrogen atmosphere. Glass plates were immersed vertically into the coating solution at constant rate 5cm /min and, after defined time, withdrawn at the same rate. The coatings were pre-dried in the dipping tube for 20 minutes and then hydrolyzed in the atmosphere of 20% of relative humidity (RH).

The coated glass slide was fired to 280°C using a heating rate of 100°C/h which was then maintained for 2hrs. The sample was then further heated to 520°C using the same heating rate and then this temperature was maintained for 1 hr before cooling.

Each coating deposited a thin film of about 70 nm of thickness depending on precursor solution concentration. Several coatings were required to get a thick, multi-layer film. Each consecutive coating was done in the same conditions as described above.

Coatings characterization methods.

The structure of deposited films was described by:

- Differential Thermal Analysis (DTA/ TGA/ TG).
- X-Ray Diffraction (XRD).
- Rutherford Backscattering Spectroscopy (RBS).

RESULTS AND DISCUSSION

All investigated compositions of sol- gel solutions have been summarized in Table 1.

As can be seen from the table 1, clear, stable for long time solutions were obtained in the range of R value 1 – 2, when concentration of zirconium propoxide was 0.5 mol/L and water concentration expressed by value W was between 2 – 3.5.

TABLE 1 Composition of sol-gel precursor solutions

$Zr(OPr)_4$ Mol/L	R	W	PEG 200 Mol/L	Precursor solution	Quality of coating
0.50	0.0	3.5	0.00	Precipitate	No deposit
0.50	0.5	3.5	0.25	Gel immediately	No deposit
0.50	1.0	4.0	0.00	Clear, moderate stable solution	Poor deposit
0.50	1.0	3.5	0.25	Stable solution	Poor quality deposit
0.50	1.0	2.0	0.25	Stable sol	Good deposit
0.50	1.0	3.0	0.25	Stable sol	Very good deposit
0.50	1.0	4.0	0.25	Transparent gel	Powder
0.50	1.0	2.0	0.50	Clear sol, stable	Good deposit
0.50	1.0	2.0	1.00	Viscous solution	Deposit
0.50	2.0	3.5	0.25	Clear, stable sol	Good deposit
0.50	4.0	3.5	0.25	White crystals	No deposit
0.75	1.0	2.0	0.25	Sol stable for short time	Poor deposit
1.00	1.0	2.0	0.25	Clear, not stable	No deposit, powder

R = ratio of [Acac] / [Zr $(OPr)_4$] W = ratio of [H_2O] / [Zr $(OPr)_4$]

When alkoxide concentration and R value were low precipitation occured [4]. The greater R, the more stable solutions were obtained except the highest value R= 4, when white crystals and no deposit were observed. Increasing water concentration showed a tendency to create a gel. This observation proves that Acac controls the kinetics of hydrolysis and condensation reactions [1-4].

The presence of second additive PEG 200 caused the further increase of stability and viscosity of precursor solutions. This last effect is of a great importance to the coatings formation because this additive is able to control the drying shrinkage by modulation of viscoelastic properties of gel. Hence, defects formation is avoided or reduced [7] and single and multi-layer coatings are of much better quality.

Coatings characterization

Thermal Analysis

The DTA/TGA and TG data have been recorded in the air at flow rate 10cm^3/min. Gel samples, prepared from original precursor solution, were dried for 24hr at 130° C. The TG plot indicates that gel loses weight at the temperature of 100 – 200°C, as a result of n-propanol removal (Fig.1). The next stage is the stage of gel dehydration followed by the burn off of the organic residues at the range of about 400 –550° C.

The large exothermic effect at about 320° C on the DTA diagram corresponds to the transformation of amorphous sample to metastable cubic form. Broad and small peaks at about 430°C and 530° C indicate that zirconia structure contains only small amounts of both metastable phases: tetragonal and monoclinic, which were not recorded by x-ray diffraction pattern (Fig.2). The most likely reason for that is that Acac and PEG-200 modify the change of structure during firing.

At this stage it is very difficult to clarify the modifying effect of both additives Acac and PEG 200 during firing. However, it seems that PEG intensifies Acac inclination to prevent the transformation of metastable cubic form to the mixture of tetragonal and monoclinic forms.

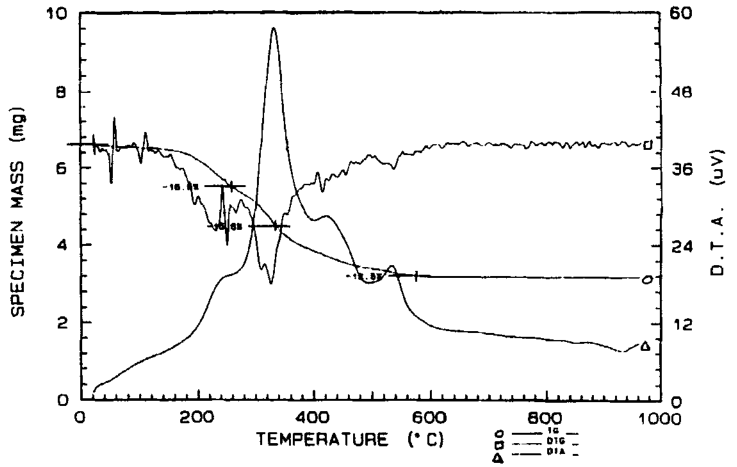

FIGURE 1 TG, DTA, and DTG analysis; Basic solution: R=1; $[Zr(OPr)_4]=0.5M/L$, W=2, [PEG 200]=0.5M/L.

X-Ray Diffraction

X-Ray diffraction of coatings (Fig.2) shows, that the metastable, cubic zirconia is in the crystalline phase, observed in coatings fired up to 540° C. According to G.Katz [8], this phase appears at 285 °C. The patterns have not shown the metastable polymorphous mixture of tetragonal and monoclinic forms, which should have been recorded between 300° and 600° C.

The best-formed x-ray pattern with all cubic zirconia characteristic peaks has been recorded for thick coat formed by seven repeated dippings.

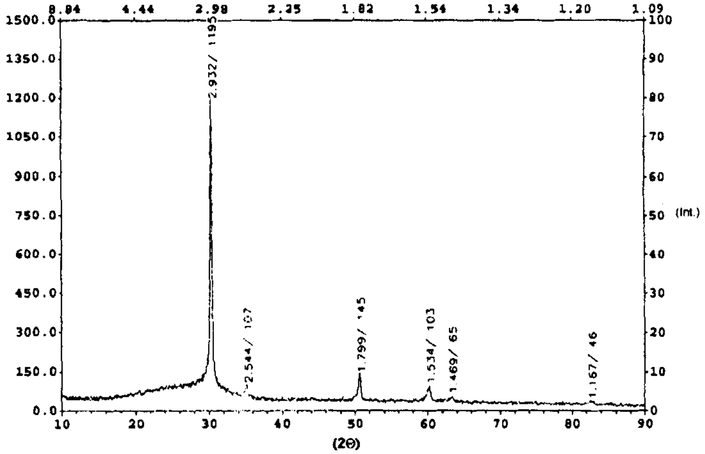

FIGURE 2 X-ray diffraction pattern of zirconia coating.R=2; $[Zr(OPr)_4]$=0.5M/L, W=3.5, [PEG 200]=0.25M/L

Thickness of coatings

The thickness of multi-layer coats has been measured using Rutherford Backscattering Spectroscopy (RBS). The analyses were done on 1.25 mm^2 area near the center of the slide.

TABLE 2. Thickness of zirconia multi-layer coatings estimated by (RBS)

R $[Acac]/[Zr(OPr)_4]$	Number of coatings	RBS Atom/cm^2	RBS D(nm)
1.0 [a]	1	650	72
As above	4	3400	375
As above	6	5150	567
1.0 [b]	1	700	77
As above	4	2900	350
As above	6	5000	550
As above	7	5650	622

a – $[Zr(OPr)_4]$ = 0.5mol/L, W= 3.0, [PEG 200] = 0.25mol/L.
b – $[Zr(OPr)_4]$ = 0.5mol/L, W =3.5, [PEG 200] = 0.25mol/L.

The thickness of deposit was determined as the value of atom/cm^2 and subsequently converted to nm assuming the density of the zirconia coating to 6.2g/cm^3 (see Table 2) [9].

It is very interesting to compare the resulting zirconia coating thickness with data measured by ellipsometry for a sol–gel derived coatings [10, 11]. The thickness of a single coating, obtained by using 0.91 mol/L zirconia precursor solution without additives, was about 55 –70 nm.

CONCLUSIONS

Both additives Acac and PEG 200 improve the quality of zirconia coats. At this stage it is difficult to give the full description of the mechanism which takes place in the presence of additives. However it seems to be possible that Acac increases stability and quality of sol-gel solution by controlling hydrolysis and condensation reactions. The second polymeric additive controls the shrinkage of gel reducing significantly the structural defects of coats.

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