Ceramics International 23 (1997) 141–148

PII: S0272-8842(96)00013-2
0272-8842/97 $17.00+.00

SiO_2–CeO_2 Coatings of Glass Substrate by Sol–Gel Process

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(Received 4 August 1995; accepted 28 November 1995)

Abstract: In the present work, the preparation of SiO_2–CeO_2 coatings by sol–gel dip coating technique was carried out. The parameters, such as different H_2O to TEOS and SiO_2 to CeO_2 ratios, viscosity of alkoxide solution, different withdrawal speed, affecting the film properties were studied. Transmittance, film thickness were determined as a function of the experimental parameters and SEM micrographs of the coated glass substrate were given. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Coating glasses, ceramics and metals with oxide films in order to gain new functions or improve the surface characteristics of substrates have been progressed in a very productive way since the introduction of the sol–gel process of metal alkoxide solutions in this field and many of the coating techniques have been developed. The dip coating technique is the one which is applied practically.

As it is known, cerium is an important element in glass and ceramic industry and its oxide-film which is obtained with different mole ratio of cerium to other elements (mostly titanium) by sol–gel process have been studied widely, though conclusions drawn about the functions of cerium element in the alkoxide solutions reveal some disagreement.[1,2] In fact, there is not much about SiO_2–CeO_2 binary system which is therefore the objective of this work.

2 EXPERIMENTAL

2.1 Apparatus and chemicals

Shimadzu UV 160A model UV–visible spectrometer, JSM-T330 model scanning electron microscope (SEM) and special designed dip coating instrument, Ubbelohde U-tube viscometer, IP71, were used in this research.

All chemicals used were reagent grade quality.

2.2 Methods

Dip coating technique has some advantages to other coating techniques. It is simple, provides highly uniform film thickness, chemical and mechanical strength, allows very complex shapes to be coated easily and gives amorphous or crystalline coatings at room temperature.

The transmittance of the coated glass slides were measured by UV–visible spectrophotometer for one dipping. For the sake of brevity, the transmittance data of 6 film types are shown in Table 1 and in Figs 1–6.

The microstructure of the oxide film was determined by scanning electron microscopy and the thickness of the film was measured by the SEM method finding a crackling part of a film. The results are shown in Table 1 and the micrographs are given in Figs 7–18.

2.3 Coating solutions

(i) Two different solutions containing H_2O/TEOS mole ratios of 7.4 and 2.2 were prepared with acid (HCl) catalyst by aging at room temperature. (ii) The solution containing cerium and silicon with mole ratios of 1 and 2 (Ce/Si), in which the mole ratios of H_2O/TEOS are constant as 7.4 and 2.2, were prepared with acid catalyst by aging at room temperature.

All the solutions prepared were freshly used for the coating experiments.

Table 1. The results of transmittance measurment

Coating procedure Fresh	24 h old	Film type	Withdrawal speed 5 cm/min		15 cm/cm		23 cm/min	
			Peak (nm)	T%	Peak (nm)	T%	Peak (nm)	T%
+		SiO_2	538	92.0	537	93.7	496	93.2
	+	SiO_2	400	92.6	585	92.5	486	90.5
+		SiO_2-CeO_2	488	92.7	460	91.5	456	88.9
	+	SiO_2-CeO_2	577	92.5	552	92.9	419	85.7
+		SiO_2-$2CeO_2$	752	77.0	392	74.6	438	66.0
	+	SiO_2-$2CeO_2$	487	73.6	438	81.2	450	82.6

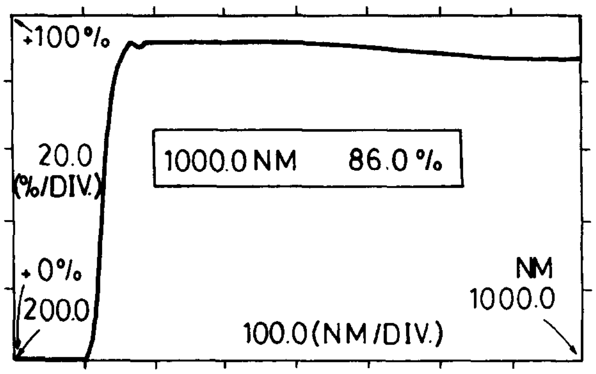

Fig. 1. SiO_2 film of fresh alkoxide solution.

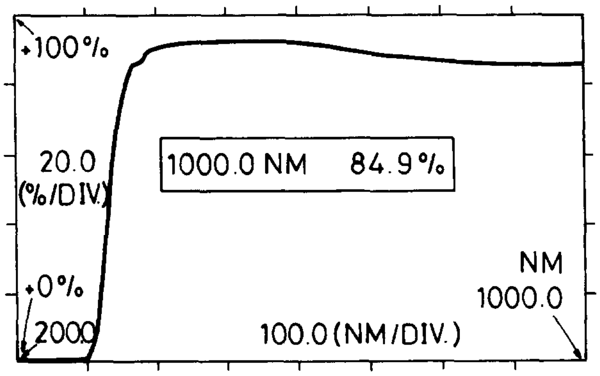

Fig. 4. SiO_2–CeO_2 film of 24 h old alkoxide solution.

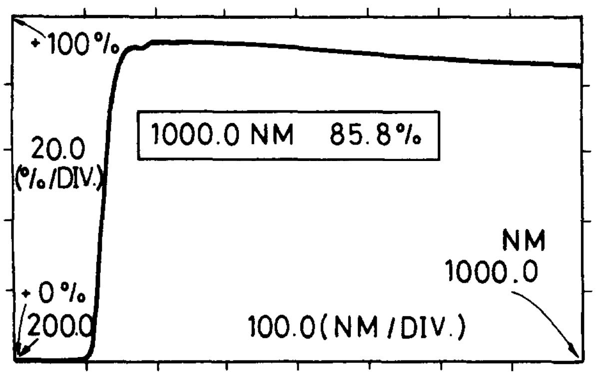

Fig. 2. SiO_2 film of 24 h old alkoxide solution.

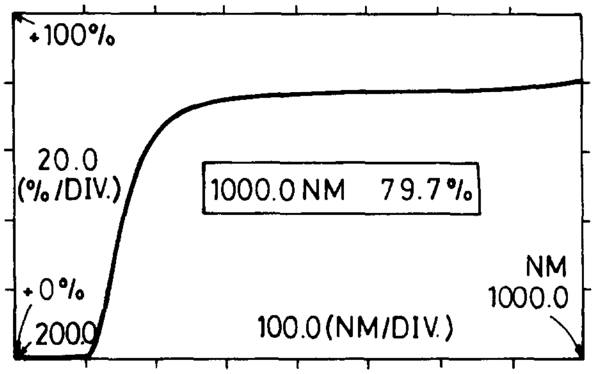

Fig. 5. SiO_2–$2CeO_2$ film of fresh alkoxide solution.

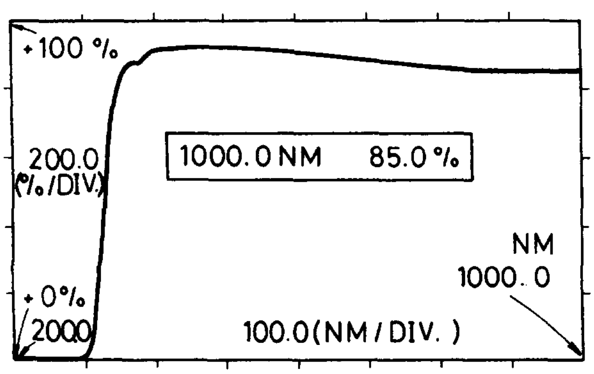

Fig. 3. SiO_2–CeO_2 film of fresh alkoxide solution.

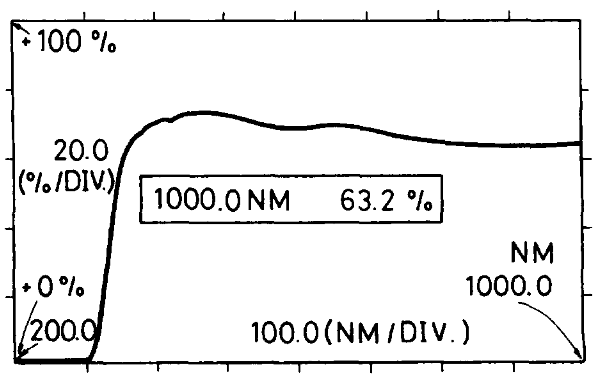

Fig. 6. SiO_2–$2CeO_2$ film of 24 h old alkoxide solution.

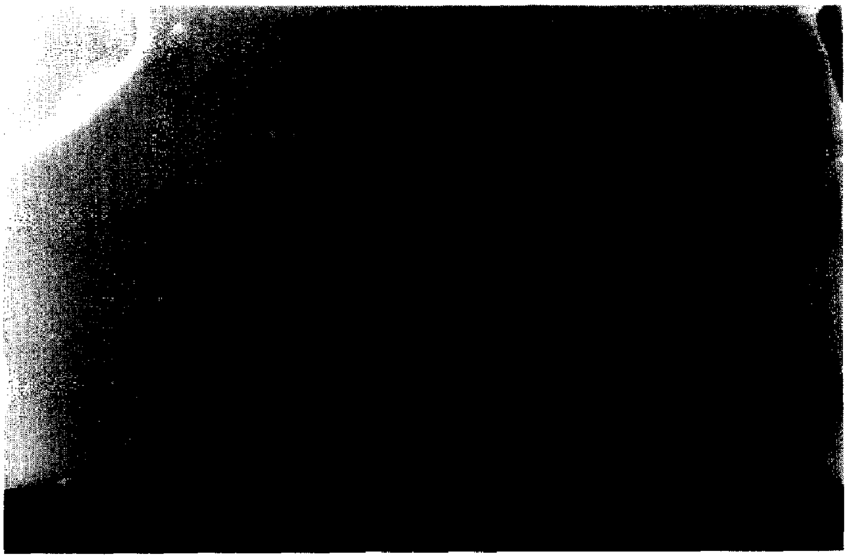

Fig. 7. SEM micrograph of SiO_2 (fresh, WS = 15 cm/min, H_2O/TEOS = 7.4).

Fig. 8. SEM micrograph of SiO_2 (fresh, WS = 23 cm/min, H_2O/TEOS = 7.4).

Fig. 9. SEM micrograph of SiO_2 (fresh, WS = 15 cm/min, H_2O/TEOS = 2.2).

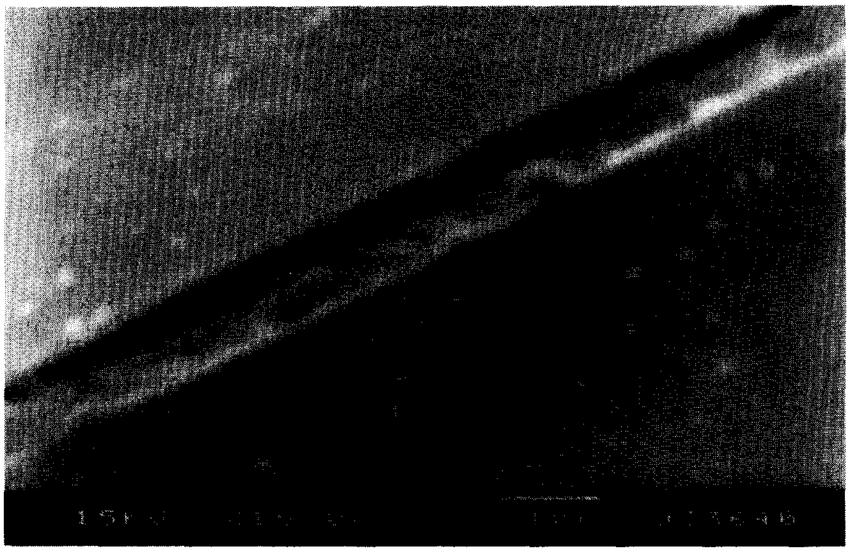

Fig. 10. SEM micrograph of SiO_2 (fresh, WS = 23 cm/min, H_2O/TEOS = 2.2).

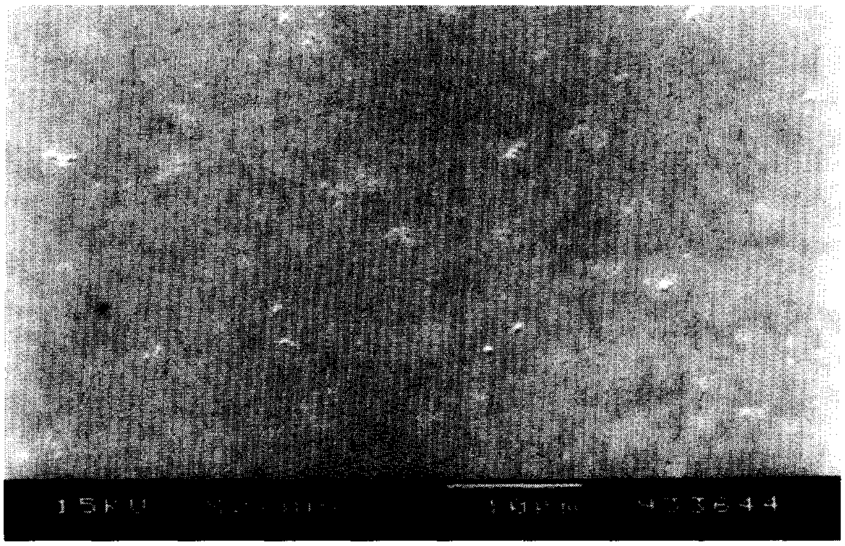

Fig. 11. SEM micrograph of SiO_2 (old, WS = 5 cm/min, H_2O/TEOS = 2.2).

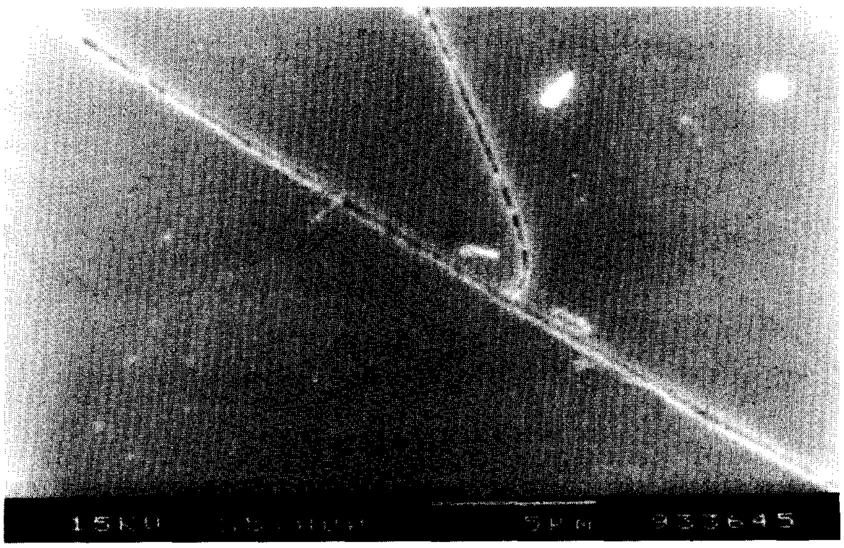

Fig. 12. SEM micrograph of SiO_2 (old, WS = 23 cm/min, H_2O/TEOS = 2.2).

Fig. 13. SEM micrograph of SiO_2 (old, WS = 23 cm/min, H_2O/TEOS = 2.2).

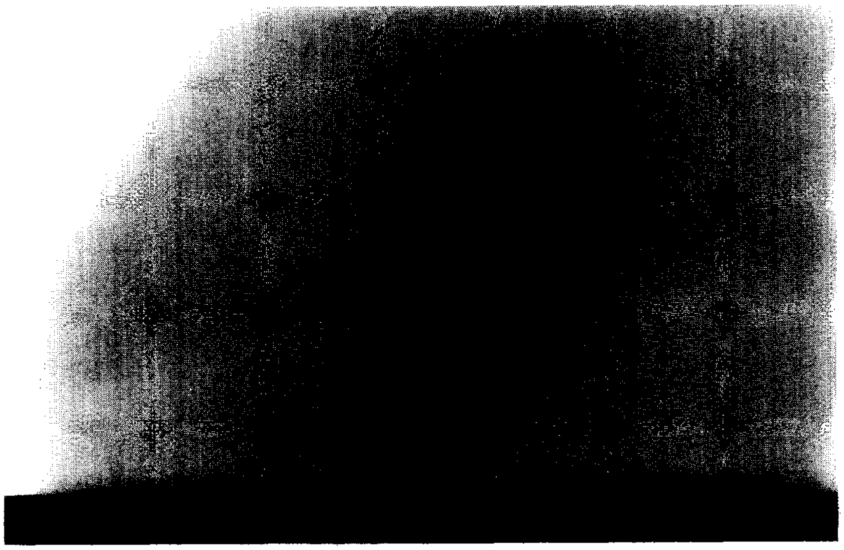

Fig. 14. SEM micrograph of SiO_2–CeO_2 (old, WS = 15 cm/min, H_2O/TEOS = 2.2).

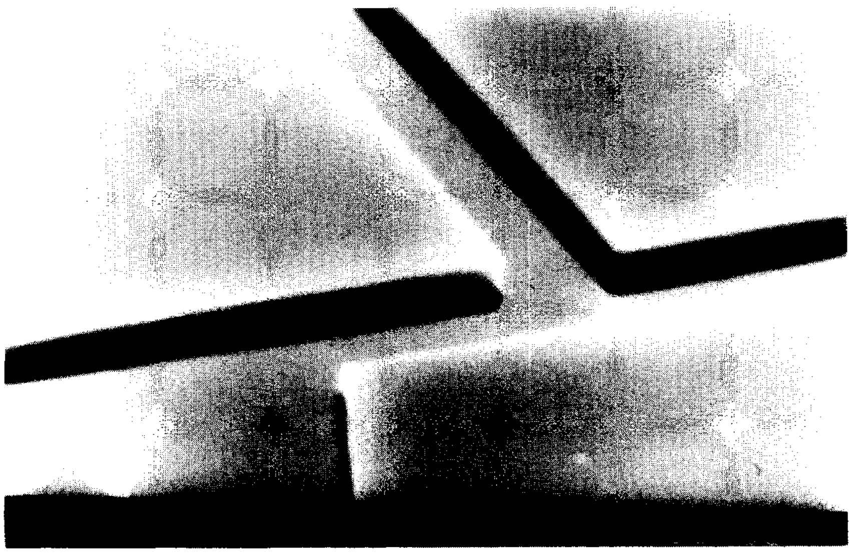

Fig. 15. SEM micrograph of SiO_2–CeO_2 (old, WS = 23 cm/min, H_2O/TEOS = 2.2).

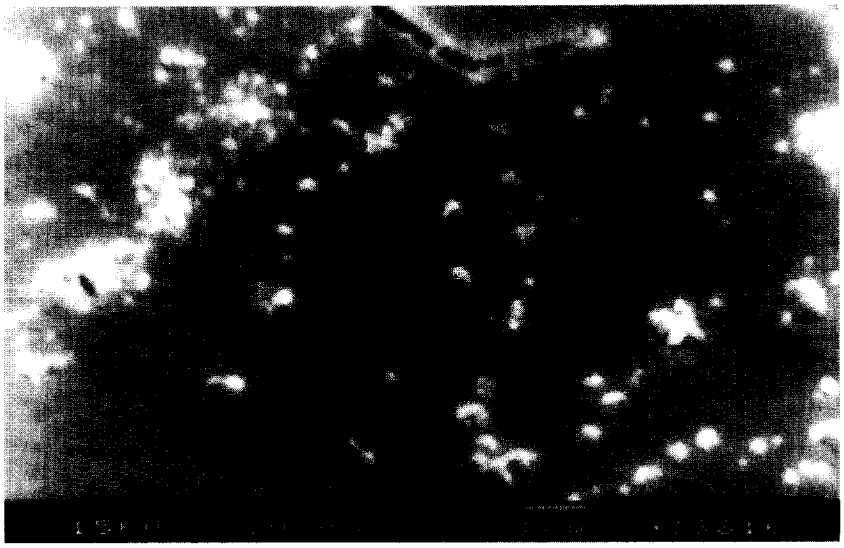

Fig. 16. SEM micrograph of SiO_2–$2CeO_2$ (fresh, WS = 5 cm/min, H_2O/TEOS = 2.2).

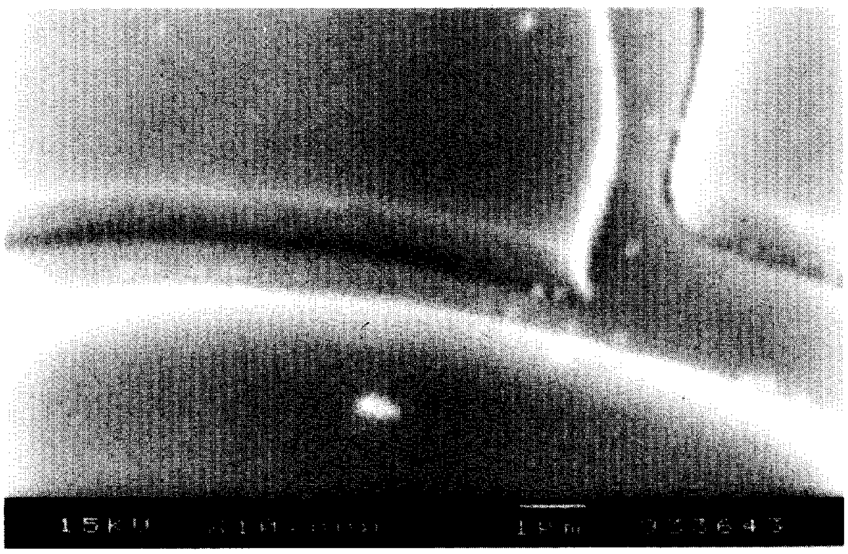

Fig. 17. SEM micrograph of SiO_2–$2CeO_2$ (fresh, WS = 23 cm/min, H_2O/TEOS = 2.2).

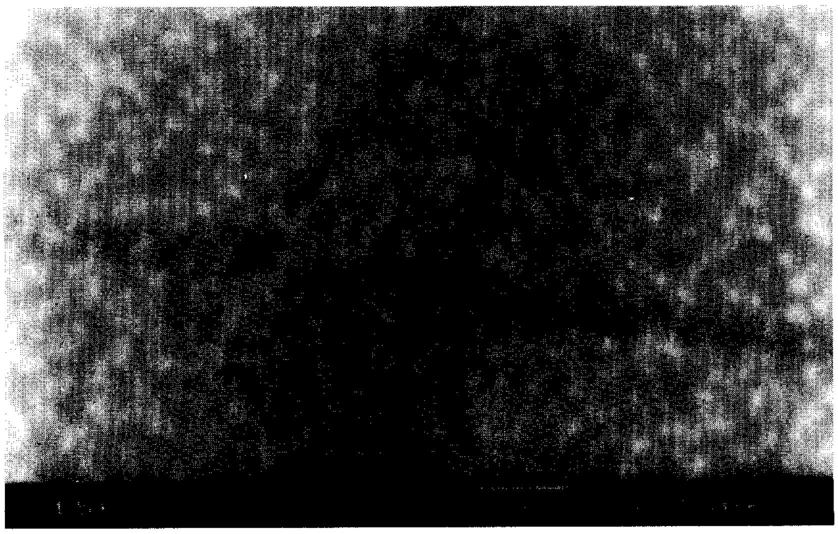

Fig. 18. SEM micrograph of SiO_2-$2CeO_2$ (old, WS = 23 cm/min, H_2O/TEOS = 2.2).

Table 2. The thickness of films

	Film type	Withdrawal speed (cm/min)	H_2O/TEOS mole ratio 7.4 Thickness (μm)	7.4 Viscosity (mm^2/S)	2.2 Thickness (μm)	2.2 Viscosity (mm^2/S)
A		5	—		2.30	
	SiO_2	15	0.84	3.1	0.94	2.9
		23	0.74		0.25	
		5	0.79		0.70	
	SiO_2–CeO_2	15	—	3.3	0.85	3.0
		23	—		1.20	
		5	—		—	
	SiO_2–$2CeO_2$	15	—	3.7	0.52	3.2
		23	—		0.94	
B	SiO_2	5	—		—	
		15	—	3.3	0.23	3.1
		23	0.41		0.67	
		5	0.82		0.59	
	SiO_2–CeO_2	15	—	3.7	0.69	3.3
		23	1.17		0.70	
		5	0.15		0.54	
	SiO_2–$2CeO_2$	15	0.82	4.4	—	3.5
		23	1.18		0.94	

2.4 Coating procedure

The glass slide, after being cleaned with alcohol ultrasonically, is dipped into the coating solution and withdrawn vertically at three different withdrawal speeds 5 cm/min, 15 cm/min and 23 cm/min. The coated sample is dried in air for a while, then in an oven at 60 °C, and after it is heated at 500 °C, is left to cool.

The same procedure is repeated with 24 h old solutions.

3 RESULTS AND DISCUSSION

Thickness and transmittance of a film are related closely to the experimental parameters. The results of the transmittance measurements show that transmittance decreases with the increase of withdrawal speed and with cerium concentration colour (Table 1 and Fig. 4). Yellow and opalescence appear when cerium concentration increases.

The thickness of the films at different withdrawal speeds are given in Table 2. Thickness varies linearly with withdrawal speed, but SiO_2 films, which are prepared from the freshly used alkoxide solutions which contain H_2O/TEOS mole ratios of 7.4 and 2.2, show that thickness decreases exponentially when the withdrawal speed increases. It is difficult to give an explanation for this result taking into consideration the composition of coating solution, because the result also shows that thickness is independent of H_2O/TEOS mole ratio. However, there is no agreement in the literature data[1–5] whether the thickness increases with withdrawal speed linearly or exponentially.

It is concluded from the SEM micrographs that a relatively good coating is obtained from both the fresh and 24 h old coating solutions used which contain a H_2O/TEOS mole ratio of 2.2. Heat treatment of the coated glass slide generally gives a satisfactory result, only a few damaged films existed. Therefore, to measure the thickness of coatings by the SEM method, it was necessary to make cracks on the coating, thus mechanical damage took place on most of the films. It is possible to differentiate the mechanical and heating failure in the SEM micrographs (Figs 7–18). The higher content of CeO_2 in the film cannot be incorporated well in the composition, so white CeO_2 is observed because of the phase separation during the drying process.

4 CONCLUSIONS

A good coating is obtained by the coating solution which is 24 h old, has lowest viscosity, less amount of water and cerium. The thickness of the films varied between 0.5 and 0.7 μm and high transmittance is reached with the lowest withdrawal speed.

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