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Dependence of thickness on the withdrawal speed for SiO_2 and TiO_2 coatings obtained by the dipping method

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SiO_2 and TiO_2 sol–gel thin films were prepared from solutions of different concentration. To fit the experimental coating thickness values, the modification of two theoretical equations, available from the literature, was used. The best-fit results were given by the approach which relates the thickness to the square root of the velocity. It was shown that, provided the same heat treatment is used for the films, the thickness of coatings obtained from solutions of different concentration and at any withdrawal speed may be predicted from just one thickness value obtained at one withdrawal speed, if the solutions' viscosity and density, are known.

1. Introduction

In the dip-coating method, the thickness of the deposited liquid film depends on some properties of the coating solution (density, viscosity, surface tension) and on the selected withdrawal speed.

Basically, there are two different theoretical approaches to the problem. One is known as the Landau and Levich (L–L) theory [1], which estimates the thickness of the liquid film by the expression

$$t_l = 0.944 C_a^{1/6} \left(\frac{\eta U}{\rho g}\right)^{1/2} \quad (1)$$

where C_a is the capillary number and is given by $C_a = \eta U/\sigma$; η, σ and ρ are the viscosity, the surface tension and the density of the liquid, U is the withdrawal speed and g is the gravitational acceleration constant. The above expression is valid for low C_a, i.e. for $C_a < 10^{-3}$ or less [2].

The second approach [2], derived by solving the flow equation for a liquid film of constant thickness, in the case of $C_a < 10^{-3}$ and for a Newtonian fluid gives the expression

$$\begin{aligned} t_l &= J\left(\frac{\eta U}{\rho g}\right)^{1/2} \\ &= J t_0 \end{aligned} \quad (2)$$

where J is the dimensionless flow.

When sol–gel coatings are deposited on a substrate, their thickness is usually measured after the initial liquid film has gelled and dried to a solid coating, or more usually even after the densification heat treatment. Because the above equations refer to the thickness of the original liquid film, t_l, this needs to be related to the heat-treated coating thickness, t_p. Guglielmi and Zenezini [3] suggested the following simple expression:

$$t_l = t_p \frac{\rho_p}{c} \quad (3)$$

where ρ_p is the density of the heat-treated coating ($g\,cm^{-3}$) and c is the concentration of the solution (g final oxide per unit volume (cm^3)).

Equations 1 and 2 for the solid film thickness became, respectively

$$t_p = 0.944 C_a^{1/6} \frac{c}{\rho_p} \left(\frac{\eta U}{\rho g}\right)^{1/2} \quad (4)$$

$$t_p = J \frac{c}{\rho_p} \left(\frac{\eta U}{\rho g}\right)^{1/2} \quad (5)$$

These two equations are different in two respects. In Equation 4 the thickness is proportional to $U^{2/3}$, while in Equation 5 it is proportional to $U^{1/2}$. Equation 4 only needs the solution and processing parameters to be used, while the dimensionless flow, J, must be experimentally determined in order to use Equation 5. Thus the L–L derived expression should be more immediate, if applicable. However, it was derived for liquids that, during the coating process, do not change their properties. This is certainly not the situation for sol–gel solutions, so the applicability of this equation is not obvious.

In this work the two expressions were used to fit experimental thicknesses of coatings obtained from SiO_2 and TiO_2 precursor solutions of different concentrations. The first aim was to test the applicability of both approaches to two kinds of solution which

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have very different chemical reactivities. The second aim was to determine whether or not the dimensionless flow may be taken as independent of the solution concentration.

2. Experimental procedure

Solutions with an SiO_2 concentration of 10, 25, 50 and 75 $g\,l^{-1}$ were prepared by mixing $Si(OC_2H_5)_4$ with ethanol, water and 1 M HCl solution. The H_2O/TEOS and HCl/TEOS molar ratios were, respectively, 5 and 0.01. $Ti(OC_4H_9)_4$ was used to prepare solutions with a TiO_2 concentration of 10, 25, 50 and 75 $g\,l^{-1}$. Acetylacetone (AcAc) was added to ethanol, water and titanium butoxide and no catalyst was introduced. The H_2O/TiBut and AcAc/TiBut molar ratios were 2 and 0.5.

After stirring the solutions for 1 h they were immediately used for coating experiments. At the same time, using different portions of the same solutions, density, viscosity and surface tension were measured at the appropriate temperature by an hydrostatic apparatus, an Hoeppler viscometer and the capillary tension method. Soda–lime slides, used as substrates, were carefully washed with a basic detergent and then rinsed with distilled water. The dipping was performed in a chamber where temperature and humidity were controlled. The relative humidity was 60% for both systems, while a temperature of 30 °C for the SiO_2 solutions, and 20 °C for the TiO_2 solutions, were chosen. The withdrawal speed ranged from 3–75 $cm\,min^{-1}$.

After a 3 h drying at 60 °C, the samples were fired at 500 °C for 72 h. The film thicknesses were measured using a stylus apparatus: several (4–6) zones of each specimen were analysed and all the samples were produced in duplicate. The density of the films was measured using Rutherford backscattering spectrometry (RBS).

3. Results

3.1. Characterization of the solutions

To match the temperature adopted for the preparation of the coatings, the characterization of the fresh solutions was performed at 30 °C for the SiO_2 system and at 20 °C for the TiO_2 one.

Tables I and II give the measured density, viscosity and surface tension values. It can be seen that the density as well as the surface tension showed a trend of linear increment towards the oxide concentration, as expected. The viscosities of the TiO_2 solutions increased with concentration more than the SiO_2 ones.

TABLE I Density, viscosity and surface tension values for SiO_2 solutions

Solution	Density ($g\,cm^{-3}$)	Viscosity (cP)	Surface tension ($dyn\,cm^{-1}$)
C10	0.7983	0.939	22.26
C25	0.8190	1.331	22.72
C50	0.8350	1.443	22.88
C75	0.8677	1.750	23.45

TABLE II Density, viscosity and surface tension values for TiO_2 solutions

Solution	Density ($g\,cm^{-3}$)	Viscosity (cP)	Surface tension ($dyn\,cm^{-1}$)
C10	0.8000	1.0780	22.06
C25	0.8204	1.3552	22.76
C50	0.8507	1.7552	23.11
C75	0.8809	2.6937	23.68

3.2. Thickness measurement

For the SiO_2 system, the measured thicknesses ranged from 25–490 nm with a maximum standard deviation of 8.5%. The films obtained from the solution with 10 g SiO_2 per litre were too thin to be measured accurately by the stylus apparatus, so the data are not reported in the work.

For the TiO_2 system the thicknesses ranged from 15–300 nm with a maximum standard deviation of 5.6%.

Films prepared with both 75 $g\,l^{-1}$ solutions at the highest speeds were of very poor quality (they were heavily cracked and the homogeneous region was not very large), but measurement of the thickness was possible and the reproducibility good.

3.3. Density measurements

The use of Equation 5 does not depend on the film density, as will be discussed later, but in the case of Equation 4 it is important to know the true density after heat treatment of the coating. The density of thin films may be obtained by combining RBS with thickness measurements.

Assuming that the chemical composition of the two investigated types of coating corresponds to SiO_2 and TiO_2, respectively (which is not far from data reported in [4] and [5]), the density was calculated from the relation

$$\rho = \frac{DPM}{t_p N_{Av}} \qquad (6)$$

where D is the number of molecules per square centimetre obtained from RBS spectra, PM is the molecular weight of the oxide, t_p is the thickness of the layer and N_{Av} is Avogadro's number ($6.02257 \times 10^{23}\,mol^{-1}$).

Up to now only few samples have been characterized in this way, but an extensive investigation is in progress to study how the coating's preparation affects its density. SiO_2 coatings prepared from C50 solution and with a thickness of about 220 nm resulted to have a density of 1.96 $g\,cm^{-3}$ after 72 h at 500 °C while TiO_2 films from C75 solution and with a thickness of about 90 nm had a density of 2.47 $g\,cm^{-3}$ after the same heat treatment.

Thus, while SiO_2 seems to reach approximately 90% theoretical density for silica glass, TiO_2 achieves only 65% theoretical value (TiO_2 was present as anatase in those films).

4. Discussion

The dimensionless flow, J, of Equation 2 is obtained by plotting the liquid film thickness, t_l, versus $(\eta U/\rho g)^{1/2}$ $(= t_o)$, but the calculation of t_l from the measured coating thickness, t_p, requires knowledge of the true film density, ρ_p. On the other hand, ρ_p is likely to depend on many factors (chemistry of the precursor solution, time and temperature of the heat treatment, structure of the coating).

It is important to notice that for Equation 5 the problem may be by-passed by directly plotting t_p/c against t_o and obtaining, as the slope of the resulting line, $J^* = J/\rho_p$. Obviously, a unique value of J^* can be used only for the evaluation of coatings of the same type and treated with the same heating schedule.

In Figs 1 and 2 the t_p/c versus t_o plots for SiO_2 and TiO_2 coatings are shown. It is interesting, and of practical utility, to note that J^* is independent on the

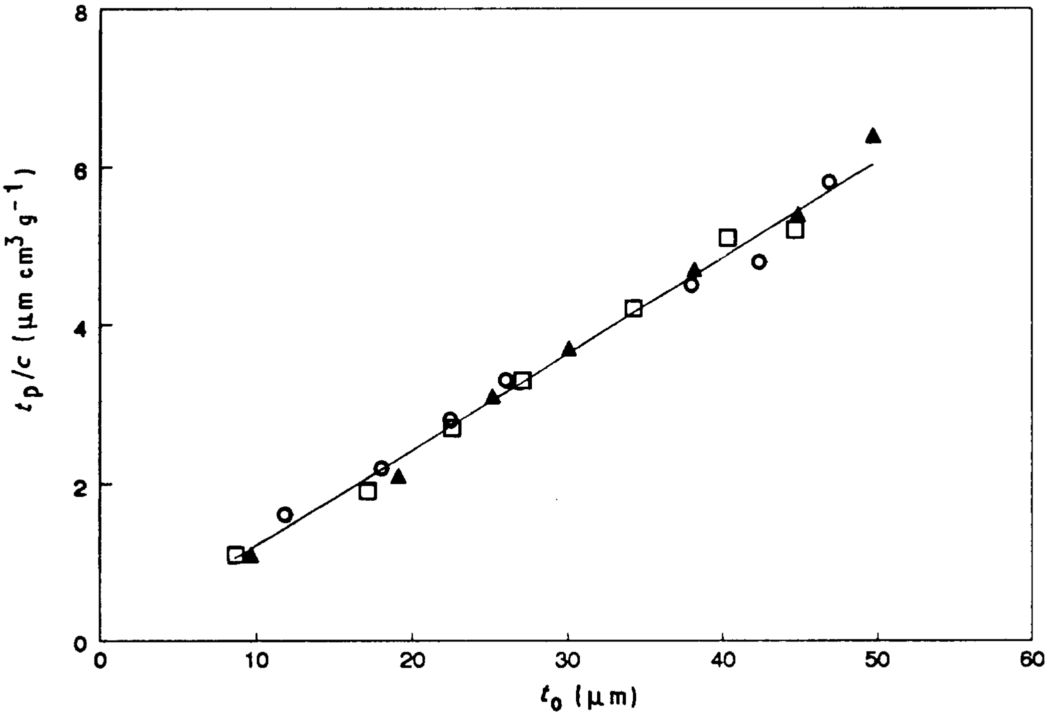

Figure 1 Plot of t_p/c versus $t_0 (= (\eta U/\rho g)^{1/2})$ values for SiO_2 coatings. Solution: (□) 25, (○) 50, (▲) 75; $J^* = 0.1213$.

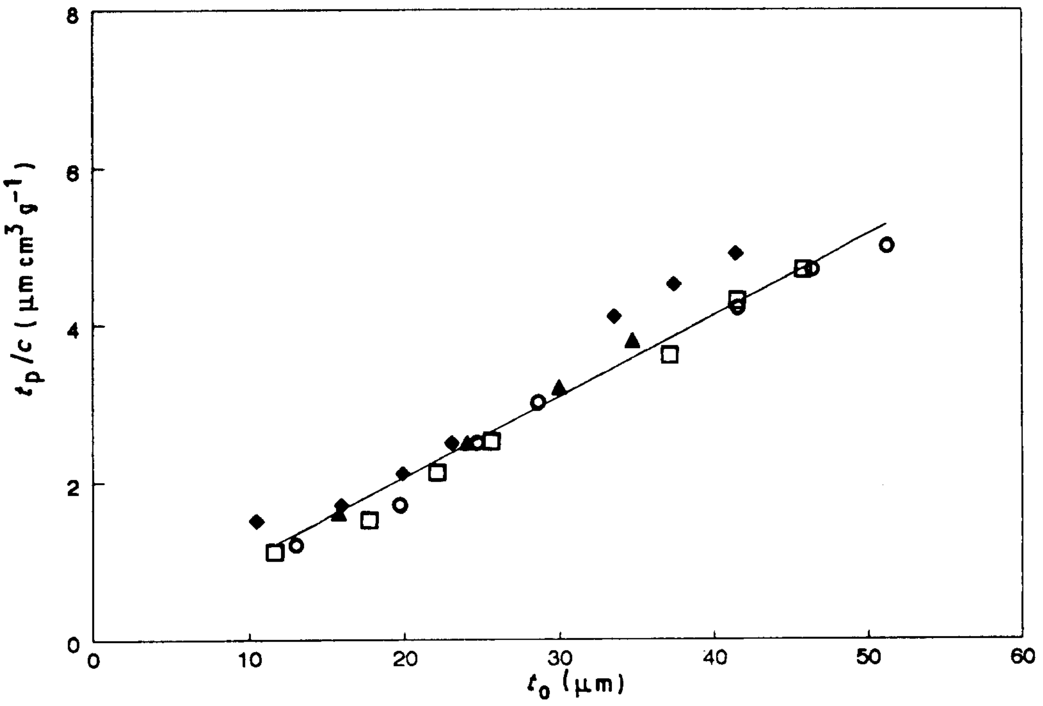

Figure 2 Plot of t_p/c versus $t_0 (= (\eta U/\rho g)^{1/2})$ values for TiO_2 coatings. Solution: (◆) 10, (□) 25, (○) 50, (▲) 75; $J^* = 0.1030$.

solution's concentration. All the experimental data are, in fact, well fitted by the same line, which gives J^* values of 0.1213 ± 0.0012 for SiO_2 and 0.1030 ± 0.0087 for TiO_2. It may be observed from Fig. 2 that the higher dispersion of data in the case of TiO_2 is due to the thickness of coatings prepared with the less concentrated solution and affected by the largest uncertainty.

In Figs 3 and 4 coating thicknesses are plotted as a function of the withdrawal speed, U, together with the curves obtained from the Landau and Levich equation (Equation 4) using the experimentally determined

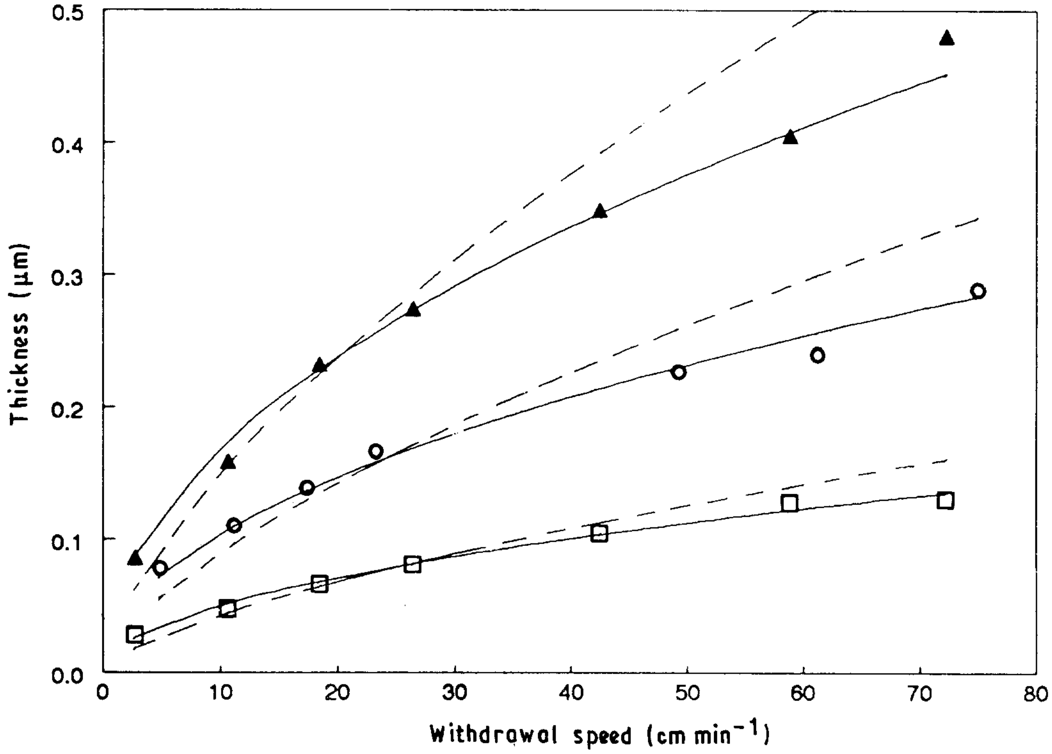

Figure 3 Plots of lifting speed versus thickness of heat-treated coatings obtained from SiO_2 solutions of different concentration. Solution: (□) 25, (○) 50, (▲) 75.

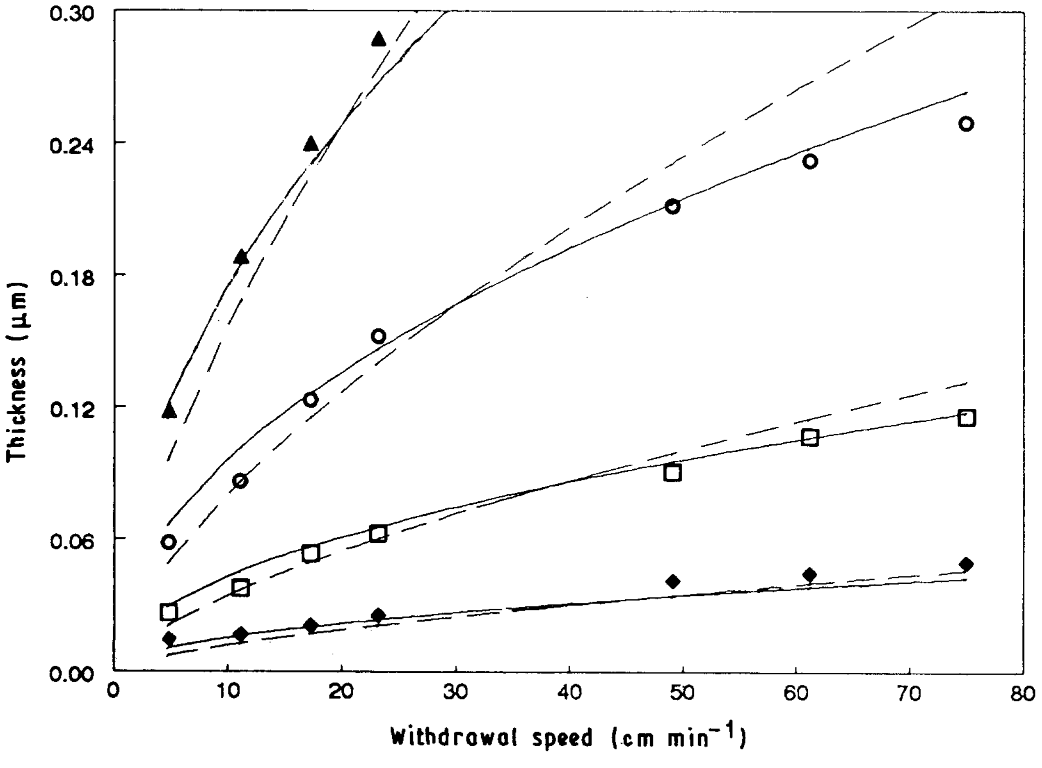

Figure 4 Plots of lifting speed versus thickness of heat-treated coatings obtained from TiO_2 solutions of different concentration. Solution: (◆) 10, (□) 25, (○) 50, (▲) 75.

solution parameters and film densities, and from Equation 5 using the above mentioned values of J^*. Equation 4 fits the data well only for low solution concentrations or for low withdrawal speeds, becoming unsatisfactory as these two parameters increase. On the contrary, Equation 5 gives a good fitting over the whole experimental ranges of c and U.

The better agreement of data with an equation having a dependence of thickness on $U^{1/2}$ instead of $U^{2/3}$ may also be checked by interpolating the data with a curve of the type $y = ax^b$. The best-fit results are $b = 0.501 \pm 0.051$ for TiO_2 coatings and $b = 0.497 \pm 0.022$ for SiO_2 coatings. As previously specified, the Landau–Levich equation is valid for low capillary number conditions. When the surface tension effect is overshadowed by the viscous drag and the gravity, the liquid film thickness depends only on the balance of these last two forces, according to $t_l = K(\eta U/\rho g)^{1/2}$, where K is a proportionality constant [6]. Looking at the reported data, it can be observed that in our experiments C_a ranged between 2×10^{-5} and 1.5×10^{-3}. An agreement with the Landau and Levich equation was obtained approximately up to $C_a = 5 \times 10^{-4}$, while strong deviations were observed at the higher values of C_a (due to the higher withdrawal speeds, and also to the higher viscosities of more concentrated solutions).

The relationship between thickness and withdrawal speed is still a matter of controversy. Brinker and Scherer [7] reported that the thickness varies approximately as $U^{2/3}$ for polymeric systems, while it seems to vary as $U^{1/2}$ for particulate species.

In this work two different solutions were used, which should be expected to behave in a different way. Although the structural characteristics of sols were not investigated, the silica sol should be a "polymeric" system, while the titania one is likely to be more similar to a "particulate" system. Nonetheless, in both cases, the thickness was found to vary with $U^{1/2}$, even in a reasonably wide range of concentrations. We have not the pretension of deriving general conclusions, as many factors could influence the process, such as change of viscosity and of concentration during film deposition. However, the results of this work suggest that a semi-empirical approach like that previously reported may be useful in predicting the thickness of coatings from a limited number of data. The constancy of J^*, in fact, enables us to predict with a good approximation the thickness of films obtainable from a solution of whatever concentration from just one thickness value acquired from a sample prepared from a solution of different concentration, provided that the solution density and viscosity are known and that the heat treatment is the same.

5. Conclusions

1. The equation giving the best-fit results for the SiO_2 and TiO_2 solutions of different concentration was that which relates the thickness of the solid coatings to the square root of the withdrawal speed: $t_p = cJ^*(\eta U/\rho g)^{1/2}$.
2. The value of J^* was found to be a characteristic of the kind of precursor solution, but was independent of the solution concentration.
3. From the practical point of view, J^* may be obtained with a good approximation simply by preparing a sample at any velocity and measuring its thickness. The computed value can be used to forecast the thickness of coatings obtainable from solutions of different concentrations and withdrawn at different speeds.

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References

1. L. LANDAU and B. LEVICH, *Physicochim.* **17** (1942) 42.
2. P. GROENVELD, *Chem. Engng Sci.* **25** (1970) 33.
3. M. GUGLIELMI and S. ZENEZINI, *J. Non-Cryst. Solids* **121** (1990) 303.
4. J. L. KEDDIE and E. P. GIANNELIS, in "Proceedings of Materials Research Society Symposium Better Ceramics Through Chemistry IV", San Francisco, CA, April 1990, edited by B. J. J. Zelinski, C. J. Brinker, D. E. Clark and D. R. Ulrich (MRS, Pittsburgh, PA 1990) Vol. 180, p. 425.
5. *Idem, Amer. Ceram. Soc. Bull.* **69** (1990) 1450.
6. L. E. SCRIVEN, in "Proceedings of Materials Research Society Symposium Better Ceramics Through Chemistry III", Reno, NV, April 1988, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (MRS, Pitssburgh, PA, 1990) Vol. 121, p. 717.
7. C. J. BRINKER and G. W. SCHERER, "Sol-gel science: the physics and chemistry of sol-gel processing" (Academic Press, San Diego, CA, 1990) p. 790.

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