JOURNAL OF MATERIALS SCIENCE 22 (1987) 1291–1294

A semi-empirical model for coating flat glass by dipping into metal–organic solutions

F. ORGAZ, F. CAPEL
Instituto de Cerámica y Vidrio, Arganda del Rey, Madrid, Spain

A sol–gel process was used to produce coloured coatings of composition $\mathrm{SiO_2} \cdot R_m\mathrm{O}_n$, where R = chromium, manganese, iron, cobalt and copper. Microscope slide glasses were dipped into the solutions and extracted vertically at different speeds. Viscosity, density and surface tension were measured for each solution. Capillary numbers and dimensionless thicknesses were then calculated. The results showed that capillary numbers did not depend on the dimensionless thicknesses. A flow rate constant for each solution was observed. A simple formula was used to calculate the heat treated coating thicknesses from the liquid coating thicknesses. Finally, a method based on a semi-empirical approach was successfully applied to predict adequately the thickness obtained as a function of the properties of the solutions and the withdrawal speed.

1. Introduction

Coating glasses, ceramics and metals with glassy films is one of the most useful applications of the sol–gel process [1–3]. The production of satisfactory coatings from a metal–organic solution requires deposition of a sufficiently adherent and thick layer in a predictable and reproducible manner. The dip-coating thickness applied from a solution depends on factors related to the solution and to the withdrawal speed. The properties of the solutions that may affect the thickness of the layer (such as viscosity, density and surface tension) in metal–organic solutions have been experimentally expressed as one parameter [4]. However, some theoretical hydrodynamic models have been proposed in polymer processing for viscous, capillary and high-Reynolds number withdrawal [5–7]. Starting from the classical Landau–Levich theory of dip-coating [8], most of the theoretical and experimental research on capillary withdrawal ($Ca \ll 1$ and $Re \ll 1$) shows a dependence of the coating phenomena on the capillary number, $Ca = \eta V/\sigma$, where η is the viscosity of the solution, V is the withdrawal speed and σ is the surface tension. For low capillary numbers ($Ca < 1$), theory fits the experimental linear relationship between dimensionless film thickness and capillary number. Several mathematical functions have been proposed for these withdrawal conditions [9, 10]. The Landau–Levich equation is expressed by

$$T = 0.944\ Ca^{1/6} \qquad (1)$$

where T is the dimensionless thickness given by $T = H(\varrho g/\eta V)^{1/2}$, ϱ is the density of the solution, g is the acceleration due to gravity and H is the thickness of the liquid coating. For high capillary numbers ($Ca > 1$), where shear effects are large (large η and V) and surface tension effects are small (small σ), a limiting value of T between 0.53 and 0.67 is obtained [11]; this depends largely on a balance between inertial and viscous forces [12].

The dimensionless flow, $J = j(\varrho g/\eta V^3)^{1/2}$ is related to the dimensionless thickness, T, by the expression $J = (T - T^2/3)$, j being the flux of liquid per unit plate width and per unit time [13].

Yang *et al.* [14] derived a model based on an empirical approach to predict the thickness of a copolymer of styrene–hexylmethacrylate film. The approach they adopted was to determine T from the experimental flow rate J using the solution of the Navier–Stokes equation for the constant thickness region. Assuming that $T = J$, they derived the equation

$$t_{\mathrm{p}} = J(\varrho_{\mathrm{s}}/\varrho_0)[(\eta - \eta_0)/\eta_0]^{0.84}(\eta V/\varrho_{\mathrm{s}} g)^{1/2} \qquad (2)$$

The objective of this paper was to derive a semi-empirical model for the sol–gel dip-coating process in order to predict the thickness of the heat-treated coating as a function of the properties of the solutions (σ, ϱ, η) and the withdrawal speed. It was then necessary to establish the empirical relationships between (a) dimensionless thickness and capillary number, and (b) between the thicknesses of the heat-treated coating and liquid coating for this type of solution.

2. Experimental methods

2.1. Preparation and properties of the solutions

Coloured coatings obtained by a sol–gel process using $80\mathrm{SiO_2}$–$20R_m\mathrm{O}_n$(wt %) compositions, where R = Co, Cr, Mn, Fe or Cu, were used. The starting solutions were prepared by mixing tetraethyl orthosilicate (TEOS), water, ethanol and nitrates of the respective transition metals. This corresponds to a 3 : 1 volume ratio of TEOS to ethanol, and approximately 5 : 1 mole ratio of water to TEOS, and concentrations of transition metal oxides of 20 wt %. Acetic acid was added to adjust the rheology of the solutions and to delay the gelling time. The mixture was left to stand for a period of time (usually 10 h), being subsequently diluted with methanol in order to obtain a final 8 to

0022–2461/87 $03.00 + .12

TABLE I Properties of the solutions

Solution (wt %)	Density ($g\,cm^{-3}$)	Viscosity (cP)*	Surface tension ($dyn\,cm^{-1}$)*
$80SiO_2$–$20Mn_2O_3$	0.9187	2.15	24.34
$80SiO_2$–$20Co_2O_3$	0.9194	2.11	27.92
$80SiO_2$–$20Cr_2O_3$	0.9267	2.96	22.20
$80SiO_2$–$20CuO$	1.0400	5.73	34.54
$60SiO_2$–$40Fe_2O_3$	0.9890	3.93	45.50

*1 cP = 1 MPa sec; 1 $dyn\,cm^{-1} = 10^{-5}\,N\,cm^{-1}$.

10 wt % oxide concentration. The experimental preparation procedure is reported elsewhere [3]. The properties of the solutions at 27° C are given in Table I. Viscosity measurements were made with an Ubbelohde viscometer. Pyknometric determinations were used to obtain the densities of the solutions. The surface tension was determined by the maximum bubble pressure method [15].

2.2. Coating technique and heat treatments

Microscope slide glasses previously cleaned with water and methanol were dipped into the solutions and extracted vertically at different speeds (varied from 5 to 40 $cm\,min^{-1}$). All the slides were permitted to remain in the solution for 30 sec before pulling up. After coating, the slides were immediately heated to 500° C at 7° $C\,min^{-1}$ in an air flow and held for one hour.

2.3. Film thickness and film density measurements

The film thickness was determined with a two-beam interference technique using the Mirau system attached to a Leitz microscope. This was done by scratching through the untreated film down to the substrate using a sharp blade. Thickness was calculated using the equation $t = (\lambda/2)m$ where λ is the wavelength of the light and m is the fractional displacement of the fringe system. The density of the heat-treated coating was determined by the relation $\varrho = P/At$ where P is the coating weight, t is the thickness and A is the covered area.

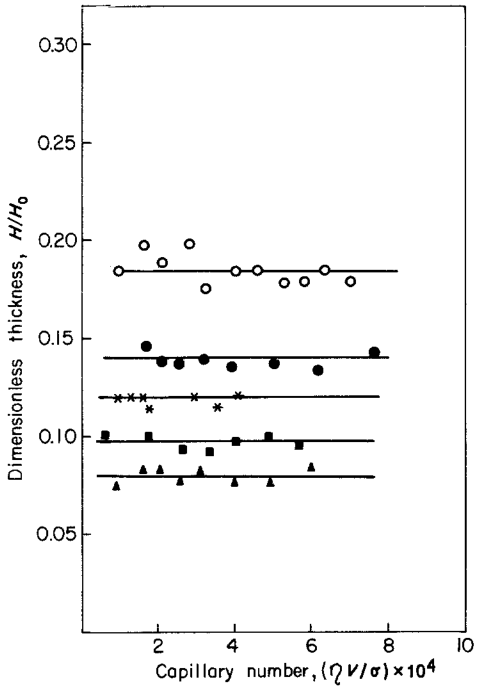

Figure 1 Dependence of dimensionless thickness, H/H_0, on the capillary number, $Ca = \eta V/\sigma$: (○) iron, (●) copper, (*) cobalt, (■) manganese, (▲) chromium.

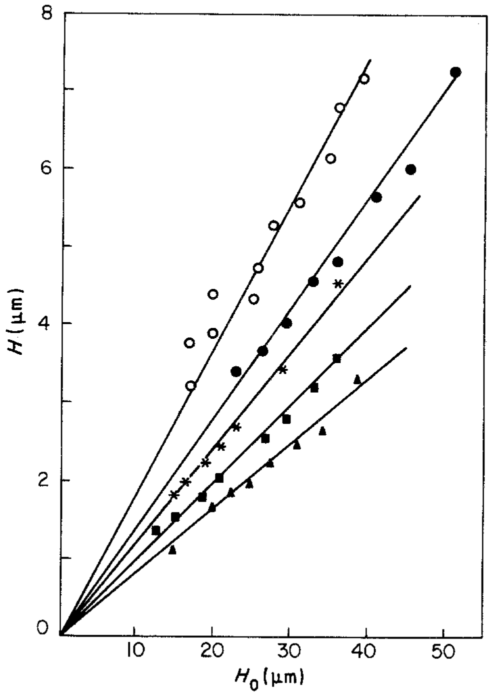

Figure 2 Variation of the liquid coating thickness, $H = P/A\varrho_s$, as a function of the characteristic thickness $H_0 = (\eta V/\varrho_s g)^{1/2}$: (○) iron, (●) copper, (*) cobalt, (■) manganese (▲) chromium.

3. Experimental results and discussion

3.1. Relationship between dimensionless film thickness and capillary number.

Fig. 1 shows the dimensionless film thickness, $T = H/H_0$, for each solution, as a function of the capillary

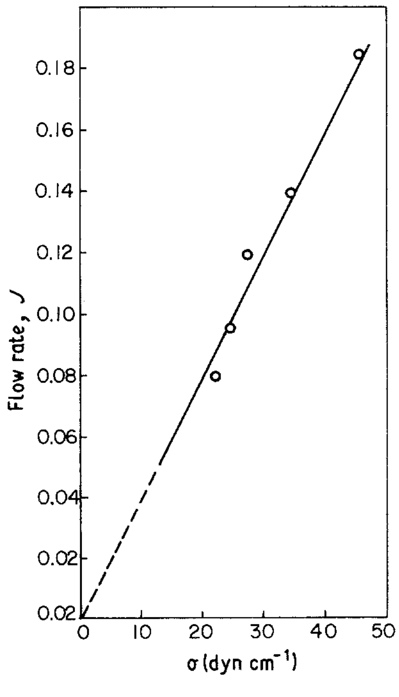

Figure 3 Experimentally determined flow rates J against surface tension of the solutions.

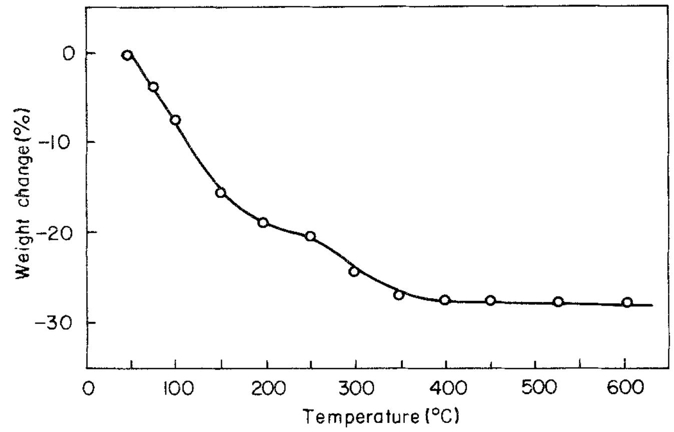

Figure 4 Percentage weight loss for SiO_2–Cr_2O_3 gels.

number, $Ca = \eta V/\sigma$. The H_0 values are given by $H_0 = (\eta V/\varrho_s g)^{1/2}$ where η and ϱ_s are the viscosity and density of the solution, respectively. The thickness of the liquid coating, H, was calculated using the expression $H = P/A\varrho_s$, where P is the liquid coating weight, A is the coated area and ϱ_s is the density of the solution. The results in Fig. 1 show that the dimensionless film thickness does not depend on the capillary number. Assuming that $T = J$, a flow rate constant J for each solution exists over the range of capillary numbers used in these experiments. The values of J were obtained from the slopes of the straight lines in Fig. 2.

Fig. 3 shows the dependence of the experimentally determined flow rates J on the surface tension of the solutions. From the slope of the $J = K\sigma$ straight line, a value of $K = 4 \times 10^{-3}$ cm dyn^{-1} (400 cm N^{-1}) was obtained. Having determined the value of K, the liquid coating thickness H could be calculated from the properties of the solutions η, ϱ_s, σ and from the withdrawal speed, using the equation

$$H = 4 \times 10^{-3}\sigma(\eta V/\varrho_s g)^{1/2} \qquad (3)$$

3.2. Gel–glass transition and relationship between liquid coating and final heat-treated coating thicknesses

The solutions are gelled on the glass substrate immediately after withdrawal and converted to glassy films by heating. Chemically and physically bound water as well as organic materials are then removed. Figs 4 and 5 show weight losses and differential thermal analysis (DTA) curves for silica–chromium oxide gels. Weight losses of approximately 30 wt % were observed when gels dried at 50° C were heat-treated at 600° C. From 50 to 110° C a weight loss of approximately 10 wt % was observed, due primarily to removal of unbound ethanol–methanol and physically adsorbed water. This corresponds to the endothermic peak observed in the DTA curve. At temperatures above 110° C carbonization and oxidation of organic compounds occurs. This gives rise to an endothermic peak near to 200° C and a broad exothermic band between 250 and 450° C depending on gel composition. Weight loss causes shrinkage and an increase of adhesion and mechanical and chemical stability. All the silica–transition metal oxide gels showed similar behaviour.

If the weight of a parallel-sided film of area A and density ϱ is P, then the film thickness t is given simply by $t = P/A\varrho$. The ratio between heat-treated t_0 and liquid coating H thicknesses can then be given by the expression

$$t_0/H = \frac{P_0/A\varrho_0}{P/A\varrho_s} = \left(\frac{\varrho_s}{\varrho_0}\right)\left(\frac{P_0}{P}\right) = \left(\frac{\varrho_s}{\varrho_0}\right) W \qquad (4)$$

where W is the ratio between heat-treated coating

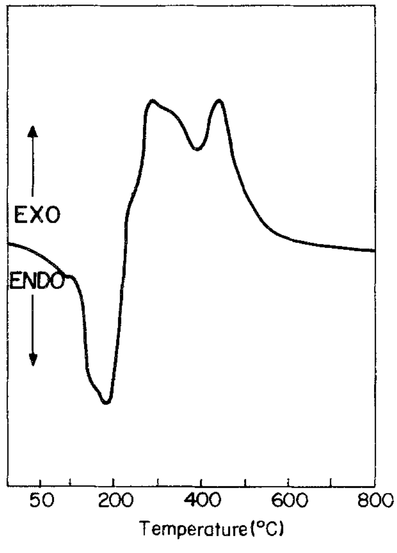

Figure 5 DTA curves for SiO_2–Cr_2O_3 gels heated in stagnant air at 7° C min^{-1}.

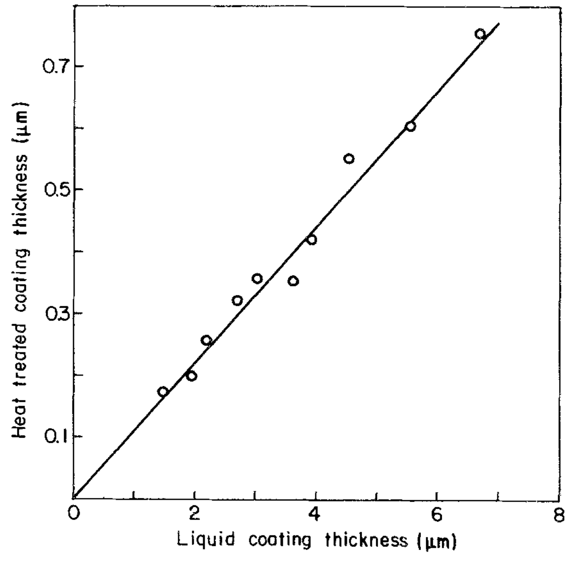

Figure 6 Theoretical and experimental relationship between heat-treated and liquid coating thicknesses for $60SiO_2$–$40Fe_2O_3$ solution.

TABLE II Density, weight losses and $(\varrho_s/\varrho_0)W$ values of heat-treated glassy films

Solution (wt %)	Density ($g\,cm^{-3}$)	$W = P_0/P$	$(\varrho_s/\varrho_0)W$
$80SiO_2$–$20Mn_2O_3$	3.1	0.45	0.13
$80SiO_2$–$20Co_2O_3$	3.6	0.49	0.12
$80SiO_2$–$20Cr_2O_3$	4.7	0.36	0.07
$80SiO_2$–$20CuO$	–	0.39	–
$60SiO_2$–$40Fe_2O_3$	2.8	0.32	0.11

weight and liquid coating weight, ϱ_s is the density of the solution and ϱ_0 is the density of the heat-treated glassy film. Table II gives the ϱ_0, W and $W(\varrho_s/\varrho_0)$ values for the different solutions studied. As an example, Fig. 6 shows that the experimental relationship between heat-treated and liquid coating thicknesses can be fitted to Equation 4 within the experimental error. This experimental relationship was observed for all metal-organic solutions.

3.3. Comparison of the theoretical with the experimental results

Using Equations 3 and 4 the analytical expression relating the glassy film thickness, the properties of the solutions and the withdrawal speed is

$$t_0 = \left(\frac{\varrho_s}{\varrho_0}\right) WK\sigma \left(\frac{\eta V}{\varrho_s g}\right)^{1/2} \qquad (5)$$

if an empirically determined value of $K = 4 \times 10^{-3}\,cm\,dyn^{-1}$ is used. Equation 5 is similar to the analytical equation derived by Yang *et al.* [14] (Equation 2), provided that J be equal to $K\sigma$ and the expression $[(\eta - \eta_s)/\eta_0]^{0.84}$ be replaced by W. In Fig. 7 the heat-treated glassy film thicknesses of coatings containing iron or manganese are plotted as a function of the square root of the substrate withdrawal speed and compared with the values obtained from Equation 5. Good agreement between the derived semi-empirical model and the experimental results was observed. Consequently, Equation 5 can be applied to predict adequately the thickness of the heat-treated sol–gel coating from the properties of the metal–organic solutions used. Only slight deviations of the experimental results from the theoretical square-root straight line were noticed.

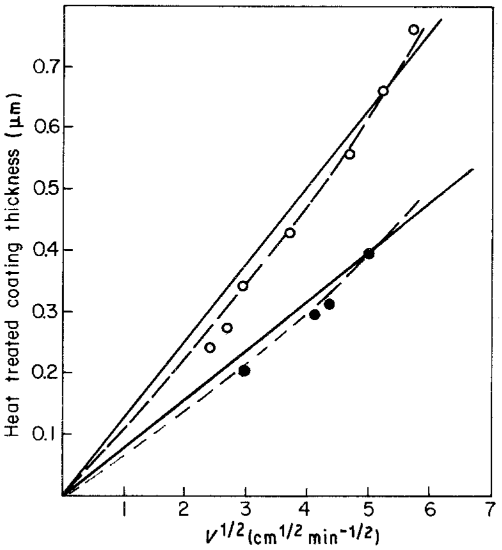

Figure 7 (——) Theoretical and (– – –) experimental coating thicknesses as a function of withdrawal rate during dipping, for (○) iron and (●) manganese solutions.

References

1. H. DISLICH, *J. Non-Cryst. Solids* **57** (1983) 371.
2. S. SAKKA, *ibid.* **73** (1985) 651.
3. F. ORGAZ and H. RAWSON, *ibid.* **82** (1986) 378.
4. H. SCHROEDER, *Thin Solids Films* **5** (1969) 87.
5. P. GROENVELD, *Chem. Eng. Sci.* **25** (1970) 1579.
6. *Idem, ibid.* **25** (1970) 33.
7. *Idem, ibid.* **25** (1970) 1259.
8. L. LANDAU and V. LEVICH, *Acta Phys. URSS* **17** (1942) 42.
9. R. SPIERS, C. SUBBARAMAN and W. WILKINSON, *Chem. Eng. Sci.* **29** (1974) 389.
10. D. WHITE and A. TALLMADGE, *ibid.* **20** (1965) 33.
11. B. DERYAGIN and A. TITIEVSKAAYA, *Dokl. Akad. Nauk. SSSR* **50** (1945) 30.
12. B. DERYAGIN and S. LEVI, "Film Coating Theory" (Focal Press, London, 1964).
13. J. VON ROSSUM. *Appl. Sci. Res.* **A7** (1958) 121.
14. C. YANG, J. JOSEFOWICZ and L. ALEXANDRU, *Thin Solids Films* **74** (1980) 117.
15. S. SUDGEN, *J. Chem. Soc.* **125** (1924) 27.

Received 3 February
and accepted 5 August 1986