Fluid Dynamic Effects in the Deposition of γ-Al_2O_3 Layers onto Metallic Supports for Structured Catalysts

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The fluid-dynamic effects involved in the deposition of γ-Al_2O_3 layers onto metallic slabs by dip coating have been investigated by means of rheological and particle size distribution measurements of the slurries. The influence of the slurry mixing method (magnetic stirring versus ball milling) is also addressed. The present results provide a rational basis for the control of the characteristics of the deposited layers.

1.Introduction

In a previous paper we have reported a procedure for the deposition of γ-Al_2O_3 coatings onto Al supports in the form of slabs, which is based on the following two steps: i) deposition of a pseudo-bohemite primer, ii) deposition of a coating layer by dipping the slabs into a slurry of γ-Al_2O_3 powders suspended in a HNO_3 aqueous solution [1]. In line with literature indications, our experience points out that the deposited coating load as well as the adhesion of the deposited layer are controlled both by chemical factors (e.g. pH and composition of the slurry) and by physical factors associated with the fluid dynamic behavior of the slurry during the dip coating procedure. In this paper we focus on such fluid dynamic aspects; specifically, we address the effects of the following variables on the characteristics of the deposited layer: 1) dipping vessel to slab size ratio; 2) rheological properties of the slurry; 3) withdrawal velocity in the dip coating procedure; 4) slurry stirring method (soft mixing by magnetic stirring versus ball milling).

2.Experimental

In this work a sub-micronic γ-Al_2O_3 powder (Sumitomo) with a bimodal particle size distribution centred a 0.3 μm and at 2 μm has been used. The alumina powder was dispersed in a HNO_3 aqueous solution under magnetic stirring or ball milling (24 hours). The rheological characteristics of the slurry as a function of the shear rate (flow curves) were determined using a rotational rheometer (Dynamic stress rheometer DSR 200 by Rheometrics). Particle size distribution measurements were collected by a Cilas laser granulometer.

For the coating deposition, metal slabs made of aluminium or Fecralloy were first primerized by deposition of thin layer (1–2μm) of pseudobohemite, and then washcoated by dipping into the slurry and withdrawing them at constant velocity, followed by flash heating at 280°C for five minutes. The washcoated samples were characterised by gravimetric analyses (to determine the deposited coating load), SEM images (Electron Scanning Microscope DSM 940 from Zeiss), BET measurements (Micromeritics Tristar instrument), using the N_2 adsorption technique, and adhesion measurements. Adhesion tests were performed by measuring the weight loss of the coated slabs upon immersion for 30 minutes in an ultrasound bath.

3.Results and discussion

3.1 Slurry rheology - The rheological behaviour of aqueous slurries with H_2O/Al_2O_3 mass ratio of 3.2 and with HNO_3 contents between 0.36 and 8.65 mmol/g has been investigated by measuring the flow curves in a rotational plane rheometer. The results are reported in Figure 1. The slurries with HNO_3 contents ≤ 1.1 mmol/g exhibited a Newtonian behaviour, the viscosity remaining almost constant on increasing the shear

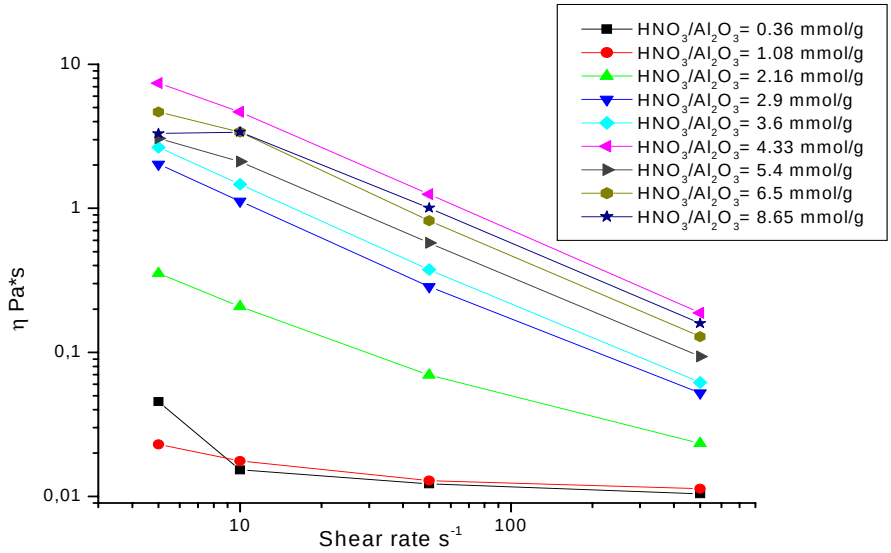

Figure 1 Flow curves of slurries with HNO_3 contents between 0.36 mmol/γAl_2O_3 and 8.65mmol/γAl_2O_3. H_2O/Al_2O_3 = 3.2 g/g

rate. For higher HNO_3 contents the slurry viscosity decreased on increasing the shear rate, indicating a non Newtonian, shear-thinning behaviour. Based on a simple power law $\mu = k\gamma^{n}$, a flow index n between –0.7 and –0.8 is estimated for all the non-Newtonian slurries. Notably, the slurry viscosity exhibited a maximum for slurry with a HNO_3 content of 4.33 mmol/g: this slurry was also associated with the highest deposited coating load, as reported in a previous work [2]. The correlation between the rheological behaviour of the slurries and the deposited coating load was then investigated.

3.2 Coating load versus slurry rheology

Literature theories regarding the coating of plane surfaces by withdrawal at constant velocity from a stationary bath of a Newtonian fluid [3] identify three distinct zones along the coated support. Among these, the upper region is characterized by an equilibrium between gravitational and viscous forces in the fluid film adherent to the support: such an equilibrium eventually results in a coating layer with constant thickness δ. In the intermediate region the gravitational forces and the viscous forces are at equilibrium with surface tension forces; this leads to a layer thickness that varies along the axial coordinate of the coated slabs. Finally, in the region nearest to the

slurry/air interface the surface tension is predominant with respect to other forces; this leads to the so called “drop effect”, a zone at the end of the slab where the coating is the thickest. According to the Landau-Levich theory [3] for free coating of slabs with Newtonian fluids, the following dependence

$$\delta \propto (\mu * U)^{2/3} \qquad (1)$$

correlates the final thickness of the deposited layer δ in the upper region 1 previously described, to the (constant) fluid viscosity μ and to the withdrawal velocity U.

Our data concerning the effect of slurry viscosity are displayed in Figure 2 for washcoats obtained from aqueous slurries with H_2O/Al_2O_3 mass ratio of 3.2, and withdrawal velocity of 3 cm/min. In view of the shear thinning behaviour of the slurries the data have been plotted considering apparent viscosities determined in the flow curves at three different shear rates of 5, 10 and 50 s^{-1}, respectively.

The data confirm that a strong correlation indeed exists between the deposited coating load and the corresponding slurry viscosity at constant shear; in particular, a bi-logarithmic plot results in a linear correlation with slopes ranging between 0.7 and 0.9, depending on the shear rate: this compares fairly well with the 2/3 power dependence on viscosity expected according to Eq. (1).

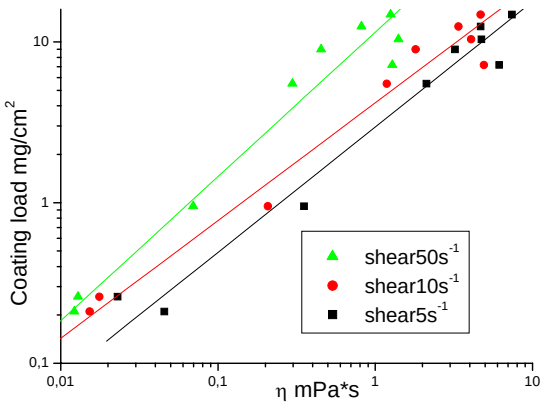

Figure 2 Correlation between slurry viscosity and coating load at different shear rates.H_2O/Al_2O_3 = 3.2 g/g, withdrawal velocity = 3 cm/min.

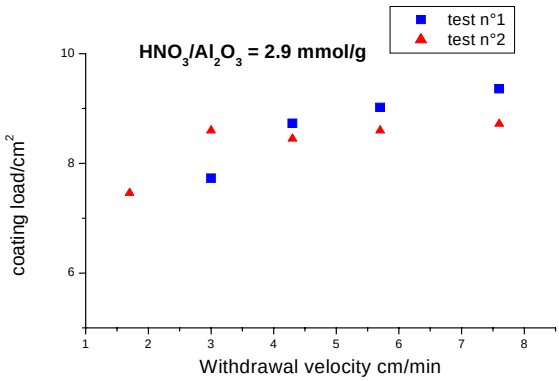

Figure 3 : Effect of withdrawal velocity on the coating load. HNO_3/Al_2O_3 = 2.9 mmol/g, H_2O/Al_2O_3 = 3.2 g

On the other hand, the experimental data on the effect of the withdrawal velocity U reported in Figure 4 show that the coating thickness depends on U according to $\delta \propto U^{0.22}$. Such a dependency is apparently at variance with Eq. (1). However, it can be rationalized considering that for our shear-thinning slurries the viscosity decreases approximately with the withdrawal velocity raised to -0.7. Introducing this dependence into the Landau-Levich equation one obtains $\delta \propto U^{0.2}$, which compares well with the experimental observations. Notably, from a practical point of view this may allow to operate at higher withdrawal velocity without major changes of the thickness of the deposited layer.

3.3 Influence of ball milling

As reported elsewhere [1], the alumina slurries involved in our coating procedure are composed of three phases, a sol, a gel and a residual powder [4] which have been observed by separation with ultracentrifugation. Based on quantification of the amounts of the different phases compared with measured consumption of HNO_3 during the slurry preparation, we have previously reported evidence that gel formation occurs mostly via other routes than a simple mechanism involving Al_2O_3 dissolution by HNO_3, followed by peptization and gelification reactions. More likely, it implies the dispersion of small Al_2O_3 aggregates of the starting powder due to chemical attack, in addition to condensation reactions to form the characteristic net of alumina gels, where eventually the residual γ-Al_2O_3 particles are entrapped [5] .

According to the patent literature, the preferred preparation methods for alumina slurries used in washcoat deposition involve treatment of a commercial powder by ball milling; apparently, this procedure results both in reducing the particle size of the starting powder and in enhancing the rate of the chemical reactions occurring inside the slurry. The reduction of the mean particle size below a few microns is clearly beneficial for the adhesion of the deposited layers. In order to investigate other effects of ball milling, associated with chemical effects, we have performed washcoat deposition experiments using a commercial "submicronic" γ-Al_2O_3 powder (mean particle size $\approx$ 2 μm), starting from slurries with two HNO_3 contents, namely 2.16 and 2.9 mmol/g. The slurries have been treated for 24 hours either with ball milling or with simple magnetic stirring, and have been characterized afterwards by rheological and particle size distribution measurements.

Particle size distribution determinations for all the sample have been performed. For both HNO_3 contents, the magnetically mixed slurries exhibited a bimodal particle size distribution with the larger fraction centred at 2.2 μm and the smaller one at 0.8 μm; the volume percentage was 90% for the particles centred at 2.2 μm and 10 % for those centred at 0.8 μm. On the other hand, the ball milled samples had the larger fraction centred again at 2.2 μm, but this fraction corresponded only to 50% of the total powder, the remaining 50% being centred at 0.3 μm: it is apparent that the ball milling procedure acts in reducing the particle size of the larger fraction.

Evidence for the formation of gel, sol and solid phases was obtained upon ultracentifugation for all of the four slurries. Figure 4 shows the flow curves of the four examined slurries.

A non Newtonian shear-thinning behaviour is evident for all samples. It is also apparent that, for the same HNO_3 content, the viscosity is greater for the magnetically mixed slurry than for the ball milled sample. Furthermore, both in the case of ball milling and of magnetic stirring the viscosity is greater for the samples with the greater HNO_3 content, as expected.

The different rheological properties of the ball milled slurries could be tentatively correlated with their smaller mean particle size. According to the DLVO theory [6] the viscosity of concentrated suspensions of a bimodal powder changes upon varying the

mean size and the relative amount of the smaller particles. In our slurries, however, the volume fraction of solid particles is below 40%; this implies that such an effect is probably marginal in changing the slurry viscosity. More likely the ball milling treatment affects primarily the chemistry of the reactions involved in the aging of the

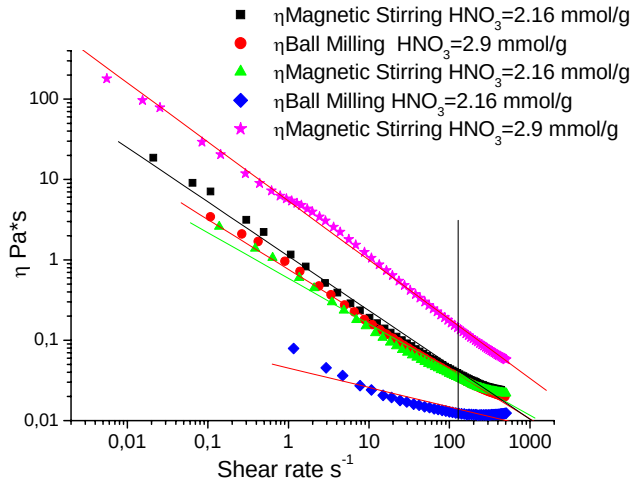

Figure 4 Flow curves of slurries with HNO_3 contents of 2.16 mmol/g and 2.9 mmol/g prepared by Ball Milling and by Magnetic Stirring.

slurry, modifying the relative amounts of the tree phases (sol, gel, powder). Indeed, previous measurements have pointed out a much faster temporal evolution of the slurry pH when the slurry was subjected to ball milling than in the case of magnetic mixing, which suggests a more effective chemical attack of HNO_3 on the alumina aggregates. Furthermore, while a submicronic alumina has been used for the purposes of the present work, it is worth considering that the effect of ball milling may depend also on the mean article size of the starting powder. In the case of bigger particles, in fact, a more significant mechanical action of the ball milling may result in local heating, thus favoring further the chemical attack. Investigation of these aspects is currently in progress.

The same four slurries characterized above have been used to deposit washcoats onto Fecralloy® slabs. The obtained coating loads are given in Table 1.

Table 1	Slurry Viscosity, Pa*s (at shear rate =10 s^{-1})	Coating Load, mg/cm^2	Weight loss after ultrasound bath test, %
Ball Milled 2.16 mmol/g HNO_3	*0.024*	*0.9*	*0*
Magnetically ixed 2.16mmol/g HNO_3	0.19	2	3
Ball Milled 2.9 mmol/g HNO_3	*0.16*	*3*	*1.9*
Magnetically Mixed 2.9 mmol/g HNO_3	1.05	7	75

Table 1: Coating Load, Adhesion and Slurry viscosity for ball milled and magnetically mixed samples

At a constant HNO_3 content, the deposited coating load for the ball milled sample is less than the load for the corresponding sample prepared with magnetic mixing, in line with the dependence of the coating thickness on the slurry viscosity outlined above.
Finally, the last column in Table 1 reports the results of adhesion tests on the coated samples, which were carried out by treating the samples in an ultrasound bath for 30 minutes. The measured weight losses were very small as long as the coating load was less than 0.2 mg/cm^2; however, the adhesion was found very poor for the sample with the greatest layer thickness. Inspection of the deposited layers by optical microscope revealed that those obtained from ball-milled slurries exhibited a more uniform surface, exempt from cracks. However, while previous data [5] support the importance of a small mean particle size for good adhesion, further investigation is necessary to establish whether the adhesion properties correlate with the layer thickness and/or with the method of slurry agitation adopted in the preparation procedure.

4.Conclusions

For dip coating of metal slabs with γ-Al_2O_3 layers, the present results document a clear correlation between the deposited coating load and the rheologic characteristics of the starting slurries. Both the observed effects of slurry viscosity and withdrawal velocity on the coating thickness are apparently in line with theoretical expectations: accordingly, this allows in practice to tailor the slurry rheology to match given specifications on the coating load. On the other hand, the theoretical predictions fail when the coating procedure is affected by border effects: in our case such effects were prevented by performing the dip coating in vessels with vessel to sample size ratios greater than four.
For a given slurry composition, the method adopted for slurry mixing (magnetic mixing versus ball milling) is critical in determining both the coating load and the coating adhesion. The influence on the coating load directly reflects the influence of the stirring method on the slurry rheology: in fact, the ball milled slurries were markedly less viscous, thus yielding thinner coating layers. However, the modifications of the slurry rheology induced by ball milling cannot be apparently ascribed only to the associated changes in the slurry particle size distribution, but are more likely related to chemical effects altering the relative amounts of the sol and the gel phases present in the slurry: this aspect is currently under investigation. The influence of ball milling on the coating adhesion also requires further analysis: on a tentative basis, one could speculate that the chemical attack on the Al_2O_3 aggregates is favored by the mechanical action of ball milling, thus enhancing the formation of sol and gel phases which eventually result in a more adherent coating.

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