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Coating of Metals by the Sol–Gel Dip-coating Method

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Abstract

The sol–gel technique to deposit coatings on metals by dipping was studied. Different metals (Cu, Ni, Fe, Al) were coated with ZrO_2, SiO_2, TiO_2 and B_2O_3–SiO_2 solutions. The influence of some dipping and solution parameters was related with the quality of the obtained coatings. A scale of quality was determined to classify the sol–gel coatings on metals. Both fresh and aged solutions, as-received and abraded substrates were used. The protection against oxidation was evaluated by XRD and by measuring the weight gain upon thermal treatment.

In dieser Arbeit wurde ein Sol–Gel-Verfahren zum Abscheiden von Beschichtungen auf Metallen mittels Eintauchen untersucht. Verschiedene Metalle (Cu, Ni, Fe, Al) wurden jeweils mit ZrO_2-, SiO_2-, TiO_2- und B_2O_3–SiO_2-Lösungen beschichtet. Der Einfluß einiger der Parameter des Tauchbades und der Lösung wurden in Zusammenhang mit der Güte der Beschichtung gesetzt. Zur Einteilung der Sol–Gel–Beschichtungen auf Metallen wurde eine Qualitätsskala bestimmt. Sowohl frische als auch ältere Lösungen wurden verwendet. Die Substrate wurden teilweise im ursprünglichen Zustand und teilweise mit abgeschliffener Oberfläche beschichtet. Der Oxidationsschutz der Beschichtung wurde einerseits mittels XRD und andererseits durch die Massezunahme beim Glühen bewertet.

La technique sol–gel de déposition d'une couche de revêtement sur des métaux par trempage a été étudiée. Différents métaux (Cu, Ni, Fe, Al) ont été recouverts avec des solutions de ZrO_2, SiO_2, TiO_2 et B_2O_3–SiO_2. L'influence de certains paramètres de trempage et de la solution a été reliée à la qualité des revêtements obtenus. Une échelle de qualité a été déterminée pour classifier les revêtements sol–gel sur métaux. A la fois des solutions neuves et vieillies, comme des substrats reçus et abrasés ont été utilisés. La protection contre l'oxydation a été évaluée par diffraction des RX et en mesurant le gain en poids après traitement thermique.

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1 Introduction

The sol–gel method is a suitable technique for obtaining coatings on different substrates. The use of sol–gel to deposit coatings on glass is widely studied and known, while only a few works are reported on thin film deposited on metallic substrates.

These coatings may be used for different purposes, such as protection against oxidation[1–4] or acid attack,[2,5] as thermal barriers,[5] water-repellent films,[6] or to enhance scratch resistance of the metallic substrates.[2]

Limitations on the use of sol–gel films on metals are the coating thickness, which cannot exceed 1 μm for a single layer, thermal mismatches between film and substrate with consequent stresses arising in the films, and the difficulty in obtaining completely densified coatings.

The technique, however, has the following attributes: facility of processing to coat metals with oxides, the possibility of obtaining films with tailored characteristics (composition, porosity, homogeneity), and lower costs with respect to other processes.

The most common coating techniques are spinning or dipping, but others, such as electrophoresis, may be used.[6,7]

In this paper the results of an investigation aimed to check the possibility of coating different metals are presented. The effect of some dipping and solution parameters on the quality of coatings and their ability to protect the substrates from high-temperature oxidation were studied. Nickel, iron, aluminium and copper, selected as substrates, were coated with ZrO_2, TiO_2, SiO_2 and a B_2O_3–SiO_2 (BS) composition.

2 Experimental

2.1 Coating solutions

Four different alkoxide solutions were prepared as precursors for ZrO_2, SiO_2, TiO_2 and B_2O_3–SiO_2 coatings. The SiO_2 solution was obtained by dissolving $Si(OC_2H_5)_4$ (TEOS) in ethanol. The ZrO_2 starting solution was prepared by dissolving $Zr(C_4H_9O)_4$ in an ethanol and acetylacetone solution (AcAc/ZrBu^t molar ratio = 1). The TiO_2 precursor solution was obtained by dissolving $Ti(C_4H_9O)_4$ in an ethanol and acetylacetone solution (AcAc/TiBu^t molar ratio = 1). All the solutions were prepared in concentrations of 10 g and 50 g oxides per litre.

The fourth solution, for BS coatings, was prepared by mixing TEOS with ethanol and distilled water, and using HNO_3 as catalyst. The molar ratios H_2O/TEOS and HNO_3/TEOS were 4 and 0·07 respectively. The obtained solution was refluxed at 100°C for 4 h, cooled and refluxed for another 4 h after the addition of $B(OC_2H_5)_3$ (TEOB). The solution concentration was 100 g oxides per litre and the molar composition was 80% SiO_2–20% B_2O_3.

All the solutions remained stable for several months. Coatings were obtained using solutions at different ageing times.

2.2 Preparation of coatings

Thin, flat, reagent grade (99·99%) metallic plates (40 mm × 20 mm × 0·125 mm) of Ni, Fe, Al and Cu were used as substrates. Coatings were prepared by dipping. Soda-lime glass slides were also coated with the same solutions and following the same procedure adopted for the metallic plates, in order to measure the film thickness by a stylus apparatus.

Before coating, the metallic substrates were washed in acetone in an ultrasonic bath and rinsed with ethanol. The surface of some samples was abraded on both sides by a fine-grained (600 grit) emery paper to increase roughness.

Dip-coating was performed in a closed box with a controlled relative humidity of 50% for ZrO_2, SiO_2 and TiO_2 solutions, and less than 20% for the BS solution. The withdrawal speed ranged from 4 to 25 cm/min.

In order to increase the film thickness, the multicoating procedure was also followed. Coated samples were heated in air, from 20 to 500°C, at a heating rate of 5°C/min and cooled at the same rate. The same schedule was followed after each deposition in the case of multicoating procedure.

2.3 Characterization

Film quality and morphology were investigated by optical and scanning electron microscopy (SEM). The oxidation resistance of coated Ni samples was tested at 800°C, measuring the weight gain (mg/cm^2) with a digital balance every 2 h. The surface area of the samples was estimated by an image analyser. XRD was also used to follow the oxidation of samples. Cu/BS samples were also preliminarily tested for oxidation resistance, at 550°C, following the oxidation by XRD.

3 Results and Discussion

3.1 Coating quality

Starting from microscopical observation of the whole set of samples, a quality scale was derived considering two parameters: the film integrity and the substrate appearance. The last one is affected by the oxidation during thermal treatment. The quality was indicated by a number, as reported in Table 1. This classification, in spite of its limitations, allows an immediate evaluation of the obtained coatings.

In Table 2 are reported the results for films prepared from ZrO_2, SiO_2 and TiO_2 solutions (50 g/litre) and from the borosilicate solution.

Due to wettability problems SiO_2 coatings obtained from fresh solutions on glass slides were not suitable for measurements. Thus the withdrawal speed rather than thickness has been reported. From the obtained results it was evident that, inde-

Table 1. Scale of quality used to characterize the coatings

Number	*Quality*
8	No cracks; substrate unaffected
7	No cracks; substrate slightly oxidized
6	No cracks; substrate strongly oxidized
5	Localized cracks; substrate unaffected
4	Localized cracks; oxidation correspondence to the positions of cracks
3	Extensive cracking
2	Film strongly damaged
1	Film completely destroyed

Table 2. Quality numbers for Ni and Al samples coated with fresh SiO_2, ZrO_2, TiO_2 (50 g/litre) and BS (100 g/litre) solutions

Substrate/coating	*Withdrawal speed (cm/min)*			
	5·5	*9·4*	*12·0*	*15·9*
Ni/SiO_2	7	5	4	3
Al/SiO_2	8	5	3	3
	Coating thickness (nm)[a]			
	60	*85*	*90*	*115*
Ni/ZrO_2	8	7	7	3
Al/ZrO_2	8	5	3	3
	65	*75*	*80*	*85*
Ni/TiO_2	8	6	3	3
Al/TiO_2	8	8	3	3
	100	*120*	*185*	*220*
$Ni/B_2O_3–SiO_2$	8	7	5	3
$Al/B_2O_3–SiO_2$	8	8	7	3

All Fe and Cu samples coated with the same solutions had quality numbers of 1 or 2.
[a] Measured on glass slides.

pendently of the type of solution used, it was not difficult to coat Ni or Al, while it was more problematic to obtain good films on Fe or Cu.

The quality of the coatings was strongly dependent on the film thickness. This is due to the fact that the probability of cracking rises with thickness increase. It is also possible to find a critical thickness for each film, as predicted by Hu *et al.*[8] Beyond the critical value the dimensions of flaws increase and the coating protective effect abruptly drops, as shown by metal oxidation of the substrate also during thermal treatment (quality number 4).

ZrO_2 and TiO_2 coatings are probably characterized by a greater intrinsic stress in comparison with BS films, as a lower critical thickness was found. This is believed to depend on their microstructural evolution more than on the concentration of precursor solutions: the borosilicate films are amorphous, while the ZrO_2 and TiO_2 ones are both crystalline.

The difference between the thermal expansion coefficients of the metals and of the films does not seem critical for the realization of well adhered and uncracked thin films. However, in the case of sol–gel coatings, it is difficult to evaluate the influence of thermal stress. The stress due to thermal expansion mismatch upon a temperature variation ΔT is given by

$$\sigma = E_f(\alpha_f - \alpha_s)\Delta T$$

where α_f and α_s are the average coefficients of expansion for the film and substrate, and E_f is the elastic modulus of the film.

A sol–gel coating is usually deposited at room temperature and, after gelation, it is dried and heated (in the present case at 500°C) for densification. During these treatments the film undergoes a great shrinkage. If the adhesion to the substrate is good, a tensile stress originates, which sums to the thermal stress.

During the cooling stage there are two possible situations. If the treatment temperature has been sufficient to relax the stress in the film, and if $\alpha_s > \alpha_f$ (as is usually the case of a glass or ceramic coating on a metal substrate), a compressive stress develops during cooling. Otherwise, if the tensile stress has not been relaxed during heat treatment, the final stress state (after cooling) will depend on how much the thermal contraction reduces the starting tensile stress. From the present results it seems that localized microcracks present in some coatings do not influence the protective effect against oxidation. However, they can represent a serious limitation for acid protection, as reported in Ref. 2.

3.2 Effect of solution ageing

Some samples were also obtained using aged solutions. The effect of this parameter is reported in Table 3. From the reported data it was possible to see that the thickness of the films increased with solution ageing, as a consequence of viscosity change. Notwithstanding the greater thickness, the coating quality was generally better. This effect was particularly evident for the sample Cu/BS, whose quality number changed from 2 to 8 in spite of an almost double thickness.

Figure 1 shows the results of the scratch test performed on Cu/BS samples with comparable thickness but prepared with fresh and aged solutions respectively. At the same load a clear delamination was observed on the coating prepared with fresh BS solution, while the other one was well adhered.

The effect of ageing should be strictly connected with the reactions proceeding in the solution, but the

Table 3. Effect of solutions ageing on the coatings quality. F and A indicate fresh and aged (30 days) solutions

Substrate/coating	*Thickness (nm)*[a]		*Quality number*	
	F	*A*	*F*	*A*
$Ni/B_2O_3–SiO_2$	185	330	5	8
$Al/B_2O_3–SiO_2$	185	330	7	8
$Cu/B_2O_3–SiO_2$	185	330	2	8
$Fe/B_2O_3–SiO_2$	185	330	2	6
Ni/SiO_2	—	230	4	7
Ni/TiO_2	80	120	3	7

All samples were coated at a withdrawal speed of 12 cm/min.
[a] Measured on glass slides.

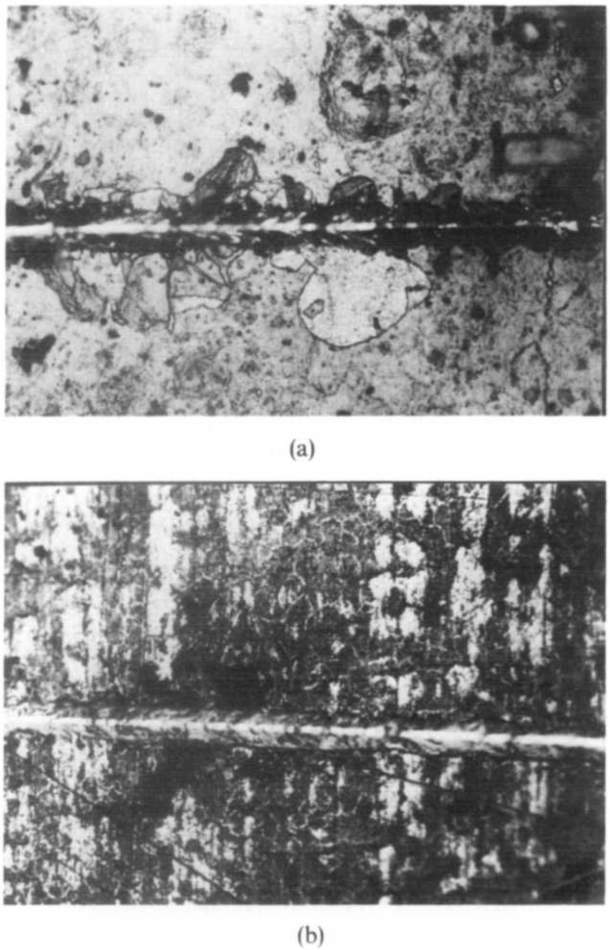

Fig. 1. Micrographs of scratches on samples of copper coated with (a) fresh and (b) aged borosilicate solutions. The scratches were obtained at the same load; the thickness of the coatings in the two samples are comparable: (a) 250 nm and (b) 330 nm. (Magnification: 400 ×).

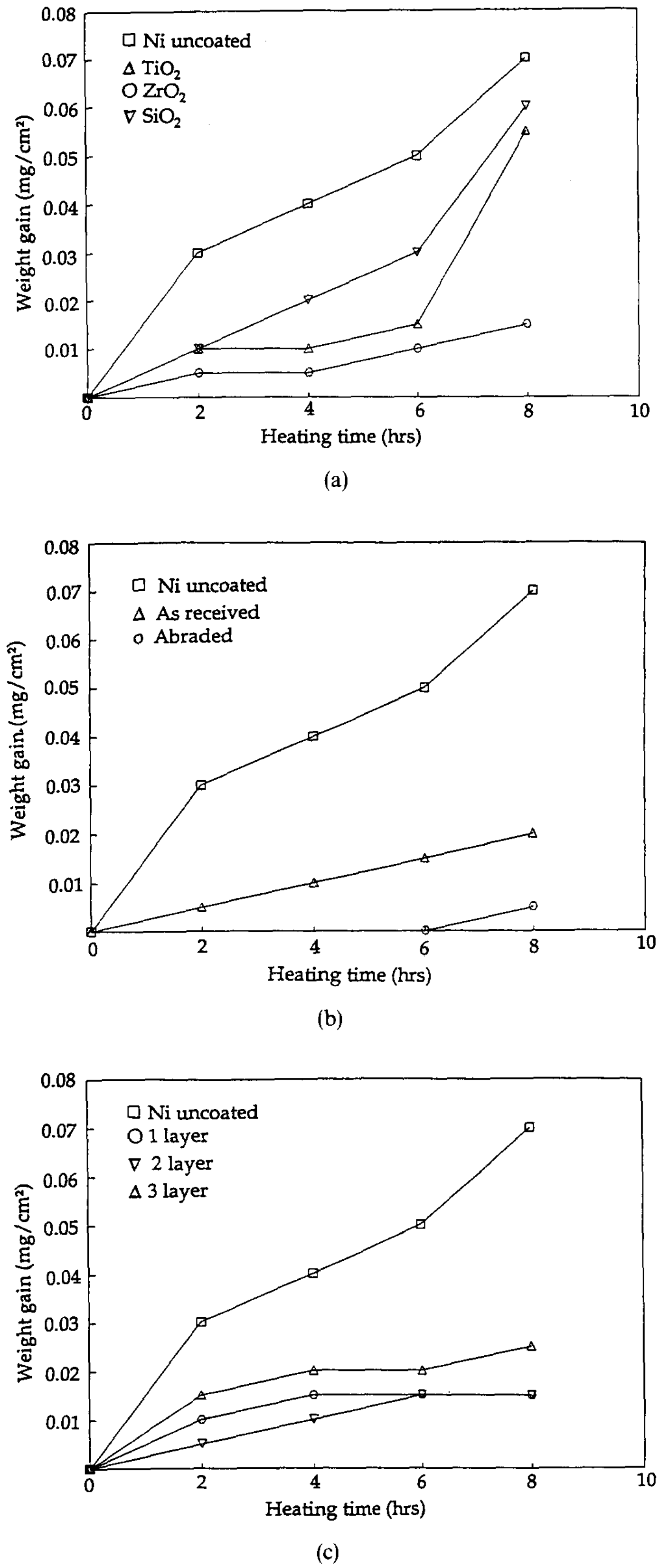

Fig. 2. Oxidation test at 800°C on Ni. (a) Comparison of TiO_2, ZrO_2 and SiO_2 coatings. (b) Borosilicate coating and effect of mechanical abrasion of the substrate. (c) Effect of increasing ZrO_2 coating thickness tested by multilayer deposition. All coatings were obtained by fresh solutions at a withdrawal speed of 9 cm/min. The error is $\pm 0{\cdot}005$ mg/cm^2. The oxidation of the bare substrate (□) is reported for comparison.

cause and effect relationship is not clear. For example, the improved adherence could be related to smaller intrinsic stresses in the film, which could be due to smaller tensile stresses developing during its shrinkage. On the other hand, the packing efficiency during coating deposition and the shrinkage upon thermal treatment can be related to the structure of the solution precursors.

The study of the effect of ageing sols was not the aim of this work, but the reported results suggest that this kind of investigation could be of practical interest.

3.3 Oxidation resistance

The oxidation resistance of coated Ni samples was tested measuring the weight gain during heat treatment in air. The test was performed on Ni/TiO_2, SiO_2, ZrO_2 systems; Ni/BS samples with smooth and abraded surfaces; and on Ni/ZrO_2 samples with different numbers of layers to investigate the effect of thickness. The results are shown in Fig. 2.

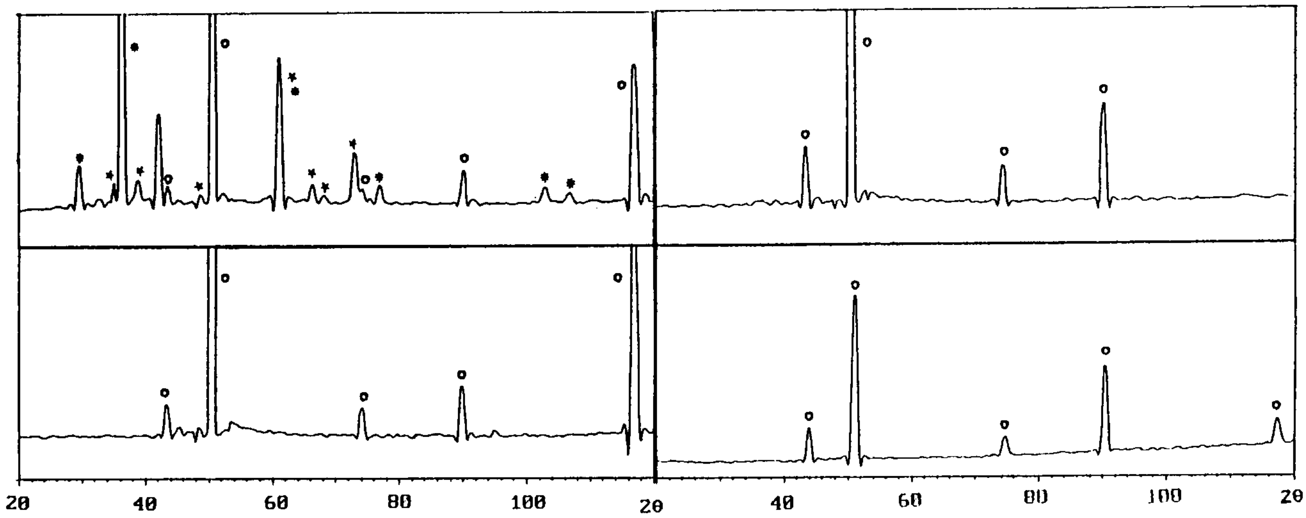

Fig. 3. X-Ray diffraction spectra of BS/Cu samples. The film thickness is 330 nm; the solution was aged 30 days. (○) Cu; (∗) Cu_2O; (☆) CuO. On the left are reported the Cu spectra as-received (bottom) and after 4 h of oxidation in air at 550°C (top); on the right the spectra of Cu coated with BS.

In Fig. 2(a) TiO_2, SiO_2 and ZrO_2 coatings on Ni are compared. It can be observed that the best protection was given by the zirconia coating, which also had the higher quality number. A comparable result was obtained with the BS coating. In this case a clear improvement was found when the film was deposited on an abraded surface, as can be seen in Fig. 2(b). In Fig. 2(c) the effect of multilayer deposition is shown in the case of Ni/ZrO_2 samples. Some improvement was observed with two layers, while the addition of a third layer decreased the oxidation resistance due to extensive cracking.

In Fig. 3 the X-ray diffraction spectra of Cu (uncoated) and Cu/BS samples after 4 h of thermal treatment at 550°C are compared. In the BS/Cu spectrum the peaks of CuO and Cu_2O, present in the spectrum of uncoated Cu, are not detectable.

In Table 4 a semiquantitative evaluation of the protective effect of the BS coatings on Ni obtained by X-ray diffraction analysis is reported. The Ni/BS and uncoated Ni samples were subjected to a thermal treatment of 4 and 8 h at 800°C in air. The protective effect is clearly indicated by the ratio between the areas of the main NiO and Ni peaks, obtained by fitting the profiles using a pseudo-Voigt representation.[9]

Table 4. Ratio between the areas of the main NiO and Ni XRD peaks for an uncoated Ni substrate and a BS/Ni sample after oxidation in air at 800°C for 4 and 8 h

Heating time (h)	*Ni*	*BS/Ni*
4	0·17	0·03
8	1·15	0·04

The film (of 330 nm) was obtained from a solution aged 30 days. Data are reported with a standard deviation of 5%.

4 Conclusions

In this work four metals (Ni, Fe, Al and Cu) were coated with ZrO_2, TiO_2, SiO_2 or B_2O_3–SiO_2 films. It was more difficult to obtain good quality coatings on Fe and Cu than on Ni and Al. An improvement was obtained using aged solutions.

The oxidation resistance of coated Ni and Cu samples was investigated by weight gain and X-ray diffraction measurements. In the case of Ni, a substantial improvement of its oxidation resistance at 800°C was obtained with a borosilicate coating on a previously abraded substrate.

Some improvement may be achieved by increasing the thickness, but there is a limit over which crack formation occurs, reducing the protective action. This limit depends mainly on the nature of the coating and it is probably related to the magnitude of intrinsic stress.

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