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Borosilicate Coatings on Mild Steel Prepared from Aqueous Amine Solutions: A Comparison with the Alkoxide Routes

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Abstract

Sol-gel coatings on metals, as barriers against oxidation of the substrate may be obtained by the dip-coating technique. Different alkoxide solutions have been previously used to deposit coating films on various metallic substrates. Borosilicate coatings gave a good protection against the oxidation of mild steel. The preparation of these coatings has however some disadvantages, such as the required low humidity during deposition and the high cost of precursors.

In this work we studied an alternative method based on aqueous amine solutions. The borosilicate solutions prepared by amines and by alkoxides were characterized by measuring viscosity and stability. Coatings were deposited on mild steel by both methods.

Samples were treated at 550°C and the oxidation was evaluated by glancing angle X-ray diffraction. Adhesion tests and microscopic observations were performed to compare the behavior of amine- and alkoxide-derived borosilicate coating films.

1 Introduction

In recent years several works have appeared on the deposition by dip-coating of sol-gel films on metal substrates. Inorganic coating films obtained via sol-gel were used as barriers against oxidation of metal surfaces. Particularly borosilicates,[1,2] silica,[3,4] alumina,[5] aluminosilicates,[6,7] zirconia,[8,9,10] and fluorine doped zirconia[11] were used as coating films on stainless steel and mild steel.

Alkoxides were always used as precursors. In previous work[12] an alternative sol-gel technique for the synthesis of oxide materials, based on aqueous solutions of amine-containing precursors,[13–15] was used. Silica coating films were deposited on mild steel by alkoxide and water–amine solutions. The use of the amine route shows important advantages such as reproducibility of the desired chemical compositions, great choice and low cost of raw materials.

In this work borosilicate coating films on mild steel were prepared starting from alcoholic and aqueous solutions. A comparative study of their properties and protective effect against oxidation is presented.

2 Experimental

2.1 Preparation of solutions

One alkoxide and two amine-based solutions were prepared for the deposition of borosilicate coating films.

The borosilicate alkoxide solution, indicated as SiBT, was prepared using tetraethoxysilane, $Si(OC_2H_5)_4$, (TEOS) and triethylborate, $B(OCH_3)_3$, (TEOB) as precursors. The TEOS/TEOB molar ratio was 80/20. TEOS was prehydrolized in ethanol (EtOH) with H_2O (H_2O/TEOS = 5), using HNO_3 as catalyst (HNO_3/TEOS = 0·07). After refluxing for 4 h, TEOB was added and the solution was refluxed for an additional 4 h. The SiBT solution had a concentration of about 10 wt%. Methylamine–Borosilicate solutions (SiBM) were prepared as follows: solid silicic acid was mixed with an aqueous solution of methylamine (MA) (20 wt%) and the obtained mixture was stirred for 1 h in a ball-mill and for one day in a magnetic stirrer.

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A methylamine–borate solution was then separately prepared by dissolving boric acid (H_3BO_3) in an aqueous solution of MA. Both solutions were mixed and diluted with water to a concentration of 8 wt% oxides. SiBM solutions with different compositions were prepared to study the effect of the content of boron.

A second type of aqueous borosilicate solution (SiBQ) was obtained using quaternary ammonium cation. A silicate of the quaternary ammonium base was prepared according to the scheme proposed by Weldes,[16] replacing ethanolamine and ethylene oxide with diethylamine (DEA) and propylene oxide (PO) respectively. A solution of diethylamine silicate was prepared by dissolving solid silicic acid in an aqueous solution of diethylamine (25 wt%), stirring the solution 1 h in a ball mill and one day in a magnetic stirrer. Then PO (2 mol per mol of DEA) was added, the solution was stirred for 4 h and heated slightly to evaporate residues of PO and to increase the SiO_2 concentration up to 7 wt%. A borate solution was prepared as previously described for SiBM and added to the silicate solution. The borosilicate solution was diluted with water to a concentration of 5·8 wt% SiO_2 and 1·6 wt% B_2O_3.

2.2 Coating films preparation

Mild steel plates were used as substrates. The steel plates were cleaned ultrasonically in acetone and rinsed with ethanol before coating. Coating films were deposited by dip-coating in a humidity controlled box. The relative humidity was less than 20% for the SiBT samples and less than 40% for the others. After deposition the samples were dried at 60°C for 15 min, heated in air at a constant rate of 5°C/min up to 500°C and immediately left to cool in the off furnace. This thermal treatment will be indicated as Procedure 1.

2.3 Characterization of solutions and coatings

The viscosity as a function of time was measured for SiBT, SiBM and SiBQ, using a rotational viscometer.

The thermal evolution of gel films was observed using a multi-plate platinum holder in a thermogravimetric apparatus (TGA). Thick layers of about 100 μm were poured onto the plates and dried for 1 h at 100°C. Then the temperature was raised up to 1000°C, at a constant rate of 5°C/min.

Coating thickness was measured at different withdrawal rates on films deposited on glass slides under the same conditions as those used for coating the mild steel substrates. The influence of the substrate was assumed to be negligible. The thickness was evaluated with a profilometer, measuring the step on the coating produced with a scratch, after drying at 60°C. Samples were observed by scanning electron microscopy (SEM) after the oxidation test.

A semiquantitative evaluation of the adhesion was done by means of a scratch test, using a microindenter. Samples were moved under the indenter, at a constant rate, using different loads. The load at which delamination was observed was considered as the critical load.

2.4 Oxidation test

The resistance against oxidation was measured on samples treated in air at 500°C (Procedure 1) and on samples reheated at 5°C/min up to 550°C and maintained at this temperature for 1 h (Procedure 2). Oxidation was evaluated by Cu K_α X-ray diffraction with a glancing angle technique. The area (A) of peaks at 2θ = 35·5 (Fe_3O_4 + α-Fe_2O_3) and 2θ = 44·6 (α-Fe) was calculated using a Pseudo-Voigt representation to fit the profiles.[17]

The area ratio of the peaks at 2θ = 35·5 and 2θ = 44·6 was evaluated for coated (R_c) and uncoated (R_u) samples. The ratio R_u/R_c was taken as a measure of the oxidation degree and indicated as the protection factor (PF):

$$PF = \frac{R_u}{R_c} = \frac{\dfrac{A_u\,(Fe_3O_4 + \alpha - Fe_2O_3)}{A_u(\alpha - Fe)}}{\dfrac{A_c\,(Fe_3O_4 + \alpha - Fe_2O_3)}{A_c(\alpha - Fe)}}$$

The kinetics of oxidation at higher temperature were also measured by evaluating the weight gain by TGA, at a constant rate of 5°C/min up to 800°C.

3 Results and Discussion

Figure 1 shows the logarithm of solution viscosity η as a function of time. In the case of SiBM and SiBQ no changes in viscosity were observed even after 60 days from the preparation. For SiBT the viscosity is stable for about 10 days and then abruptly rises.

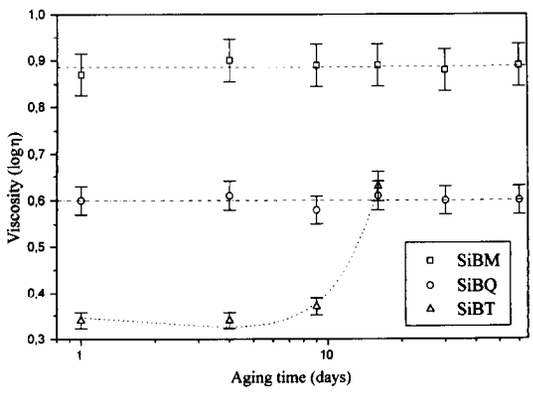


Fig. 1. Viscosity as a function of time for solutions SiBM, SiBQ and SiBT.

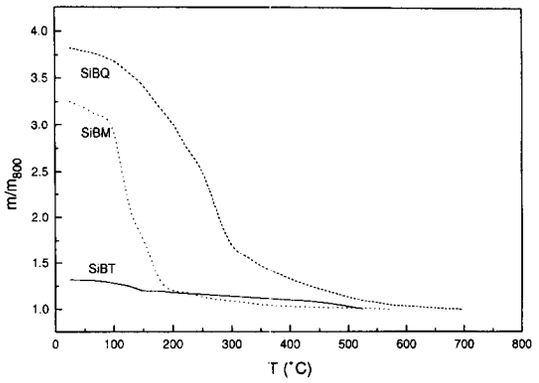


Fig. 2. TGA curves of gels obtained from solutions SiBM, SiBQ and SiBT pre-heated at 100°C for 1 h. m_{800} is referred to the mass value at 800°C.

This different behavior is ascribed to the different chemical character of alkoxide and amine solutions. SiBT, prepared from TEOS and TEOB, undergoes the sol-gel transformation by hydrolysis and condensation of alkoxides. This process continues in time giving the gelation of the solution. For alkoxide borosilicate solutions[18,19] a delaying in the gelation time proportional to the B_2O_3 content was observed and it was ascribed to the decreasing of potential condensation sites due to the trigonal coordinated boron. This can explain the stability of SiBT for about ten days, a longer time than that found with silica solutions. A much higher stability was however observed in the amine solutions, where the high pH values (11–12·5) displace the polycondensation equilibrium to low polymerized silicate and borate anions, which are stable in aqueous solutions. The viscosity of SiBM is higher than SiBQ because of the higher concentration of organic substances in the solution.

Thermogravimetric results are reported in Fig. 2. The curves relative to SiBM and SiBQ show one main effect, associated with an endothermic peak in the DTA. This effect ends at about 200°C for SiBM and 300°C for SiBQ. The weight loss is attributed to the escape of water in the case of SiBT and water

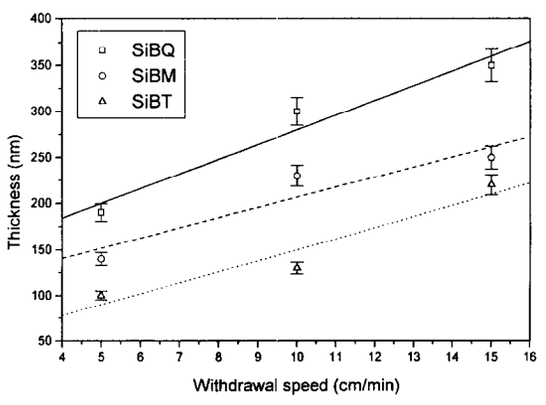


Fig. 3. Thickness as a function of withdrawal speed for coatings obtained from borosilicate solutions SiBM, SiBQ and SiBT.

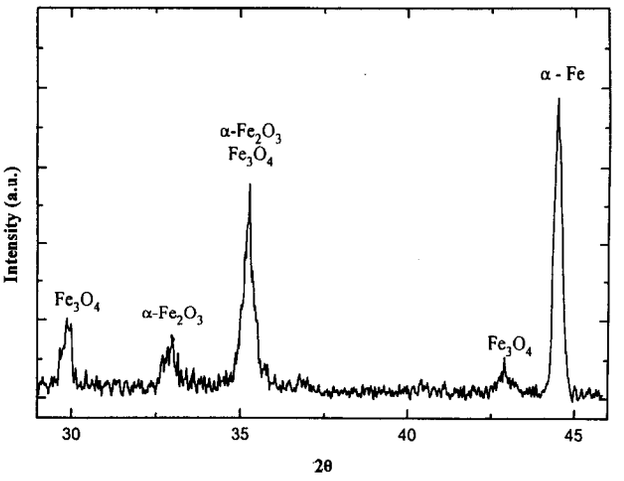


Fig. 4. Typical XRD spectra of a coated sample with partial oxidation of the substrate.

plus MA for SiBM and SiBQ. The difference in the mass loss between SiBM and SiBT may be explained by the quite strong chemical connection of MA and H_2O to the silicate network. Wet SiBT gels contain only non-bonded volatiles (ethanol and water) which are easily removed at 60°C. The mass loss over 60°C is due to the water which results from the reactions of polycondensation that continue up to higher temperatures. The SiBQ curve shows a supplementary mass loss in the range of temperature 400–600°C, accompanied by an exothermic DTA effect. This loss may be attributed to the oxidation decomposition of resin-like residuals of the quaternary ammonium silicate.

Figure 3 shows the thicknesses of the coatings deposited from solutions SiBT, SiBM and SiBQ, at three different withdrawal speeds. In the dip coating process the thickness depends on such solution properties as concentration, viscosity, density and surface tension.[20–22]

In the present case, the thickness differences are mainly due to viscosity (Fig. 1), which increases from SiBT to SiBQ.

Figure 4 shows a typical diffraction pattern obtained from X-ray glancing angle measurements on the coated samples.

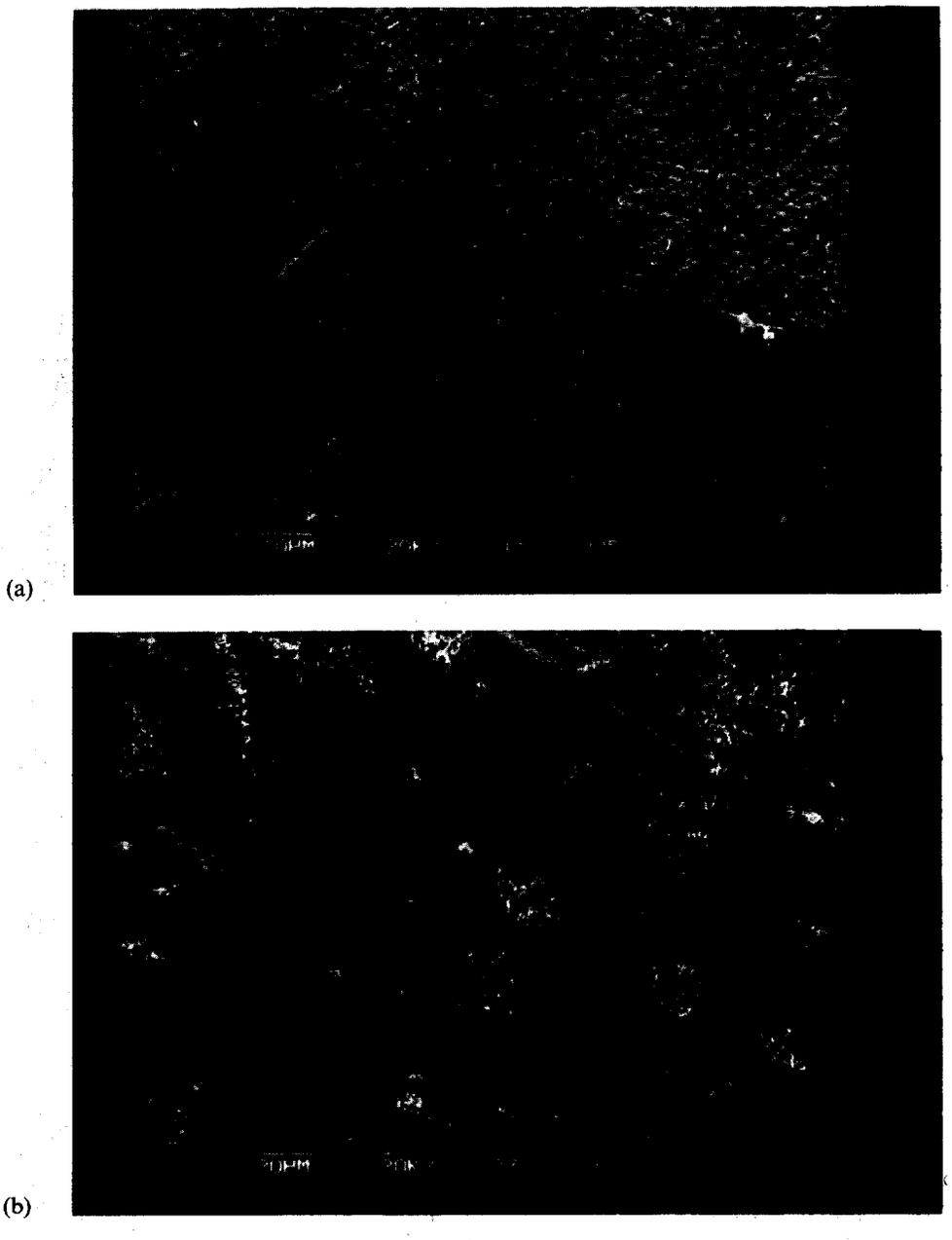
Comparative XRD data, obtained in the oxidation tests are reported in Table 1. The data in the table refer to samples after firing at 550°C (Procedure 1) and to samples re-heated at 550°C for 1 h, (Procedure 2). The thickness of the coating films was tailored to obtain almost the same thickness value for SiBT, SiBM, and SiBQ. In the table the data from previous work,[12] where silica coatings were studied, are also reported. The thickness values are quite different in this case, but the data may be useful for comparison. Coatings containing boron may, in general, give higher protection, compared with SiO_2 films. As observed previously,[1] boron probably has the effect of reducing

Table 1. Comparative XRD data relative to the oxidation tests. The reported data are referred to samples after firing at 500°C (Scheme 1) and to samples re-heated at 550°C for 1 h (Procedure 2). Data referred to silica coating films on mild steel[12] are also reported for a comparison.

	Alkoxide-derived		*QAB-derived*		*MA-derived*	
	without B_2O_3[a]	*SiBT*	*without* B_2O_3[a]	*SiBQ*	*without* B_2O_3[a]	*SiBM*
Film thickness (nm)	30	200	250	190	68	230
Protection factor (Procedure 1)	4	78	27	24	24	62
Protection factor (Procedure 2)	3	39	2·5	18	6	39

[a] Data from[12].

the intrinsic stress in the sol-gel films. As a matter of fact the critical thickness, t_c, i.e. the maximum thickness achievable free of cracks,[22] is higher. Sol-gel borosilicate coatings, prepared from fresh solutions, have a critical thickness of about 350–400 nm, while typically for silica coatings t_c is about 200–250 nm.[23] Furthermore the lower intrinsic stress may reduce the presence of microcracks in the coatings[1,3] thus increasing the protective action.



(a)

(b)

Fig. 5. SEM micrographs of a sample coated with solutions (a) SiBT 200 nm, (b) SiBM 230 nm and (c) SiBQ 190 nm. All samples were treated following Procedure 2.

(c)

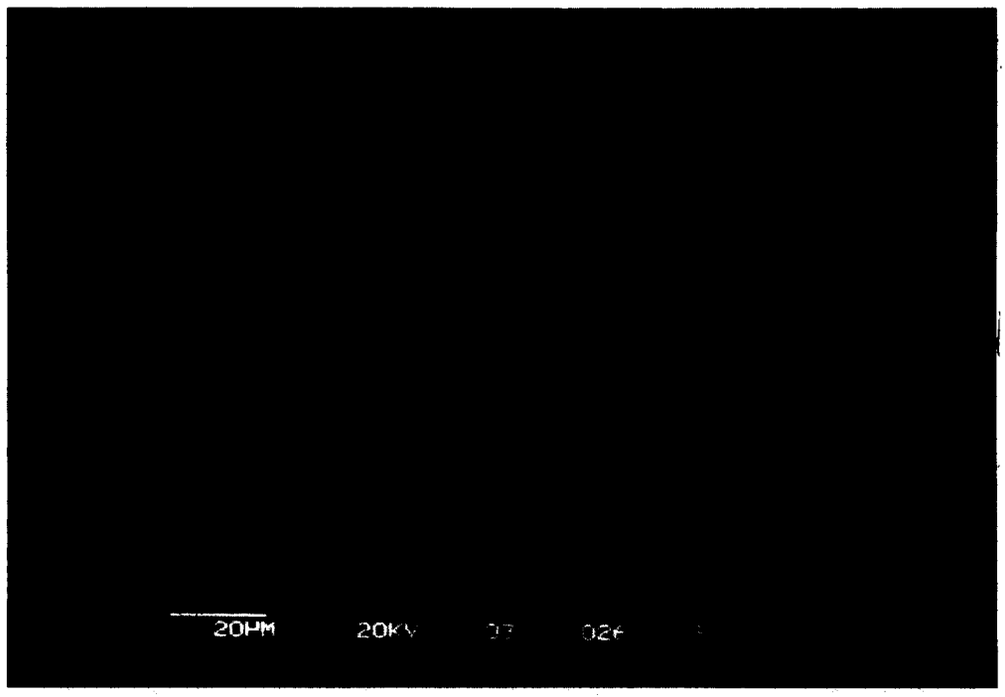


Fig. 5—*contd.*

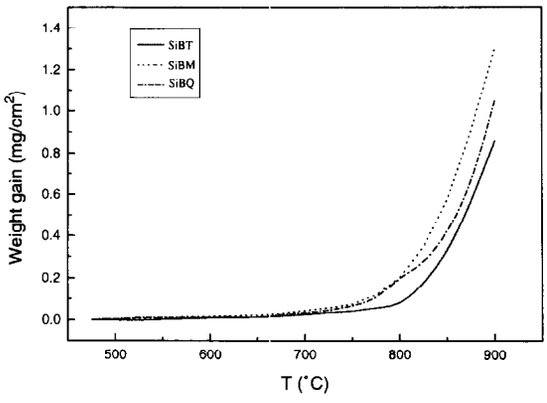


Fig. 6. Weight gain as a function of temperature for samples coated with solutions SiBT, SiBQ and SiBM.

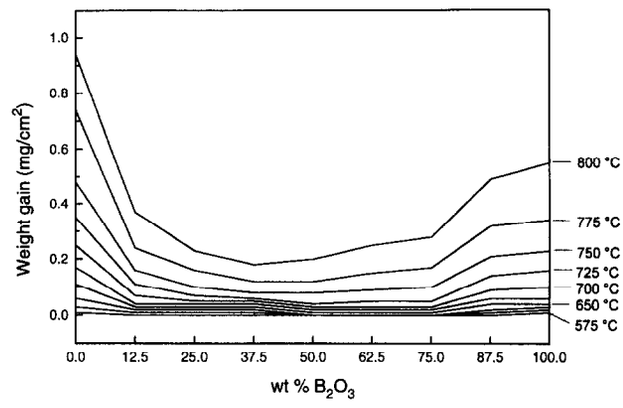


Fig. 7. Weight gain as a function of thermal treatment, for samples coated using SiBM solutions with different B_2O_3 contents.

SiBT and SiBM gave better protection against oxidation, with a quite similar PF; also SiBQ has a good protective effect, even if this is about half that of SiBM and SiBT. As the thicknesses for SiBT, SiBM and SiBQ are quite similar, the differences in the protective effect should be attributed to structural differences in the coatings.

As revealed by SEM observations, SiBT and SiBM coatings were mostly uncracked (Fig. 5(a) and (b)) differently from SiBQ (Fig. 5(c)). Also a different porosity between SiBM and SiBQ might be supposed, due to the different concentration of organic substances in the xerogels. However, due to difficulties in obtaining measures of thin film porosity, a direct proof is not available.

The kinetic results from TGA for the oxidation of samples in the high temperature region (up to 900°C) are shown in Fig. 6. Weight gain up to 750°C is negligible. At higher temperatures, the oxidation of the metallic substrate rapidly increases. In this test no significant difference between samples could be detected.

Figure 7 shows the weight gain as a function of temperature and B_2O_3 content for SiBM samples.

In Table 2, data relative to adhesion tests are reported. For every sample the adhesion was found to be good. SiBM provides the best adhesion.

Table 2. Critical load measured on samples after thermal treatment at 500°C.

Sample	$L_c(g)$
SiBQ	200
SiBT	300
SiBM	500

4 Conclusions

Borosilicate alkoxide and amine derived coatings were prepared on mild steel. Differences in the protective effect against oxidation of the metallic substrate were investigated. The anti-oxidation protective action of coatings was studied by XRD and TGA measurements up to 800°C. Amine derived films showed a protection comparable to that of coatings obtained from alkoxide solutions.

Furthermore, amine derived solutions have much higher stability, and lower costs than alkoxide ones. They are, therefore, more suitable for practical applications.

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