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Multi-elemental depth profiling by microbeam PIXE of phenolic coatings exposed to sulphuric acid

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The phenolic coatings used to protect the steel of railway tanks during the shipment of concentrated sulphuric acid have been studied by microbeam PIXE and a.c. impedance measurements. After repeated washing and filling cycles, these coatings begin to lose their resistance to corrosion but the breakdown mechanism is not presently well understood. A 20 μm focused proton beam has been used to scan the approximately 200 μm thick coatings to obtain the depth profiles of sulphur, which, as sulphate ions, are thought to migrate towards the steel–coating interface and initiate the breakdown process. Parallel electrochemical impedance spectroscopy (EIS) measurements have been performed to determine the electrical properties of the metal–coating system. Samples were exposed to concentrated sulphuric acid for periods of up to six months.

The microbeam PIXE results indicate that the sulphur concentration has reached a saturation level after about ten weeks, which coincides with the onset of appreciable corrosion as determined from the impedance measurements. Two additional samples, which were treated to repeated cycles of immersion in acid followed by rinses in water, lost a large fraction of titanium at the exposed surface and after some twenty cycles were easily delaminated from the substrate, suggesting one possible breakdown mechanism. The use of an inexpensive proton microprobe provides a simple and rapid quantitative evaluation of sulphur concentrations and depth profiles.

1. Introduction

The phenolic coatings used to protect the steel surface of railway tanks during the transport of concentrated sulphuric acid are composed of pigments and mineral charges that are extremely resistant to degradation. Nevertheless, after repeated washing with water (during safety inspections) and filling cycles they begin to break down and offer less effective protection, leading to corrosion at the steel–coating interface. While the exact nature of the breakdown is not well understood it is probably related to the migration of sulphate ions through the protective layer which is typically 150 to 250 μm thick. The coatings studied are composed of pigments (a mixture of TiO_2 and Fe_2O_3) to which a mineral charge of kaolin [$Al_2Si_2O_5(OH)_4$] has been added and their study by conventional electron microscopy and X-ray fluorescence techniques is difficult since they are excellent electrical insulators. To probe the steel–coating interface EIS measurements can be used [1, 2] but for a more complete understanding of the breakdown process the concentrations of key elements, especially sulphur, needs to be determined across the coating.

A relatively new technique, the proton microprobe, with a beam spot size of around 20 μm and good sensitivity for the elements of interest offers many advantages. Proton induced X-ray emission (PIXE) is now well understood and is routinely applied to the study of thick targets [3, 4]. The main advantages of PIXE are a minimum of target preparation and measurement time, so that a large number of samples can be analysed on a routine basis, with sensitivity down to the p.p.m. level. In this paper the application of microbeam PIXE to the measurement of the distributions of sulphur and other major elements in phenolic coatings is explored and the results are compared with a.c. impedance measurements.

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2. Experimental methods

2.1. Microbeam PIXE

The Université de Montréal proton microprobe has been described in a previous paper [5] and only a brief review is given here. A 4.5 MV Dynamitron accelerator focusses a 1 MeV proton beam onto a set of slits (500 μm × 500 μm) which forms the object for an electrostatic quadrupole triplet lens [6]. The lens (focal length $\approx$ 10 cm) produces a beam spot on target with a diameter of about 20 μm and with a typical beam current on the target of 1 nA. The target chamber consists of a standard Dependex cross with six 4″ diameter ports and two additional 1″ ports at 135° to the beam direction. An HPT040 micromanipulator is used for positioning the target.

A 30 mm^2 Link* Si(Li) X-ray detector (energy resolution 155 eV at 5.9 keV) is mounted at 135° to the beam direction. An electron flood gun in the second 1″ port is used to reduce the Bremsstrahlung due to target charging by the beam. The X-ray detector has an 8 μm thick beryllium window and additional filters are mounted on a support in front of the detector. To view the target a zoom microscope is used to look at a retractable mirror (with a hole in the centre for the beam) in front of the target. A pulse processor, which includes a comprehensive pulse pile-up rejector, is used to process the signals from the detector.

The bombarding energy of 1 MeV provides optimum sensitivity for the elements of interest (aluminium, silicon, sulphur and titanium) and the system is calibrated with a set of standard thin foils† by determining the yields of X-rays per μC of beam charge per μg cm^{-2} of target thickness for a range of elements between sodium ($Z = 11$) and copper ($Z = 29$).

Eight targets, each consisting of a cylindrical steel core with a phenolic coating, were exposed to concentrated sulphuric acid for periods ranging up to six months. EIS measurements were used (see the following section) to determine the equivalent electrical circuit of each sample after which the phenolic coating cross-section was exposed by cutting through the cylindrical sample with a diamond blade. A photograph of one of the samples is shown in Fig. 1, while Fig. 2 illustrates the inner steel core with the approximately 200 μm thick coating. The targets were mounted on a plastic target holder and scanned across the proton beam in steps of 25 μm from the inner steel core to the outer surface.

2.2. Electrochemical impedance spectroscopy (EIS)

A Princeton Applied Research a.c. impedance system‡, interfaced to an Apple II computer through an IEEE-488 interface, was used to make all the EIS measurements. The data were acquired with a two-electrode set-up at the steady state potential of the coated sample and the signal amplitude applied between the electrodes was 10 mV. The data were transferred to a VAX 11/785 for analysis.

Figure 1 A photograph of one of the samples used in this study for the EIS measurements. The diameter of the sample is 10 mm.

In all the EIS measurements, the painted rods were completely immersed in a 93% H_2SO_4 solution. The surface area in contact with the acid was 2.8 cm^2. The counter electrode was a platinum wire and in order to get results in a reasonably short time, the experimental temperature was 90° c. A more detailed description can be found elsewhere [7].

3. Results

3.1. PIXE results

Some typical X-ray spectra are shown in Fig. 3, taken (a) in the steel core, (b) in the centre of a coating and (c) at the coating surface. Also shown are the X-ray spectra from (d) the centre of the coating of an unexposed sample and (e) a sample which showed signs of excessive corrosion and pitting at the surface. The rapid decrease in the iron concentration marks the core–coating interface, with a corresponding increase in the titanium, aluminium, silicon and sulphur concentrations from the coating (the coatings used in the present study all contained a mineral charge of kaolin). This is best illustrated in Fig. 4, for three of the samples, where the concentrations of iron, titanium, aluminium, silicon and sulphur are shown as a function of the target position. The concentrations are fairly constant for a single coating over a 100 μm region in the centre but show an increase in the sulphur concentrations at the surface. This might be due to surface irregularities or might indicate that complete saturation has not yet occurred.

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‡Princeton Applied Research, PO Box 2565, Princeton, New Jersey 08540, USA.

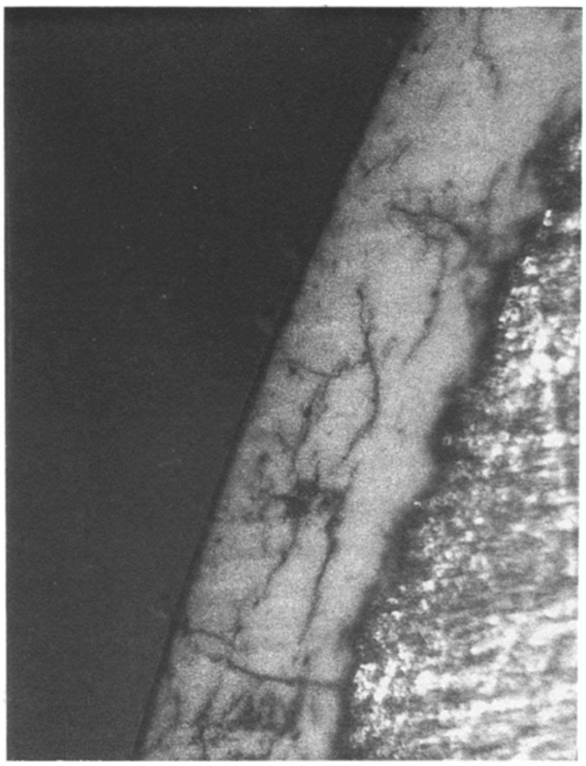

Figure 2 A photograph showing the central steel core and the phenolic coating of one sample prepared for scanning with the proton microprobe. The coating thickness varied between 150 and 250 μm.

In Table I the measured concentrations of aluminium, silicon, titanium and sulphur are presented, taken as the average at the centre of the coating. Also shown are the average sulphur concentrations at the surface of each coating. In the absence of information on the proprietary formulation of the coatings, the matrix composition was fixed in the analysis at 20% Ti with the remainder divided equally between oxygen and carbon. The results are not very sensitive to small deviations from these values. The averages of the titanium, aluminium and silicon concentrations are 27, 2.05 and 1.75%, respectively, and do not appear to be dependent on the exposure time. The variations observed probably reflect more the slightly different compositions of the coatings for different samples and small systematic errors in the positions of the targets relative to the detector. The pigment and the mineral charge of kaolin are, therefore, quite stable in the presence of the acid. The sulphur concentrations, on the other hand, show an increase with exposure time which reaches a peak value in the centre of the coating of about 2.5% after ten weeks. Correlations with the coating thickness, which might give rise to variations in the sulphur distributions, were not examined in the present work. The results obtained for sulphur at the surface are more difficult to interpret since irregularities at the target surface are expected and can affect drastically the applied X-ray absorbtion corrections. Nevertheless, a saturation level of about 4% appears to be reached for periods greater than six weeks.

The sulphur concentrations in two additional coatings, exposed to repeated cycles of immersion in acid followed by rinses in water, were also measured on the inner and outer surfaces after the coating had been stripped from the steel core. The results are presented in Table II. While the aluminium, silicon and sulphur concentrations are fairly constant (1.7, 2.0 and 4.25%, respectively), there is a huge reduction in the titanium content from an average concentration of 27% for non-washed samples, down to less than 3% at the outer surface. In addition the inner surface concentration averages 16.7% which is also considerably lower

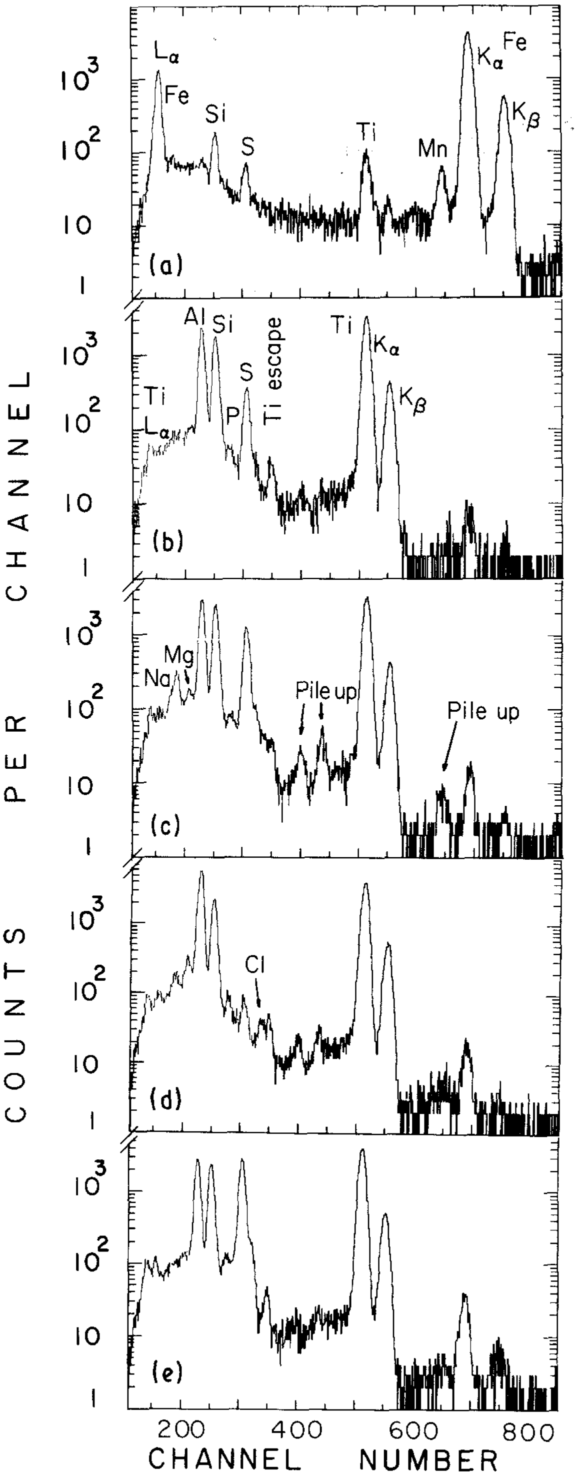

Figure 3 Some typical PIXE spectra taken at (a) the steel core, (b) the centre of the phenolic coating and (c) the surface of the phenolic coating. Also shown for comparison in (d) is a PIXE spectrum taken at the centre of a virgin coating unexposed to sulphuric acid and in (e) the spectrum from a badly corroded sample. The peaks are labelled by the chemical symbol and the corresponding X-ray line. The proton bombarding energy was 1 MeV.

TABLE I The concentrations (wt %) of titanium, aluminium, silicon and sulphur, obtained by microbeam PIXE at 1 MeV bombarding energy on phenolic coatings exposed to sulphuric acid for periods ranging up to six months. The results are the average values measured across the centre of each coating. The average concentrations of sulphur at the surface of the coatings are also shown. The errors are typically 10 to 15%. To the right are included the results of the a.c. impedance measurements, presented as the electrical component equivalent values.

Immersion time	PIXE results					EIS results				
	Centre				Surface	R_{pore} (Ω)	R_t (Ω)	C_c (F)	C_{dl} (F)	Z_0
	Ti	Al	Si	S	S					
Unexposed	23	1.5	1.5	0.06	0.11	–	–	–	–	–
2 h	–	–	–	–	–	10^7	–	10^{-9}	–	–
2 d	–	–	–	–	–	10^7	–	2×10^{-7}	–	–
1 week	–	–	–	–	–	4×10^6	–	8×10^{-7}	–	–
2 weeks	25	1.8	1.5	0.2	0.8	300	10^3	1×10^{-6}	10^{-6}	10^6
4 weeks	35	4.0	3.0	0.6	1.5	200	700	1×10^{-6}	8×10^{-6}	10^5
6 weeks	30	1.8	1.5	0.6	4.0	150	600	3×10^{-6}	10^{-5}	10^5
2 months	25	2.0	1.5	0.4	2.5	–	–	–	–	–
10 weeks	28	2.0	2.0	2.5	2.0	70	120	5×10^{-6}	5×10^{-4}	5×10^4
3 months	23	1.7	1.3	2.0	5.0	25	50	2×10^{-5}	5×10^{-4}	5×10^4
6 months	24	1.6	1.5	1.3	3.8	–	–	–	–	–

than the average value of 27%, indicating that the pigment is readily attacked by the acid and is leached out of the coating. The importance of discharging the targets with the electron-gun in these measurements should be stressed. With the electron-gun turned off, the measured titanium and iron concentrations rose by factors of 2.6 and 4.5, respectively, due to target charging.

3.2. Alternating current or impedance results

The results of the a.c. impedance measurements, in circuit equivalent form, are also shown in Fig. 4, while the calculated values of the electrical components, which have been fully described in a previous paper [7], are given in Table I. Calculated values are determined using the complex non linear least squares fitting program of MacDonald [8] and represent mean values obtained from different samples with the same exposure period.

For less than seven days, the a.c. impedance spectra represent essentially the coating: a high R_{pore}, the coating electrical resistance, in parallel with a small C_c, its capacitance. This is Model I. For the period between 1 and 2 weeks, a diffusion process across the coating begins to appear and the corresponding electrical circuit is given by Model II. The diffusion impedance (or Warburg impedance) is given by [9]

$$Z_d = Z_0 \frac{\tanh (i\omega k)^\alpha}{(i\omega k)^\alpha}$$

where ω is the angular frequency of the a.c. signal, k a constant containing the physical parameters of the diffusion process, Z_0 the modulus at $\omega = 0$ and α a constant between 0 and 1 ($\alpha = 0.5$ for pure uniform diffusion).

R_t and C_{dl} represent, respectively, the charge transfer resistance and the electrochemical double layer of the electrochemical (corrosion) reactions at the metal–coating interface. The R_t values remain high and the C_{dl} values low showing almost nonexistant corrosion reactions. Between 15 days and 6 months all the preceeding values evolve, showing an acceleration of both the diffusion process and corrosion reactions as described by Model III, which is the model commonly used for the metal–coating system [2].

TABLE II The concentrations (wt %) of aluminium, silicon, sulphur, titanium and iron measured by microbeam PIXE at 1 MeV bombarding energy in two samples of a phenolic coating repeatedly immersed in sulphuric acid and washed with water over a period of three weeks. The errors are typically 10 to 15%.

	Sample 1 Inside surface	Sample 1 Outside surface	Sample 2 Inside surface	Sample 2 Outside surface
Al	1.44	1.86	1.74	1.91
Si	1.55	2.18	2.02	2.29
S	4.02	4.28	4.50	4.21
Ti	14.6	2.67	18.8	2.84
Fe	0.75	0.30	0.62	1.19

4. Discussion

Combining the results obtained by PIXE and EIS the following degradation mechanism can be deduced.

4.1. Samples continuously exposed to sulphuric acid

During the first two weeks, the main phenomenon is the slow penetration of the acid into the coating towards the metal as reflected by the EIS measurements with a decreasing R_{pore} and an increasing value of C_c. No corrosion on the steel can be observed and the coating provides excellent protection. Very little sulphur ($\approx 0.2\%$) is detected in the coating at depths greater than 50 μm from the surface.

For the following weeks and up to two months, the acid is still penetrating the coating towards the metal. The process of corrosion is just beginning but is severely limited by the very slow diffusion of the acid. This is shown by the high values of R_t and Z_0. The sulphur concentration, always higher near the surface, has increased to around 1% in the centre and has now reached the metal–coating interface.

For periods greater than two months, the acid has finally reached sufficient quantity to provoke detectable corrosion, as indicated by the low values of R_t and the sulphur concentration has reached a steady state value around 2.5% at the centre, imposed by the physical properties of the coating.

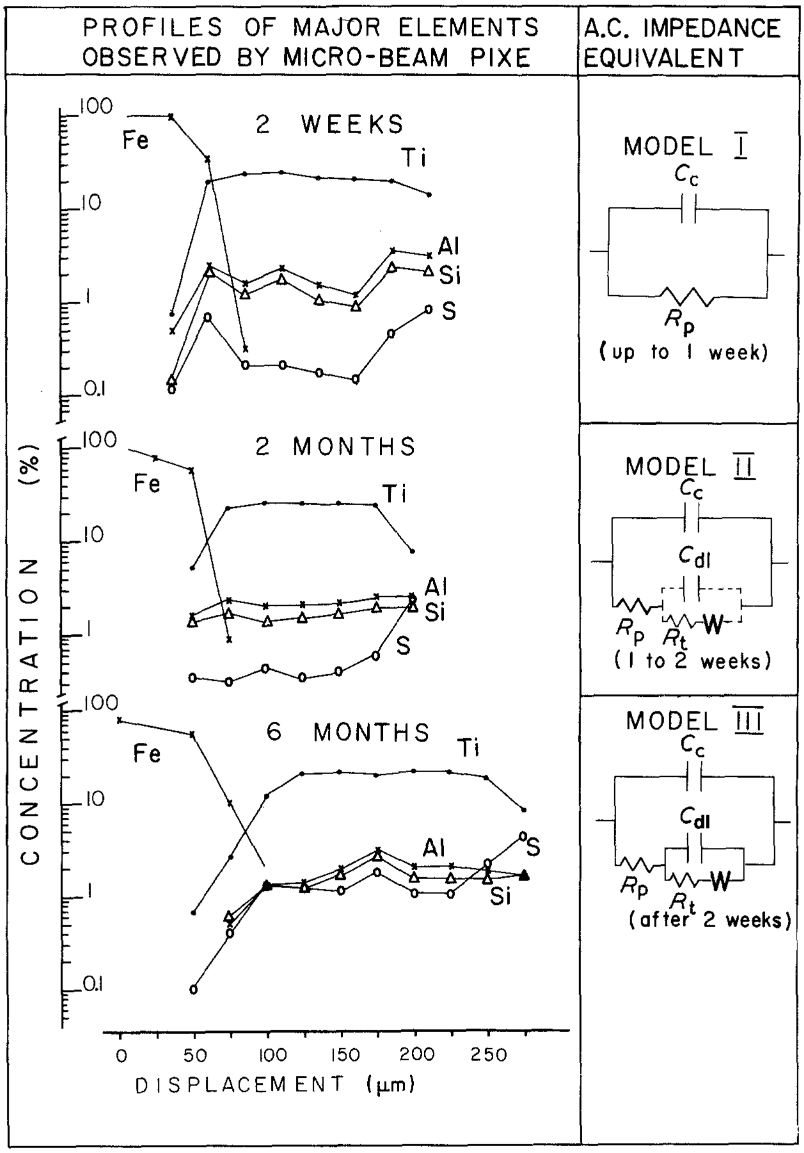

Figure 4 The concentrations (wt%) of iron, titanium, aluminium, silicon and sulphur as a function of the position across the surface of three phenolic coatings exposed to sulphuric acid for two weeks, two months and six months, respectively. The errors in the concentrations are typically 10 to 15%. To the right of the figure the equivalent electrical circuit is shown, as determined by EIS measurements.

The phenolic coating offers effective protection, acting as a barrier which strongly inhibits the diffusion of corrosive species towards the metal. Since the corrosion process is very slow, the lifetime of the coating will be determined by the chemical resistance of the coating.

4.2. Rinsed samples

The EIS results for these samples showed accelerated degradation with the appearance of Model III after only about two weeks and around ten washings in water. During the third week large cracks appeared and the whole coating peeled off after some twenty rinses, leading to complete loss of corrosion protection. The loss of titanium from the coating, as evinced from the PIXE measurements, suggests the following explanation. In contact with concentrated sulphuric acid TiO_2 reacts to give complex sulphates whose composition depends on the acid concentration and its temperature [10]. The most common sulphate is $TiOSO_4 \cdot 2H_2O$ which is slightly soluble in very concentrated acid but whose solubility increases rapidly when the water content of the acid increases. When washed with water, therefore, the solubility of the sulphate increases and titanium is leached out of the coating. When the coating is again immersed into the acid, TiO_2 deeper inside the coating forms again a sulphate which is leached out during the following washing. The formation and dissolution of this sulphate can also be explained by the EIS measurements: the resistance of the coating increases slowly after a washing from a value which is much lower than before the washing [11]. The leaching out of the TiO_2 increases considerably the porosity of the coating and facilitates the diffusion of sulphuric acid through the coating, leading to rapid corrosion phenomena at the metal–coating interface. This is in accordance with the sulphur content of around 4.5% found in these samples on both the outer and inner surfaces of the coating which is much higher than the sulphur content found in the non-washed samples. The build-up of a large volume of corrosion products then causes the cracks in the coating and finally its complete delamination.

5. Conclusion

The use of a proton microprobe to investigate the onset of corrosion in phenolic coatings exposed to sulphuric acid has been investigated and the results are found to be in qualitative agreement with EIS measurements. The PIXE results show that the sulphur concentration in the centre of the coatings increases with exposure time, reaching a value of about 2.5% after about ten weeks. A large reduction in the titanium concentration occurs for samples that have been repeatedly washed in water and immersed in acid. The sulphur concentration reaches a value as high as 4.25% in these samples while the concentrations of silicon and aluminium do not appear to be affected. These measurements reveal the chemical evolution of the coating during degradation and provide for an explanation of the EIS results and the degradation mechanism.

The diffusion of sulphur into the coating can be measured in a relatively simple and rapid fashion by this technique and yields quantitative results which should prove extremely useful in developing more efficient uses of these coatings.

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