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The application of X-ray photoelectron spectroscopy to the study of polymer-to-metal adhesion

Part 3 *The influence of substrate surface chemistry on the cathodic disbondment process*

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The cathodic disbondment of a fusion-bonded epoxy coating applied to mild steel treated with a phosphoric acid wash has been investigated. The interfacial chemistry of disbondment has been studied by X-ray photoelectron spectrscopy (XPS), which shows the locus of failure to alternate between cohesive failure of the polymer coating and a phosphate-bearing layer. The kinetics of delamination are substantially reduced compared with data obtained for epoxy applied to a bare steel substrate. It is concluded that the application of an acid wash treatment results in a stronger, more durable, polymer-to-substrate bond. The process parameters of the wash treatment control both the substrate surface chemistry prior to coating and the eventual failure mode.

1. Introduction

In a recent paper, the adhesion failure of a fusion-bonded epoxy coating applied to cathodically protected mild steel has been described [1]. It was shown that the substrate surface topography has a marked effect on the kinetics, but not the mechanism of failure. Such coatings systems are widely employed in the oil and gas industries for the corrosion protection of transmission line-pipe [2]. In exceptionally arduous conditions the steel substrate may be pre-treated chemically prior to coatings application to enhance adhesion. One such example of this procedure is the application of a dilute phosphoric acid wash immediately before coating [3, 4].

The work reported here presents complementary results to those cited above which extend the area of interest to the effect of substrate surface chemistry on the kinetics and the mechanism of failure. This has been achieved by the careful characterization of the steel substrate after exposure to a dilute H_3PO_4 solution, and following heat treatment prior to coating. The kinetics of disbondment of a commercial fusion-bonded epoxy*, from such substrates, has been investigated and the loci of failure determined by the surface-sensitive technique of XPS.

2. Experimental details

2.1. Specimen preparation

Mild steel panels were blast cleaned with G12 chilled iron grit and immersed in a 2% H_3PO_4 solution at 85° C for 2 or 10 min, followed by a 30 sec wash in boiling, deionized water. The panels were then heated in air at 240° C for 30 min prior to powder coating to a thickness of approximately 380 μm using a compressed air gun. The coated panels were then returned to the oven for a further 2 min to cure the polymer and then quenched in cold water.

Samples were cut from uncoated panels at each stage of the pre-treatment so that the changes in surface chemistry could be monitored by XPS.

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*3M Company, Scotchkote 206N.

TABLE I Effect of phosphoric acid wash and subsequent heat treatment on the surface chemistry of grit-blasted steel

Immersion time (min)	Heat treatment	At.%				
		C	O	Fe	P*	Fe/P
Grit-blasted only	No	42.0	43.7	14.3	0	–
2	No	36.4	53.0	8.8	1.8	4.9
10	No	36.5	51.6	9.4	2.5	3.8
Grit-blasted only	Yes	35.5	50.3	14.2	0	–
2	Yes	33.3	53.6	12.1	1.5	8.1
10	Yes	33.8	53.0	10.8	2.4	4.5

*As PO_4^{3-}.

2.2. Cathodic disbondment tests and surface analysis

The procedures adopted for the cathodic disbondment experiments and subsequent XPS analysis have been described previously [1]. Only the salient points of each technique will be described here.

The cathodic disbondment tests were carried out according to the relevant British Gas Corporation specification [5]. Coated, pre-damaged panels were polarized cathodically (– 1500 mV, vs SCE) in aqueous 0.52 M sodium chloride solution. Following testing the extent of disbondment was assessed by cutting the coating back radially from the defect. Specimens were then cut from both substrate and coating for XPS analysis which was carried out in a V.G. Scientific ESCA 3 Mk II electron spectrometer. Aluminium $K\alpha$ X-rays ($h\nu =$ 1486.6 eV) and an analyser pass energy of 50 eV, operating in a vacuum of 5×10^{-10} torr were employed. Quantification of the photoelectron spectra was achieved using peak areas (following a linear background subtraction routine), and the appropriate sensitivity factors.

The uncoated steel surfaces were examined by scanning electron microscopy to determine the effect of the acid wash treatment on surface topography.

3. Results

3.1. Effect of substrate pretreatment

Mild steel coupons were examined by XPS after grit blasting and following immersion in the acid solution for 2 or 10 min. The effect of heating in air at 240° C, the temperature employed prior to powder coating, was also studied. The quantitative surface analyses for this set of specimens are presented in Table I.

The morphology of the grit-blasted surfaces after heat treatment is shown in Fig. 1. Although somewhat similar at low magnifications, it is clear, from the higher magnification micrographs, that some metal dissolution has occurred during the phosphating process. This has the effect of reducing the surface roughness on a micro-scale (as seen in the SEM images), but has little effect on the macro-roughness as determined by surface profilometry.

3.2. The kinetics of cathodic disbondment

The extent of disbondment was recorded at the end of each test and is reported as the radius of the circular disbondment zone. The exposure times were chosen so that specimens large enough for XPS analysis could be cut from substrate and coating. The values of cathodic delamination recorded are listed in Table II. Following previous philosophy [1], an interfacial disbondment velocity, D_k, can be calculated, where

$$D_k = \frac{\text{disbondment radius}}{\text{disbondment time}} \times \tau \,\text{mm day}^{-1};$$

τ is a tortuosity related parameter, the ratio of interfacial path length to apparent length.

The use of this type of relationship in assessing coatings failure has been discussed [1] and a value of 0.40 ± 0.08 mm day^{-1} recorded for the epoxy/

TABLE II Kinetics of cathodic disbondment of the epoxy coating on acid-washed mild steel

Specimen code	Immersion time (min)	Length of test (day)	Radius of disbond (mm)	D_k
D14	2	90	6	0.313
D19	2	138	7	0.238
D24	10	203	9	0.208
D26	10	197	12	0.285

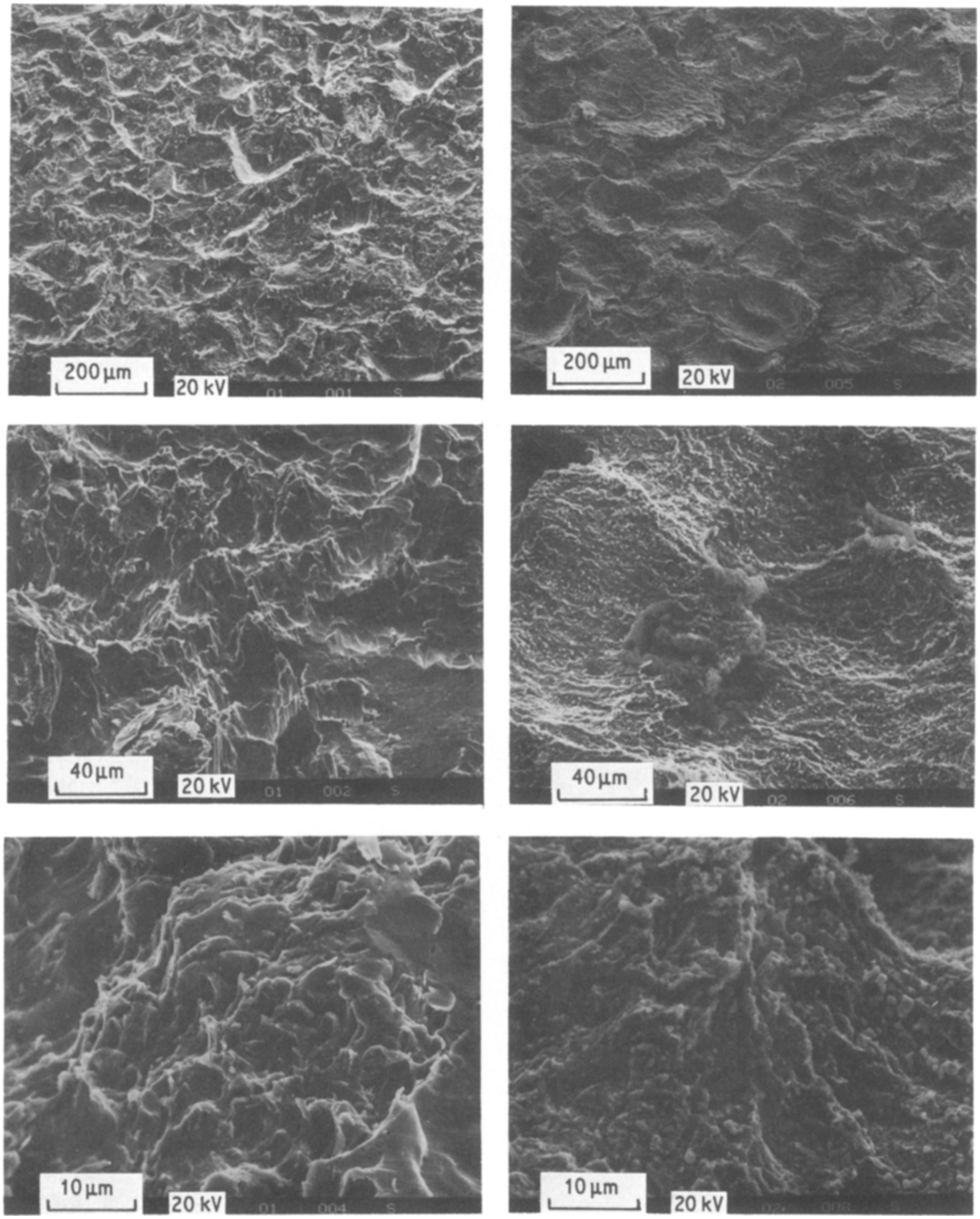

Figure 1 Scanning electron micrographs of the steel substrate following 30 min at 240° C in air. The left-hand set are for the bare steel, those on the right for steel which had received a 10 min phosphoric acid treatment.

mild steel system. The mean values of D_k for epoxy applied to grit-blasted steel immersed in 2% H_3PO_4 for 2 or 10 min are 0.275 and 0.246 mm day^{-1}, respectively, a reduction of 31% and 38% on the value recorded for untreated substrates.

3.3. Surface analysis of the failed interface

The elemental compositions of the specimens taken from both substrate and coating, following disbondment, are presented in Table III.

The high resolution carbon 1s spectra highlight

TABLE III Interfacial surface analyses of specimens taken from cathodic disbondment test panels

Specimen code	Interfacial surface	At.%							Fe/P
		C	O	Fe	N	Na	Cl	P*	
D14M1	Metal	42.3	47.7	2.0	1.5	4.5	0.4	1.7	1.18
D14P1	Polymer	59.3	32.1	1.1	1.3	5.7	0.1	0.4	2.75
D19M1	Metal	36.0	44.5	4.4	1.0	10.8	1.7	1.7	2.59
D19P1	Polymer	56.5	31.6	1.4	1.6	8.5	0.3	0.2	7.00
D24M1	Metal	47.7	40.5	3.9	2.8	4.2	0.3	0.5	7.80
D24P1	Polymer	61.7	30.4	0.9	3.0	3.7	0.1	0.2	4.50
D26M1	Metal	44.0	42.9	3.1	3.6	5.3	0.2	0.8	3.87
D26P1	Polymer	53.6	35.2	1.3	3.8	4.6	0.3	1.1	3.45

*As PO_4^{3-}.

important differences in substrate behaviour during the disbondment tests. Those panels which had received a 2 min acid wash show a minor component at 289.2 eV, characteristic of carbonate species [1]. As can be seen from the spectra of Fig. 2, for specimens taken from panels which had received a 10 min treatment, no such component is discernible in the XPS spectrum.

Nitrogen is consistently present in the analysis from both metal and polymer specimens. This may be nitrogen from the epoxy, but in our experience, corrosion specimens exposed to aerated solutions for long periods of time frequently exhibit nitrogen in the XPS spectrum. Furthermore, the level of nitrogen is, for the most part, higher than the 1.2% seen in an epoxide film detached from the surface.

A more reliable guide to the presence of epoxy residues on the metal surface can be seen in the curve fitting of the high-resolution oxygen 1s spectra. An example of such curve fitting is shown in Fig. 3. All the substrate O1s spectra can be treated in this manner to show the presence of a small amount of epoxy (generally around 10% of the O1s signal). In assignment of peaks of the O1s spectrum of Fig. 3 some ambiguity occurs in the component centred at 532.0 eV. This is most likely a convolution of an hydroxide component (531.8 eV) and a phosphate component; a binding energy of 532.2 eV has been reported for $FePO_4$

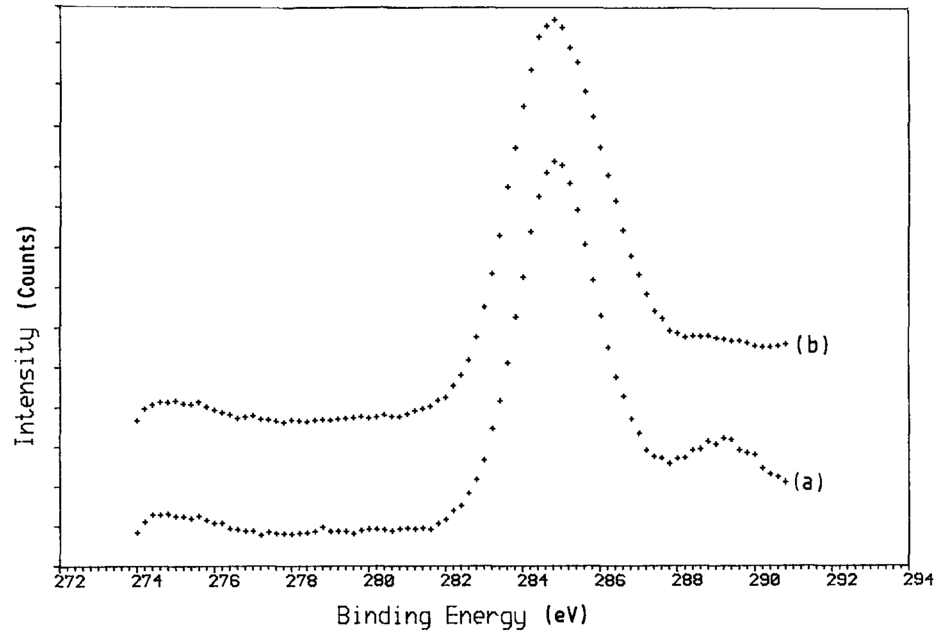

Figure 2 Substrate carbon 1s spectra from disbondment specimens. Phosphoric acid times were (a) 2 min, (b) 10 min. Note the presence of carbonate residues (at $\simeq$ 289.2 eV) on the 2 min specimen.

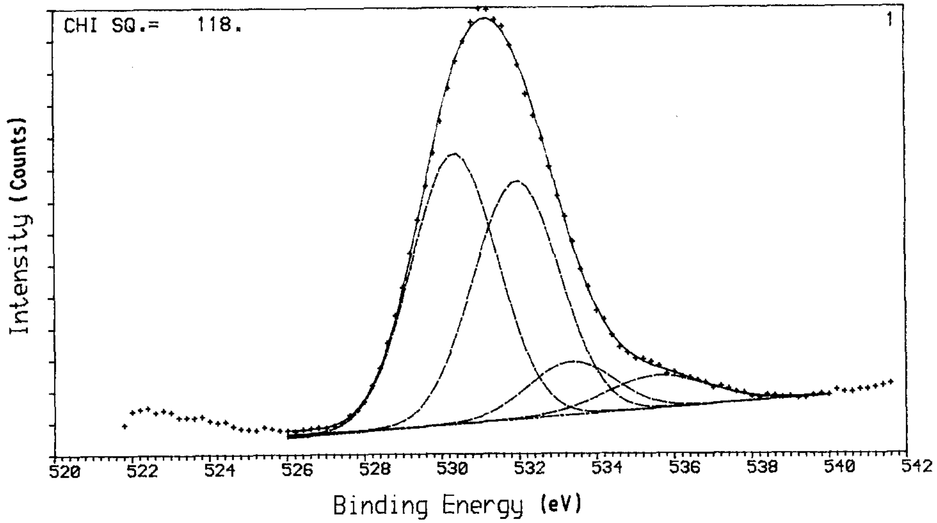

Figure 3 Curve fitting of a substrate oxygen 1s spectrum. Components are (left to right): oxide, hydroxide/phosphate, epoxy, sodium $KL_1L_{2,3}$ Auger transition.

[6]. For this reason it is unrealistic to comment on the relative contributions of oxide and hydroxide to each spectrum, but merely to say that all substrate spectra show a small contribution from epoxide residues.

4. Discussion

The surface analysis results for mild steel treated with an acid wash (Table I) do not show any marked difference between the 2 and 10 min immersion times, although both show a slight reduction in carbon and increase in oxygen when compared with the grit-blasted standard.

On heating, however, differences between the two immersion times become apparent. In the case of the shorter acid treatment, the iron concentration increases by some 40% while the phosphorus value is slightly reduced. The specimen which had received the longer acid treatment shows little change when compared with the unheated sample, the only difference being the expected reduction in adventitious carbon. The changes which occur on heating are best characterized by the Fe:P ratios of Table I. Initially, values of approximately 4 are recorded. On heating the 10 min specimen is little affected but the 2 min sample shows an Fe:P value of 8.1. These results indicate that the shorter immersion time gives incomplete coverage of the steel surface by a phosphate deposit. On heating, oxide growth is promoted which, in places, overgrows the iron phosphate deposit giving the increased level of iron in the analysis. The longer acid immersion affords more complete coverage of the substrate by the phosphate deposit and consequently little change is seen on heating – merely the removal of some of the loosely bound contaminant material.

Thus the Fe:P ratios of Table I present an empirical means of estimating the proportion of iron present as $FePO_4$. A value of about 4 indicates a large proportion of surface iron is present on the conversion coating. This situation exists for both specimens prior to heat treatment, and for the 10 min specimen after heating.

The XPS results point to the formation of an iron phosphate layer which may be overgrown by iron oxide, depending on the acid immersion time. The scanning electron micrographs (Fig. 1) show that metal dissolution has occurred during the phosphating process. This is in marked contrast to a commercial Fe/Zn phosphating treatment which leads to the precipitation of acicular hoepite ($Zn_3(PO_4)_2 \cdot 4H_2O$) crystals, readily apparent in the SEM [7]. In terms of coating/substrate interaction such metal dissolution may be expected to lead to a reduced interfacial path length (τ). These effects, however, are not reflected in surface profilometry measurements, thus in terms of the D_k philosophy the two surfaces can be treated in a similar manner.

The disbondment velocity is clearly reduced by acid pre-treatment of the substrate. Although cathodic disbondment tests give results which generally fall into a wide scatter band, it is

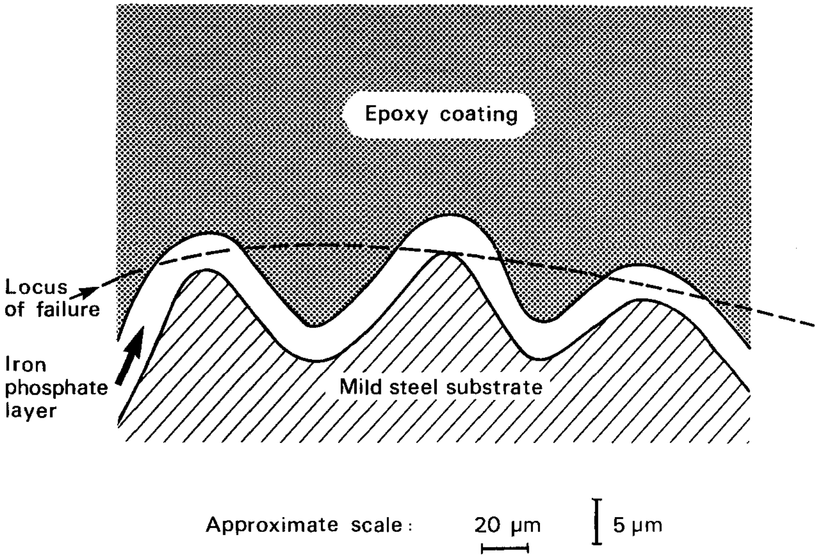

Figure 4 Schematic representation of failure mode for the epoxy applied to a phosphated steel stubstrate. The thickness of the phosphate layer is exaggerated for clarity.

apparent that the longer immersion time gives a greater reduction in the disbondment velocity, D_k.

The interfacial analyses of Table III provide a means of assessing the manner in which this failure has occurred. As we have observed in previous work [1, 8] cathodic disbondment from bare steel substrates leads to underfilm alkaline conditions, reflected in the excess of sodium to chloride ions in the surface analysis. The situation is unchanged when a phosphated substrate is employed, all the analyses of Table III show a large excess of sodium to chlorine.

The Fe:P ratio of the interfacial surfaces for the 10 min specimens is close to 4:1 (Table III). As has been indicated above, this shows that the exposed surface is mainly iron phosphate – detachment or loss of the phosphate material would have increased the iron relative to phosphorus and this is seen on one specimen (D24M1). On the other hand, concentrations of both elements are depressed within the total analysis, suggesting the phosphate layer is partially covered by epoxide and the analysis of the O1s spectra confirms this. Thus the locus of failure for these specimens passes from within the polymer to within the phosphate layer, sometimes removing the phosphate deposit entirely. This regime of failure is shown schematically in Fig. 4. This failure mode is in marked contrast to the mainly adhesive failure observed for the bare steel substrate [1]. It is similar to that proposed by Gettings *et al.* [9] for a dry epoxy/mild steel adhesive joint. These workers showed that fracture occurred in both the epoxy and iron oxide, the locus of failure passing from one zone to the other at random. In the presence of an aqueous environment adhesive failure of these joints was reported.

The analyses from the 2 min specimens show rather different relative concentrations of iron and phosphorus. One polymer surface shows a large excess of iron as a result of a large proportion of oxide in the locus of failure. The other specimens all show an excess of phosphate species. It is proposed that the high underfilm pH (probably of around 13) results in dissolution of some of the phosphate deposit which is then precipitated on the exposed oxide. It has been shown, both by electron microscopy and traditional analytical techniques, that a commercial phosphate deposit is attacked by alkaline solution [7].

5. Conclusions

The application of a dilute phosphoric acid wash treatment to mild steel leads to the formation of an iron phosphate layer at both 2 and 10 min immersion times. On heating there is little change in the surface composition for the longer treatment. The shorter immersion time specimen shows an increase in iron together with a reduction in phosphorus; results consistent with the overgrowth of the phosphate layer by an iron oxide. Thus the immersion time is crucial for the formation of a uniform substrate surface to which the coating can then be applied.

The cathodic delamination of a fusion-bonded epoxy from such a surface shows a complex, mixed-mode failure as illustrated in Fig. 4. The locus of failure passes, at random, between cohesive failure of the polymer and phosphate layer, sometimes separating the phosphate from the substrate completely. The rate at which this type of failure proceeds, when assessed by an interfacial disbondment velocity, is 40% less than the value recorded for the epoxy/bare steel system.

If the phosphate coverage is incomplete, as for example with the 2 min wash, analysis of the failure mode is complicated by dissolution of the phosphate. The rate of delamination is still considerably slower than for the untreated steel.

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