

# Surface analysis of polysiloxane/metal oxide interfaces

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The interfaces between various types of silane-based primers and abraded mild-steel surfaces have been investigated using two surface-specific techniques in an attempt to ascertain the bonding mechanism between primer and metal. The XPS technique gave semi-quantitative information about the relative concentrations of primer and exposed steel while the SSIMS technique enabled the chemical state of the first few monolayers of surface to be elucidated. From some primer/metal systems the presence of  $\text{FeSiO}^+$  radicals was detected by SSIMS and it was found that the environmental resistance of structural adhesive joints, employing the various silane-based primers, could be directly related to the presence or absence of this radical.

## 1. Introduction

A serious limitation frequently encountered in the use of structural adhesives is the adverse effect moisture may have upon the strength of an adhesively bonded component [1, 2]. Further, it has been argued on a thermodynamic basis that if only secondary forces are acting across an adhesive-metal substrate interface water will virtually always desorb an organic adhesive from a metal oxide surface. Thus, either water must be prevented from reaching the interface in sufficient concentration to displace the adhesive or stronger primary interfacial forces must be forged which are resistant to water.

However, it has recently been demonstrated that the environmental resistance of joints consisting of aluminium alloy and mild-steel substrates, bonded with a simple epoxide adhesive, may be considerably increased by applying a silane-based primer to the substrate surface prior to joint formation [1, 2]. Previous work [3] has shown that silane primer films are usually polymeric and essentially composed of a polysiloxane network but there has been no direct evidence as to the type of bonding between the polysiloxane and metallic substrate, i.e. whether the polysiloxane is attached

to the substrate by some form of primary chemical bond. The purpose of the present work was therefore to determine the type of bonding between different silane-based primers and a mild-steel substrate and attempt to correlate this with the durability of joints.

Two surface-specific techniques have been used: X-ray photoelectron spectroscopy (XPS) [4] and static secondary ion mass spectroscopy (SSIMS) [5]. The XPS technique yields information on the elemental composition of the top 20 to 40 Å of a surface and on the chemical binding states of the principal components of the surface. The concentrations of the various elements existing at a surface can be estimated to  $\pm 20\%$  while variations in the binding energy of the emitted photoelectron can be equated to variations in the valence band of the atom caused by chemical effects. With SSIMS, ionized particles ejected from the surface by the action of an argon beam are mass analysed. As the current densities used in SSIMS are low ( $\sim 10^{-10} \text{ A cm}^{-2}$ ) the first one or two monolayers of the surface can be investigated. Either atoms or molecules can be ionized and thus details about the chemical state of atoms in a surface can be inferred.

## 2. Experimental

### 2.1. Sample preparation

#### 2.1.1. Joint durability studies

The epoxide adhesive employed was a diglycidyl ether of bisphenol A crosslinked with 9.4 wt % of a tertiary amine curing agent (tri-2-ethyl hexanoate of 2, 4, 6-tris (dimethylamino-methyl) phenol).

The substrate was mild steel to specification BS9, EN3B and was in the form of cubes, of side 2.54 cm. The surfaces to be bonded were always first subjected to a liquid and vapour degreasing bath of trichloroethane, grit-blasted with 180 to 220 mesh alumina, degreased again and finally allowed to air-dry. The surfaces were then subjected to one of the treatments listed in Table I. Adhesive was spread on the treated faces and the two blocks were pressed lightly together to form a coaxial butt joint. Small lengths of copper wire, previously inserted in the adhesive near the centre of the joint, were employed to control the adhesive layer thickness to  $0.50 \pm 0.06$  mm. To effect cure of the adhesive, the joint was held at 23°C for 96 h, followed by 1.25 h at 100°C and finally 2.5 h at 180°C, and then allowed to cool slowly.

After assembly, the joints were immersed in water at 60°C and removed at intervals of 0, 500 and 1500 h. They were then kept at 20°C, 55% r.h. for about 30 min, and finally fracture in tension at 20°C and a strain rate of  $6.67 \times 10^{-3} \text{ sec}^{-1}$ .

#### 2.1.2. Surface analysis studies

For the surface analysis studies mild-steel subs, 3.7 mm in diameter and 8 mm long, were cleaned as described above and surface-treated on the end faces, as indicated in Table I. However, previous work [6] had shown that to obtain polymerization of the silane primers outside of the joint environment, addition of a small amount of the amine

curing agent was required. Therefore, typically an amount of amine, equal to that the silane, was added to the primer solution for these surface analysis experiments.

### 2.2. The analysis system

The XPS/SSIMS system has been described in detail elsewhere [7, 8] and only the salient points of each technique will be discussed here. In XPS, photoelectrons generated by X-ray photons of energy 1486.6 eV ( $\text{AlK}\alpha$ ) from a spot  $\sim 2.5$  mm diameter are energy-analysed in a double pass cylindrical mirror analyser having pre-retardation grids. The XPS technique lends itself to a quantification of the elements existing near the surface since the number of photoelectrons detected in a certain peak from a particular element is directly proportional to the concentration of that element existing in the surface. However, errors in determining the constant of proportionality result in a total error of about  $\pm 20\%$  in the estimates of concentration of elements.

Both the XPS and the SSIMS equipment were housed in one UHV chamber and by rotating the sample through 60° "static" SIMS could be performed. In this technique a 3 keV Argon ion beam irradiates an elliptical area 4 mm  $\times$  3 mm and current densities are kept small ( $\sim 10^{-10} \text{ A cm}^{-2}$ ) so that the first one or two monolayers can be investigated. Positive and negative ions are mass analysed in a modified residual gas analyser and masses up to 511 atoms mass unit (amu) were detectable. However, while problems of quantification are difficult for XPS, they are almost unsurmountable for SSIMS. Secondary ion yields from an element bear little relation to the concentration of that element at the surface, thus this technique is used here in a purely qualitative manner.

TABLE I Substrate surface treatments

Chemical Type	Code in Text	Method of Application
None (i.e. degreasing and grit-blasting only)	—	—
$\gamma$ -glycidoxypropyltrimethoxy silane	A	Brush-coated using 1 vol % aqueous soln.
A styrene-functional amine hydrochloride silane	B	Brush-coated using 10 vol % methanol soln.
$\gamma$ -aminopropyltriethoxy silane	C	Brush-coated using (i) 10 vol % aqueous soln. (ii) 1 vol % (iii) 0.01 vol %

TABLE II Concentrations of the elements found on variously primed surfaces (estimated error  $\pm 20\%$ )

Primer	Element (at. %)							
	Fe	O	C	Al	Si	Cr	Ni	Cl
1% Primer A	4.2	32.0	47.0	—	16.8	—	—	—
10% Primer B	1.6	28.3	49.8	2.1	11.4	—	6.8	—
10% Primer C	3.9	15.2	68.6	—	4.0	—	5.8	2.5
1% Primer C	17.4	41.4	23.3	12.2	3.7	—	2.0	—
0.01% Primer C	14.5	48.3	23.0	14.2	—	—	—	—
Mild-Steel Ref.	9.9	53.2	29.1	6.2	—	1.6	—	—

TABLE III Binding energies (eV) of principal elements found on the variously primed surfaces. The figures in brackets represent the energy positions of shoulders observed on the Fe  $2p$  peak

Sample	Fe $2p_{3/2}$	O1s	Cl1s	Si2s	Al2s
1% A	711.3	531.9	284.7	153.4	—
10% B	708.1	532.4	285.4	154.4	—
10% C	709.6	532.1	285.1	154.6	—
1% C	707.1 (710.3)	530.6	285.1	154.6	121.2
0.01% C	707.1 (710.3)	530.6	285.6	—	—
Mild-Steel Ref.	709.3	530.4	285.4	—	120.0

### 3. Results

#### 3.1. XPS analysis

Six samples (five primed and one unprimed mild-steel reference sample) were analysed using XPS and SSIMS. The results from the XPS analysis are shown in Table II and III. In Table II concentrations have been calculated for elements detected near the surface while Table III contains the binding energies of the principal photoelectron peaks of the elements.

Silicon was not detected on the mild-steel reference sample but was found on all the silane primed surfaces except for the 0.01% primer C surface. However, the binding energies for the Si2s peak are different for the different silanes indicating different chemical states in each primer.

Iron was present on all the primed surfaces indicating incomplete coverage by the silane primer. Further, the chemical state of the iron varied considerably for the different surfaces, as is evident from the wide variations in binding energy of the iron  $2p_{3/2}$  peak. For the 1% and 0.01% concentrations of primer C, the iron is almost in the pure elemental form ( $\sim 706.5$  eV) while for the 1% primer A sample the iron is heavily oxidized.

The binding energy position of the Cls photoelectron peak was the same for the carbon present on the reference and primed samples but the full width half-maximum of the Cls peak found on the

primed samples was much greater than that for the mild-steel reference sample (5 eV cf 2.4 eV). While some peak broadening would be expected due to the electrical insulating nature of the primed surface, it is thought that the majority of the broadening can be attributed to the existence of carbon species whose photoelectron peaks are unresolved.

The presence of aluminium must be due to alumina particles embedded in the metal surface during the grit-blasting process.

#### 3.2. SSIMS analysis

It is evident from Fig. 1 that the surface of the mild-steel reference sample contains traces of many elements such as  $N^{++}$ ,  $Ti^+$ ,  $Cr^+$ ,  $Si^+$ ,  $Mn^+$  and  $Cu^+$ . These elements exist as traces on the surface (probably about  $10^{-3}$  to  $10^{-5}$  at. %) as removal of the first few Å by ion-bombardment using 2 keV Ar ions dramatically reduced the trace metal ion yields. The  $Al^+$  and its associated oxide radicals were attributable to the presence of alumina particles embedded in the surface of the mild steel as a result of the grit-blasting step in the cleaning process.

Comparing Fig. 1 and 2 it is obvious that the level of Si and its oxides is higher on the 1% primer A coated sample than on the reference sample. While such radicals as  $SiO_2H^-$ ,  $SiOH^+$ ,  $SiO_2^-$  may be attributed to the polysiloxane primer the radical

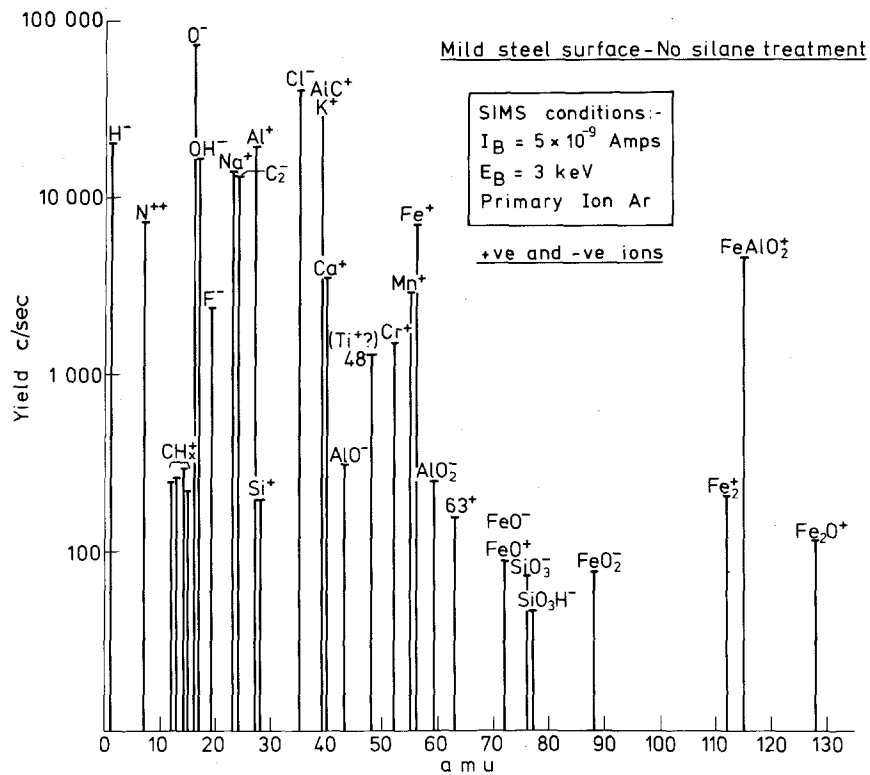


Figure 1 Positive and negative SSIMS spectrum from a mild-steel reference samples cleaned as described in text.

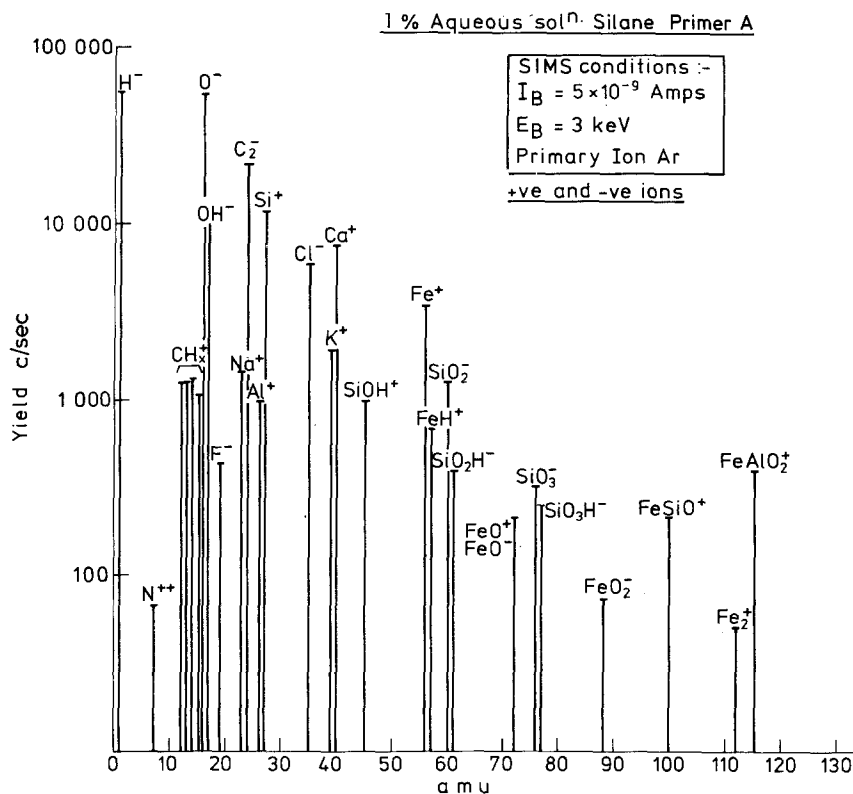


Figure 2 Positive and negative SSIMS spectrum from a mild-steel sample covered with 1% Primer A.

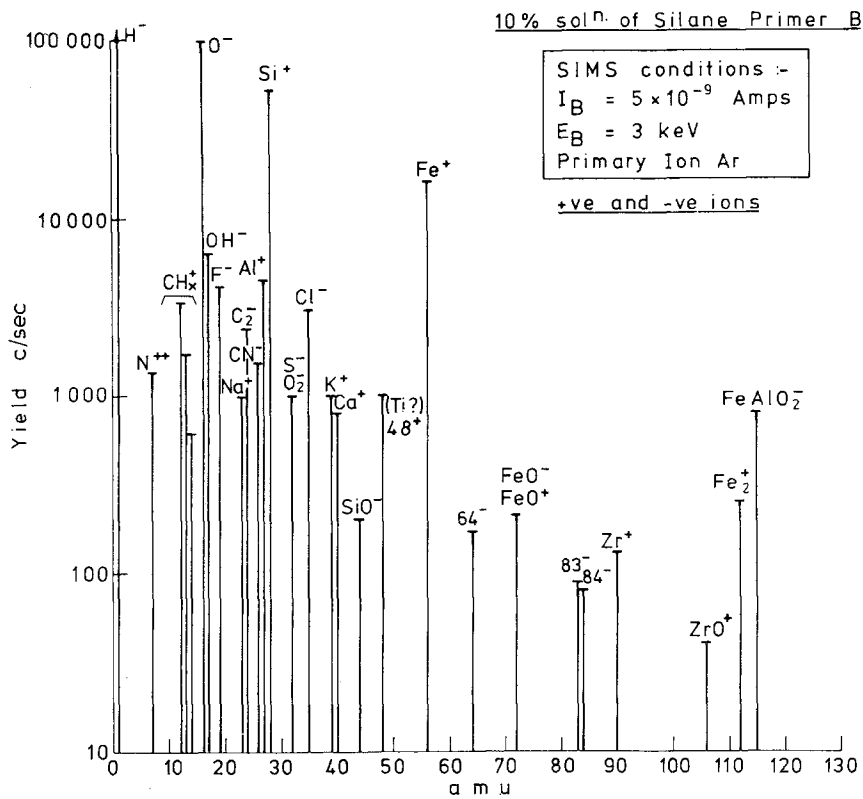


Figure 3 Positive and negative SSIMS spectrum from a mild-steel sample covered with 10% Primer B.

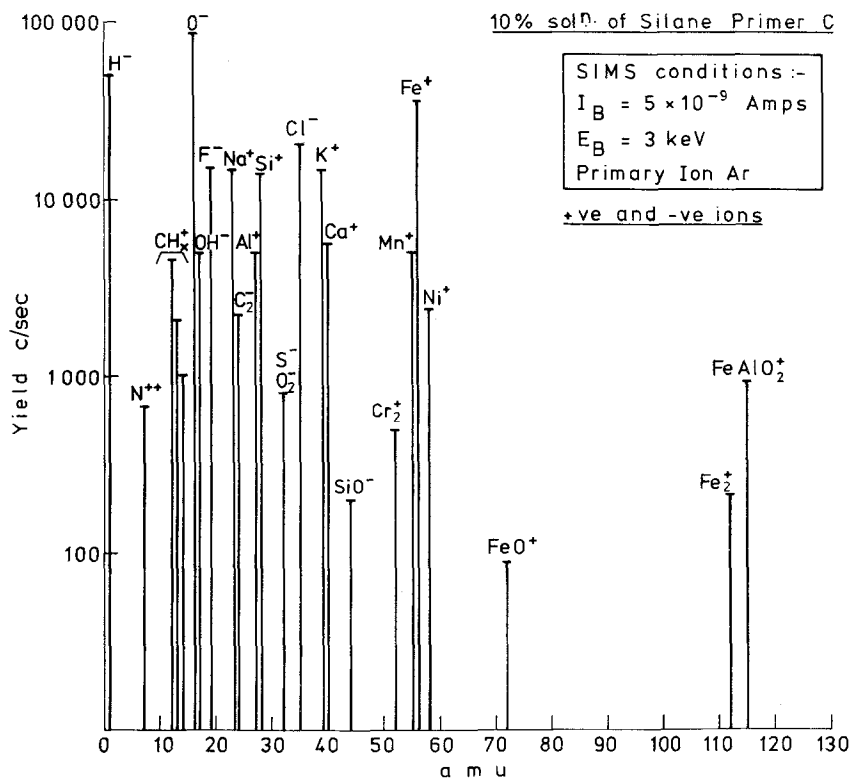


Figure 4 Positive and negative SSIMS spectrum from a mild-steel sample covered with 10% Primer C.

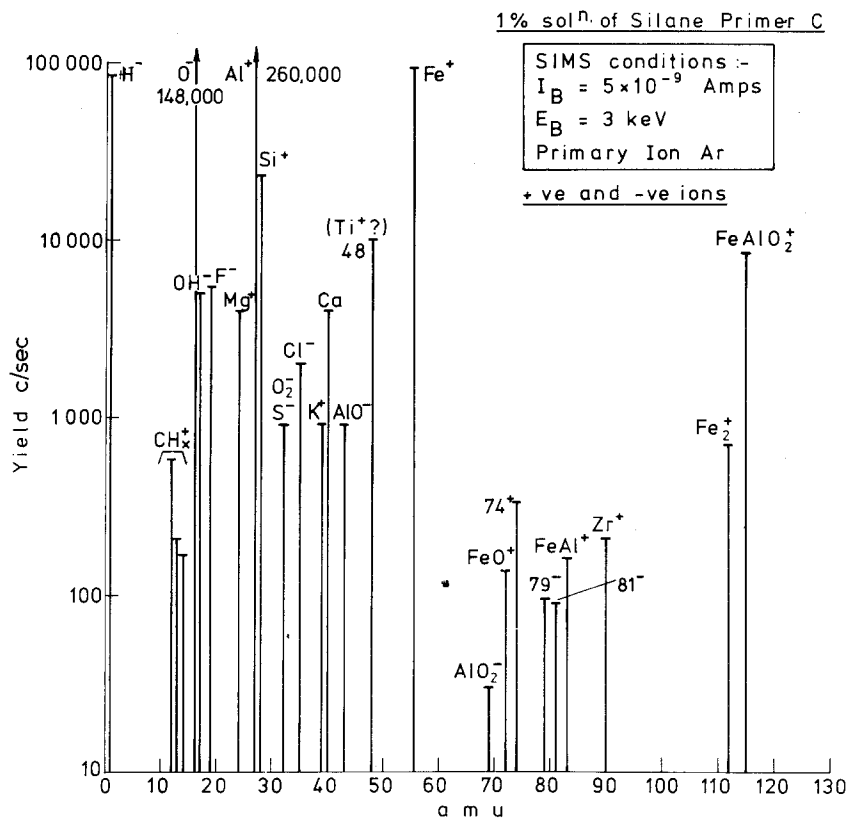


Figure 5 Positive and negative SSIMS spectrum from a mild-steel sample covered with 1% Primer C.

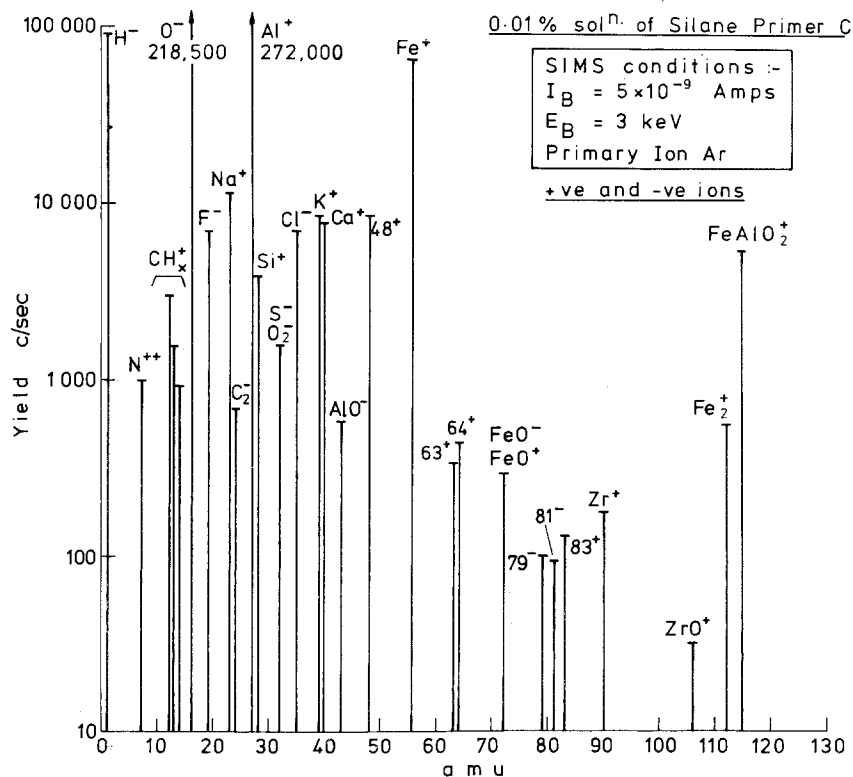


Figure 6 Positive and negative SSIMS spectrum from a mild-steel sample covered with 0.01% Primer C.

$\text{FeSiO}^+$  must be associated with the interaction of the iron oxide surface with the polysiloxane primer.

For the 10% primer B sample, the results shown in Fig. 3 reveal the presence of a high  $\text{Si}^+$  radical (11.4% Si was detected using XPS) but virtually no silicon-oxygen radicals despite the high yield of  $\text{O}^-$  ions detected. Also no  $\text{FeSiO}^+$  radicals were detected.

Surfaces treated with primer C (Fig. 4, 5 and 6) exhibited similar behaviour upon examination by SSIMS to primer B in that although silicon levels were high on both the 10% and 1% primer C samples, little evidence was available for the existence of silicon oxides at the surface and no  $\text{FeSiO}^+$  radical was detected. It is obvious from the high yields of  $\text{Al}^+$  and  $\text{Fe}^+$  that the 1% and 0.01% primer C solutions had not completely covered the substrate surfaces.

### 3.3. Durability studies

The effect of water immersion on the strength of various joints is shown in Figs. 7 and 8. A significant improvement in joint durability was only achieved by the application of a 1% aqueous solution of primer A to the substrate surface prior to bonding. Primer B resulted in joints possessing both low initial strengths and poor environmental resistance and none of the concentrations of primer C employed resulted in significant increased joint durability.

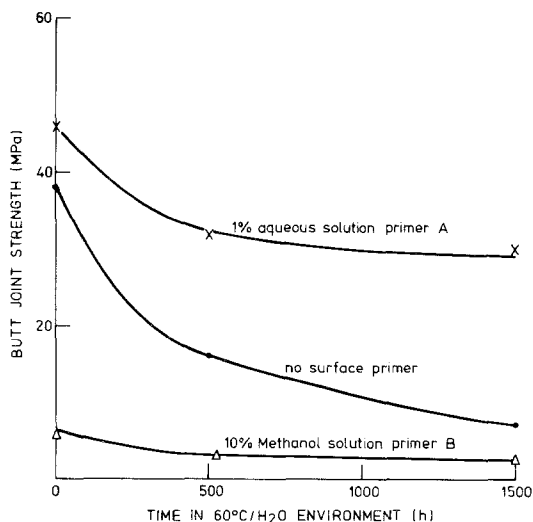


Figure 7 Results of durability study comparing strengths of unprimed joint to those primed with 1% Primer A and 10% Primer B as a function of time in a water environment.

## 4. Discussion and conclusions

From XPS analysis differences were found in the concentration of silicon present on the various primed surfaces. For the 1% primer A surface a concentration of 17% was found; the value calculated assuming complete coverage by polymerized primer was 16%. Thus, the polysiloxane derived from primer A probably exists as a uniform or almost uniform film over the mild-steel surface. A similar value (i.e. approx. 16%) would be expected if polymerized primer C covered the whole surface but the low concentration of the element detected indicated incomplete coverage. This may arise from lack of polymerization since if polymerization does not occur, it has been found [6] that the low molecular weight primer monomer is readily desorbed in the UHV environment. As the exact structure of primer B is unknown, the 11% of silicon detected may be from either a polymeric or monomeric species.

Both the XPS and SSIMS also revealed other differences between primer A (which exhibited relatively high joint strengths after water immersion) and primers B and C (which showed poor joint durability). The main difference found by XPS between the good primer (1% primer A) and the others was in the shifts observed in the binding energy of the iron  $2p_{3/2}$  photoelectron peak. For the 1% primer A coated surface a binding energy of 711.3 eV was observed which is 4.8 eV from the ascribed pure metal position (706.5 eV). This compares to shifts of 1.6 eV and 3.1 eV for 10% primer B and 10% primer C. For these two latter

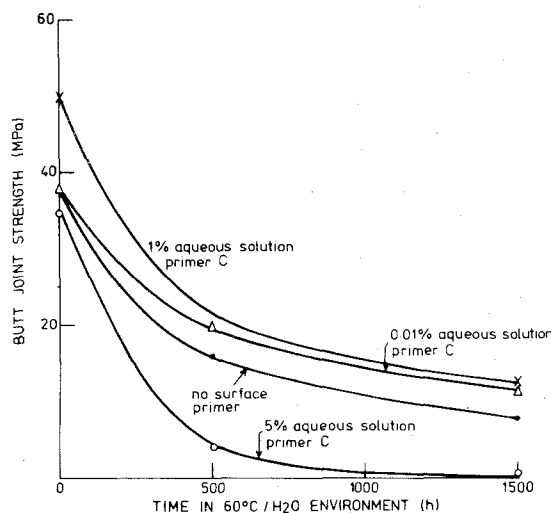


Figure 8 Comparison of strengths of unprimed joints with joints primed with various concentrations of Primer C.

cases the shifts can be ascribed to the formation of different types of the iron oxides. However, a shift of 4.8 eV is too large to be due to iron oxide formation and must be due to a more complex bonding possibly between silicon, iron and oxygen.

The SSIMS data revealed more differences between primer A and primers B and C. The most striking difference was the presence of  $\text{SiO}_2\text{H}^-$  and  $\text{SiO}_2^-$  radicals on primer A surfaces but the absence of such silicon-oxygen radicals on primer B and C surfaces, despite the presence of strong  $\text{Si}^+$  and  $\text{O}^-$  signals. A possible explanation is that only with primer A has polymerization occurred to a give polysiloxane structure on the metal substrate surface and these radicals arise from the polysiloxane.

A further difference revealed by the SSIMS analysis is the detection of  $\text{FeSiO}^+$  radicals from the primer A coated surface. This is strong direct evidence for the formation of a chemical bond, probably  $-\text{Fe}-\text{O}-\text{Si} \equiv$  between the metal oxide and polysiloxane primer. No such radicals were detected from primer B or C coated surfaces and, indeed, for these primer/metal oxide interfaces there was no evidence whatsoever of any chemical bonding between the primer and oxide. Thus only for the silane primer which results in improved joint durability is there any evidence for chemical,

rather than purely secondary, bonding between the primer and metal oxide.

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