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ESCA study on the destruction mechanism of metal–resin adhesion due to water penetrating through the resin

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The mechanism destroying the adhesion between PMMA and mild steel, and the action of water molecules reaching the adhesion interface was investigated. Mild steel and a thin PMMA film were bonded with dental adhesive (4-META resin). After immersion in water, the adhesive layer was peeled from the metal surface. The surface was analysed by ESCA, reflection electron diffraction, and X-ray diffraction to elucidate changes in surface structure. After 2 weeks immersion, there was a very thin brown product and after 2 months a thick black corrosion product composed of Fe_3O_4 formed at the adhesion interface. The thin brown layer showed no X-ray diffraction pattern but reflection electron diffraction showed it to be FeO(OH). After 3 days immersion, the mild steel surface appeared unchanged through the clear resin layer, and ESCA analysis showed the same chemical state as the surface of the specimen immersed for 2 weeks. Destruction of adhesion between metal and adhesive is caused by destruction of the chemical bond by the water molecules permeating through the resin layer. It is followed by corrosion of mild steel which produced iron oxide hydrate.

1. Introduction

Generally, joints of dental adhesive resin bonded to dental alloys weaken in wet environments, though adhesion is strong in dry environments. There have been some reports discussing the mechanism of degradation at the adhesion interface [1–7]. We have reported that in specimens bonding a polymethyl methacrylate (PMMA) film with a dental adhesive resin to mild steel, water enters the interface by diffusion through the resin rather than by passage along the interface [8]. Adhesion at the interface is destroyed when the water content at the interface reaches 48% of the equilibrium water concentration of PMMA. Observation through the transparent resin film showed no change in the mild steel surface at 48% equilibrium water concentration. At 93% water content, many small white spots appeared on the surface, and the surface colour further changed to brown and black [8].

The present study clarifies how the surface chemical state changes with water immersion. The changes in chemical states of the mild steel surface at the adhesion interface of the PMMA film bonded with 4-methacryloxy ethyl trimellitate anhydride (4-META) resin were studied by analytical methods, including electron spectroscopy for chemical analysis (ESCA), reflection electron diffraction, and X-ray diffraction (XRD).

2. Materials and methods

2.1. X-ray and reflection electron diffraction

A 0.2 mm thick PMMA film was bonded with 0.05 mm thick adhesive resin containing 4-META [9] on the 18 mm × 18 mm metallographically polished mild steel plate. The bonded specimens were stored in a dry chamber at 37 °C for 24 h and then immersed in 37 °C distilled water until corrosion products were observed on the mild steel surface through the transparent resin layer. Identification of the corrosion products at the adhesion interface was carried out by X-ray diffraction with a diffractometer under FeK_α radiation with a manganese filter, 35 kV tube voltage, and 20 mA current.

Products on the specimen exhibiting no diffraction pattern in the X-ray diffraction were identified using reflection high-energy electron diffraction patterns which were taken using an electron microscope with an accelerating voltage of 100 kV.

2.2. ESCA analysis

Mild steel was soldered on an ESCA (Shimadzu ESCA-850) 18-8 stainless steel specimen holder. The mild steel surface was polished metallographically and a 0.2 mm thick PMMA film was bonded to the mild steel with 0.05 mm thick 4-META resin. After storage for 24 h in a dry atmosphere at 37 °C, the specimen was immersed in distilled water for 3 or 4 days. The specimen was formed by bonding the PMMA block on the PMMA film, as shown in Fig. 1 in order to create a large thermal stress at the interface. The specimen was then sealed in a quartz glass tube filled with ultra-high purity argon gas (purity 99.999%; oxygen content < 0.2 p.p.m; dew point below $-70\,^{\circ}\mathrm{C}$), and the specimen in the quartz tube was subjected to thermal shock with thermal cycles from liquid nitrogen ($-196\,^{\circ}\mathrm{C}$) to $40\,^{\circ}\mathrm{C}$ water to separate the resin layer from the mild steel surface. After the thermal shocks, the quartz glasss tube was broken in a polyethylene chamber which was attached to the ESCA specimen chamber, filled with ultra-high purity argon gas. The ESCA specimen was introduced into the specimen chamber without exposure to air, and ESCA measurements were performed with $\mathrm{Mg}K_{\alpha}$ radiation (1253.6 eV) at 2×10^{-6} Pa maintained by a turbo-molecular pump. The specimen surface was subjected to argon-ion etching at 2 kV and 20 mA under a pressure of 5×10^{-4} Pa in the spectrometer. The etching rate was $0.1\ \mathrm{nm\,s^{-1}}$ on pure silver under these conditions. The measurements and the argon-ion etching were performed alternately to determine both the amounts and chemical states of the elements with depth. The amounts of the elements were calculated by considering only the photoelectron cross-section.

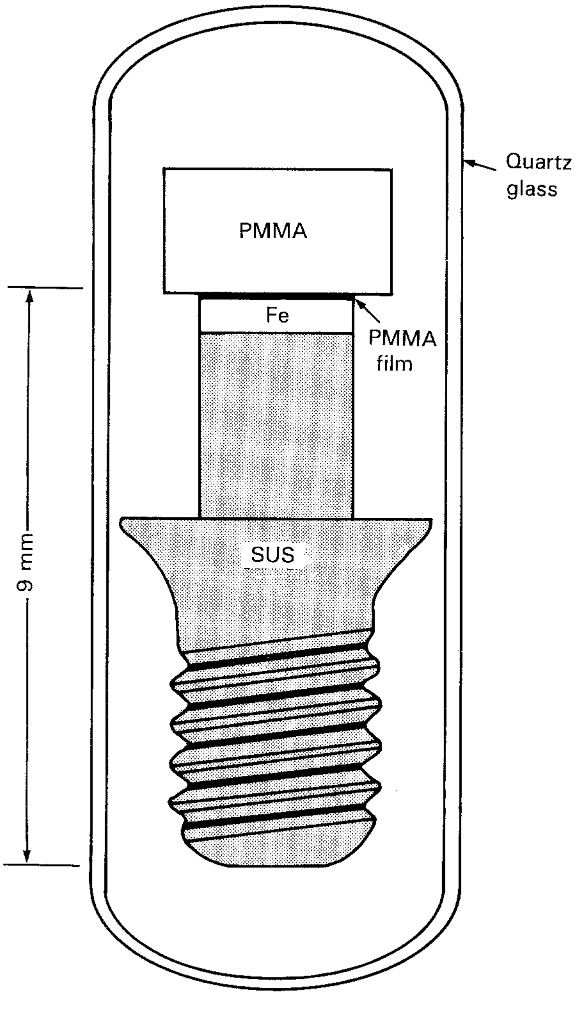

Figure 1 ESCA specimen with soldered mild steel sealed in quartz glass tube filled with ultra-high purity argon gas.

3. Results

3.1. X-ray and reflection electron diffraction

Fig. 2a shows XRD patterns of the slightly brown surface of the specimen immersed in water for 2 weeks and Fig. 2b is the diffraction pattern of the black surface found after 2 months immersion. Diffraction pattern (a) shows only the iron structure, while (b) shows a mixture of iron and Fe_3O_4.

Fig. 3 shows the reflection high energy electron diffraction pattern obtained from the surface of the 2 week specimen. In Table I, the observed lattice spacings and intensities of the diffraction pattern are shown and compared with the data for iron and iron oxide hydrate, FeO(OH). The diffraction from iron shows a ring pattern and that from FeO(OH) has a spotty pattern.

3.2. ESCA analysis

Fig. 4 shows the very similar Fe $2p_{3/2}$ spectra obtained after 3 days (a) and 2 weeks (b) water immersion. Spectrum (c) was obtained from the 2 week immersed specimen after 100×60 s argon-ion etching in the ESCA spectrometer, showing an almost pure iron state. As the surface state of the 2 week specimen was identified as iron oxide hydrate, the same chemical state may be assumed after 3 days immersion. Fig.5 shows the changes in concentrations (at %) of iron, oxygen and carbon with depth, for the specimens immersed for 3 and 4 days. The carbon concentration of the 3 day specimen is higher than after 4 days of immersion, while the oxygen concentration is lower in the 3 day specimen.

Fig. 6 shows the Fe $2p_{3/2}$ spectra obtained at different depths after 3 and 4 days water immersion with varying argon-ion etching times. The peak at 707.2 eV is metallic iron, and the peak and shoulder at 710.0 and 711.2 eV indicate oxidation states. The spectra show a mixture of metallic and oxidation states. To obtain the fraction of oxidation states, the spectrum of the oxidation states was graphically separated from the measured spectrum, and the results are shown in Fig. 7. The amount of oxidation state after 4 days immersion is higher than after 3 days.

4. Discussion

The bond strength of the adhesive joints is strongly influenced by water and humidity in the environment [1]. There are many investigations of industrial applications on degradation due to moisture intrusion into bonded joints: after exposure to water, the fracture path is exactly along the adhesive–metal oxide interface, and there is a considerable increases in the iron oxide thickness [2]. For aluminium, moisture intrusion at the bond line causes the oxide to convert to hydroxide with an accompanying change in morphology and bond strength [1, 3]. The durability in wet environments, such as the oral cavity, is also of prime importance in bonding dental adhesive materials to teeth and dental alloys.

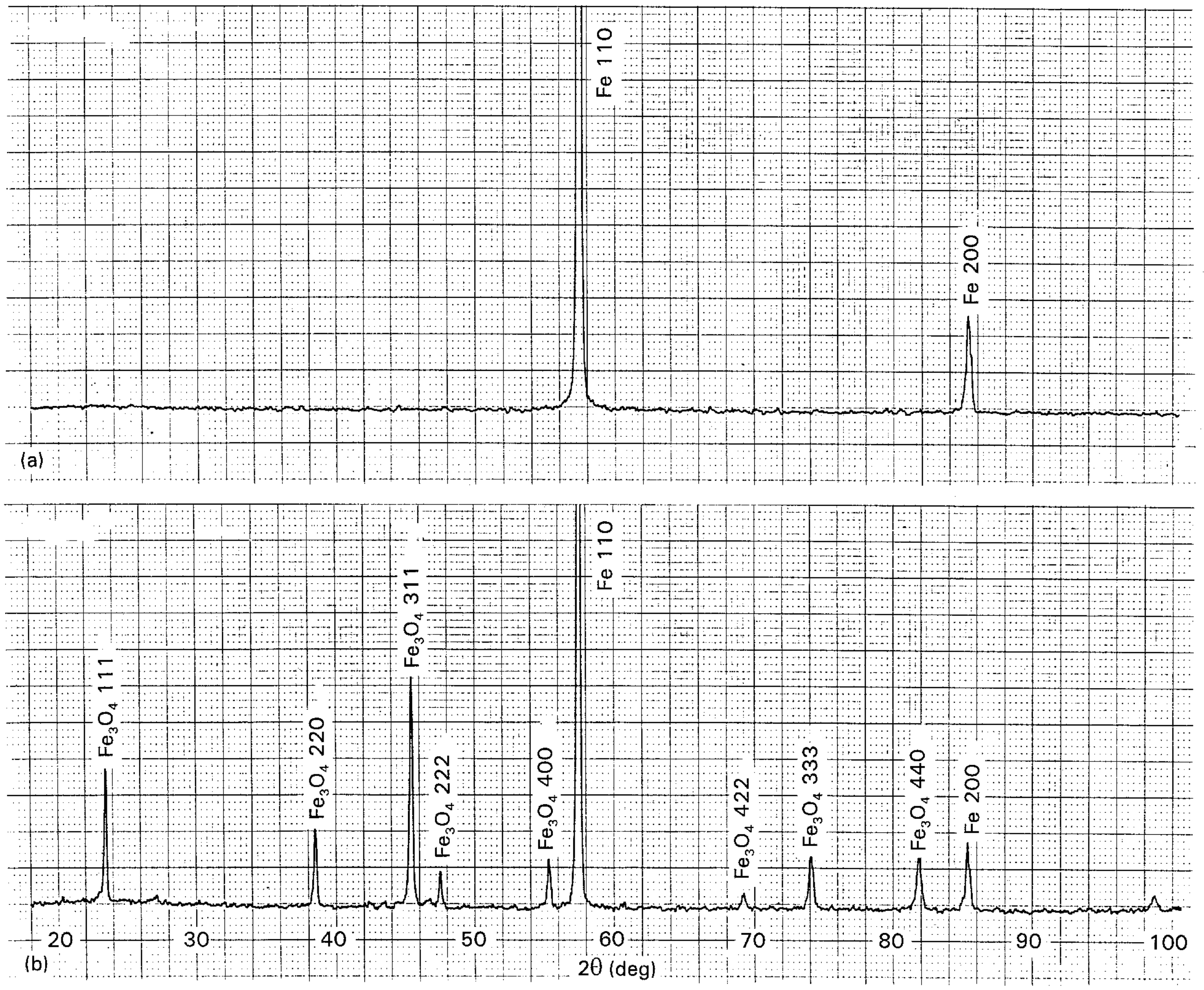

Figure 2 X-ray diffraction patterns obtained from the water immersed specimens for (a) 2 weeks and (b) 2 months.

TABLE I Observed lattice spacings and intensities with JCPDS data for ion and lepidocrocite obtained from the 2 week water immersed specimen

Observed values	Reference substances						
	Iron(α)				FeO(OH)		
d (nm)	I	d (nm)	I/I_1	hkl	d (nm)	I/I_1	hkl
	–[a]				0.626	100	020
	–[a]				0.329	90	120
0.268	[b]				0.279	10	011
0.252	[b]				0.247	80	031
0.228	[b]				0.236	20	111
0.201	vs	2.027	100	110			
0.143	m	1.433	20	200			
0.116	s	1.170	30	211			
0.101	w	1.013	10	220			
0.090	m	0.906	12	310			
0.082	vw	0.828	6	222			

[a] Not observed.
[b] Spotty.

It has been established that the water molecules reach the adhesion interface by diffusion through the resin layer rather than by passage along the interface [4, 8, 9]. The destruction of adhesion depends on the velocity of water diffusion [1, 6, 7]. The water content at the interface has been calculated from Fick's second equation by Ohno *et al.* [8]: the interface is destroyed by water when the water content at the interface reaches 48% of the equilibrium water concentration of PMMA.

Observations through the transparent resin layer of the adhesion interface on mild steel showed no surface changes with 48% water content. The chemical state at the adhesion interface could not be determined

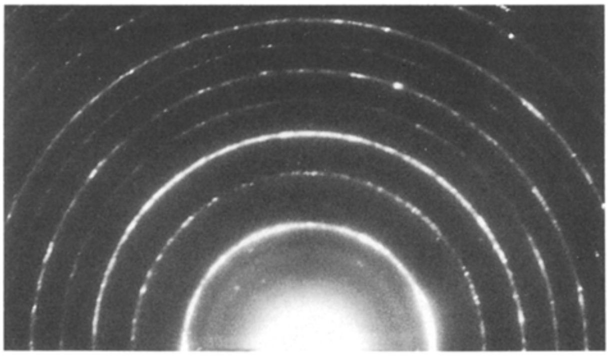

Figure 3 Reflection high-energy electron diffraction pattern obtained from the 2 week specimen.

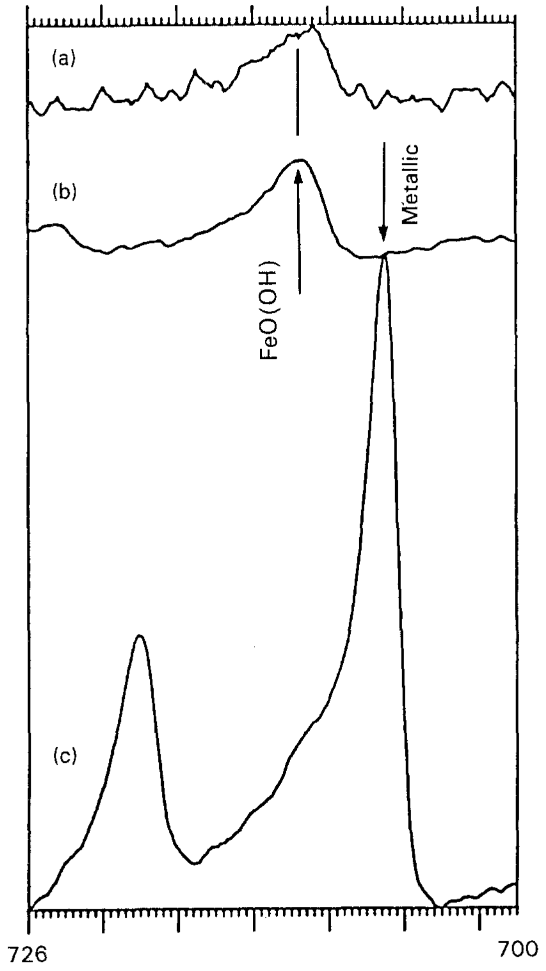

Figure 4 Fe $2p_{3/2}$ ESCA spectra obtained after (a) 3 days and (b) 2 weeks of water immersion; (c) shows the 2 week specimen after 100 × 60 s argon-ion etching.

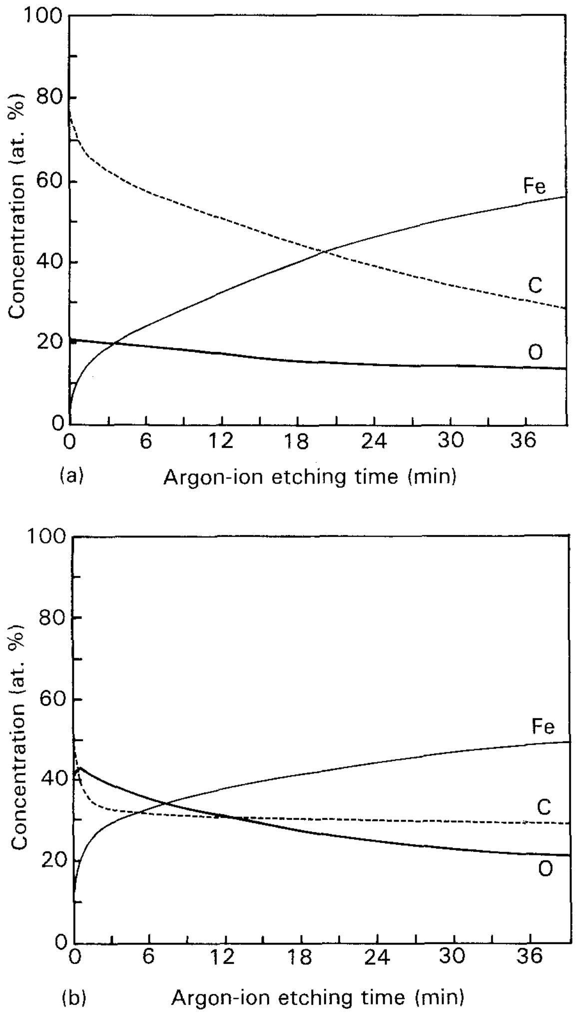

Figure 5 Concentration variations (at %) with depth for the (a) 3 day and (b) 4 day water immersed specimens.

because the PMMA film could not be separated from the mild steel substrate by thermal shocking for the specimen sealed in the quartz glass tube with a small adhered area as shown in Fig. 1.

The surface of the mild steel developed white spots at 95% water content and these then changed to brown ones. After 3 days immersion, the water content at the adhesion interface reaches close to the equilibrium water concentration, and it was determined that iron oxide hydrate was formed at the adhesion interface after 3 days and also 2 weeks immersion. This was followed by the appearance of a black corrosion product, Fe_3O_4. The critical point, forming the corrosion product of Fe_3O_4, was not determined here.

Carbon is derived chiefly from contamination and the adhesive resin. The steep decrease in carbon concentration after a few minutes of argon etching shown in Fig. 5a and b shows the extent of carbon contamination. The carbon content of the 3 day specimen is higher than that of the 4 day specimen, indicating a large amount of residual resin on the 3 day specimen. The amount of residual resin bonded to the mild steel surface decreases as destruction due to water molecules progresses.

Oxygen comes from absorbed water molecules (the contamination) and iron oxide hydrate. The high oxygen content in the 4 day specimen shows that much oxygen is due to iron hydroxide, as there is a large amount of residual resin in the 3 day specimen and absorbed water, because contamination is similar for the two specimens, as also shown in Fig. 7.

Side chains of 4-META bond to hydroxyl groups on the metal surface by forming hydrogen bonds [10]. These chemical bonds may be destroyed slowly with water diffusion. Destruction of adhesion occurs when water molecules which permeate to the interface reached 48% of the equilibrium water concentration. This is followed by corrosion and formation of iron hydroxides such as FeO(OH), resulting in a complete destruction of the adhesion interface.

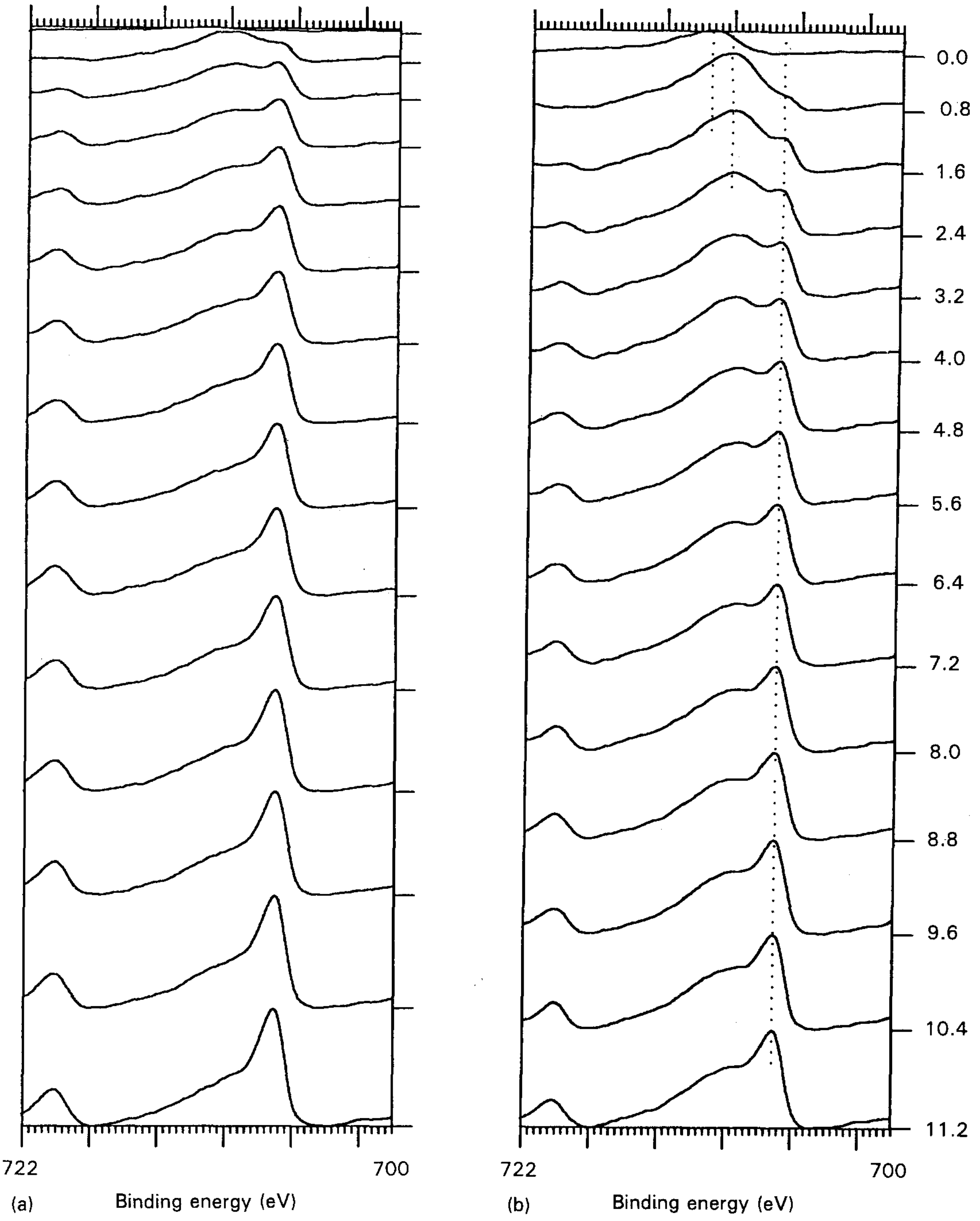

Figure 6 Fe $2p_{3/2}$ spectra obtained from the (a) 3 day and (b) 4 day water immersed specimens after varying argon-ion etching times.

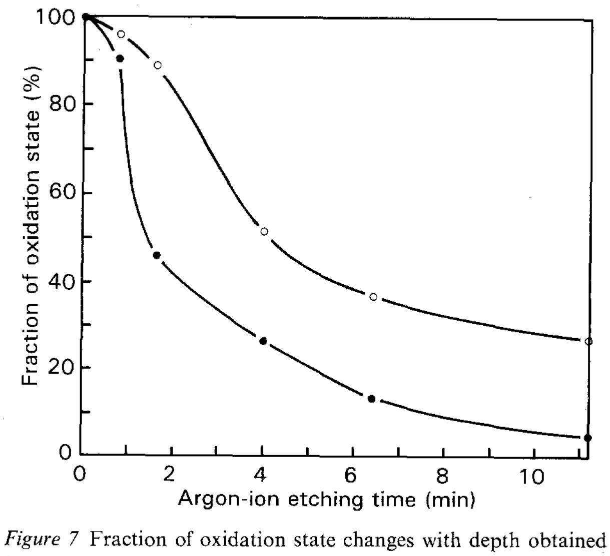

Figure 7 Fraction of oxidation state changes with depth obtained from the (●) 3 and (○) 4 day water immersed specimens.

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