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RHEED, AES AND XPS STUDIES OF THE PASSIVE FILMS FORMED ON ION-IMPLANTED STAINLESS STEEL†

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ABSTRACT

P-implantation (10^{17} ions cm^{-2}, 40 Kev) into 304 stainless steel (ss) has been carried out, and an amorphous surface alloy was formed. Polarization studies in deaerated 1N H_2SO_4 + 2% NaCl showed that P-implantation improved both the general and localized corrosion resistance of 304 ss. A comparative study has been carried out between the implanted and unimplanted steel to determine what influence P-implantation has upon the properties of the passive film formed in 1N H_2SO_4. The influence of Cl ions on pre-formed passive films was also studied. RHEED, XPS and AES were used to evaluate the nature of the passive films formed in these studies.

KEYWORDS

Ion implantation, X-ray Photoelectron Spectroscopy, Auger Electron Spectroscopy, Reflection High Energy Electron Diffraction, passivity.

INTRODUCTION

In a previous study (1) TEM analysis was carried out on pre-thinned 3 mm. diameter discs of 304 (ss) which had been implanted with 10^{17} P+ ions cm^{-2} at 40 Kev. The microstructure of the surface alloy showed a mottled structure which could be interpreted as evidence of microcrystallinity with grains of ca. 50 Å in diameter. Electron diffraction analysis produced a single diffraction halo, indicative of either an amorphous or microcrystalline surface alloy. The electrochemical behavior of the surface alloy was studied in deaerated 1N H_2SO_4 and in 0.1 N NaCl solution. Little improvement was found in the active-passive behavior in the acid, and poor resistance to pitting was observed in the chloride solution. This behavior was not typical of the ultra-high corrosion resistance which has been observed in amorphous Cr bearing ferrous alloys (2,3), and was taken as further evidence that the surface alloy was indeed microcrystalline.

Recently we have improved the heat sinking of 304 ss samples during ion implantation with P, by bonding the samples with silver adhesive to a water-cooled copper plate. This has resulted in significant improvements in the

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passivation behavior of the P-implanted 304 ss in deaerated 1N H_2SO_4 and 1N H_2SO_4 + 2% NaCl solution. This study is concerned with the compositional and structural nature of the passive films formed on P-implanted and unimplanted 304 ss.

EXPERIMENTAL

The composition of the stainless steel used in this work is given in Table 1.

Table 1. Composition of 304 Stainless Steel

% Cr	% Ni	% Mn	% Si	% Mo	% C	% N	% S	% P
18.18	8.48	1.75	0.5	0.36	0.055	0.05	0.005	0.028

Sample preparation was the same as that reported earlier (1). As mentioned above, heat sinking was improved to insure that the power input (1 watt cm^{-2}) during implantation did not raise the temperature of the sample to above 50°C. A composition depth profile was carried out using Auger Electron Spectroscopy (AES) with Ar^+ ion etching (6 Kev, 15 $\mu A\ cm^{-2}$). This profile, which is given in Fig. 1, indicates that > 90% of the P is distributed within a depth of ca. 120 Å and that the peak distribution is located at ca. 40 Å from the surface. In agreement with the previous work (1) in which X-ray Photoelectron Spectroscopy (XPS) was used to profile the surface alloy, no sign was found of the redistribution of Fe, Cr or Ni due to selective sputtering or radiation enhanced segregation. However, the second maxima found in the P-profile of the previous work was not observed in this study.

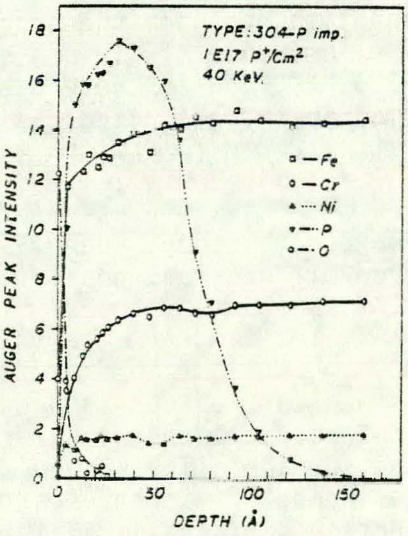

Fig. 1. AES composition depth profile of P^+-implanted 304 stainless steel.

ELECTROCHEMICAL ANALYSIS

The details of the technique of anodic polarization used in this study have been published earlier (1). In this work the active-passive behavior was observed in a deaerated solution of 1N H_2SO_4 + 2% NaCl. All electrode potentials were measured against the Saturated Calomel Electrode (SCE). Fig. 2 shows the polarization curves for 304 and P-implanted 304 ss. In this electrolyte a marked lowering of the passivation potential and a decrease in the critical and passive current densities due to P-implantation was observed. A second anodic current maximum was also observed at -50 mV. Whereas no pits were observed in the implanted steel, pitting did occur on the unimplanted steel where breakdown of passivity took place transpassively.

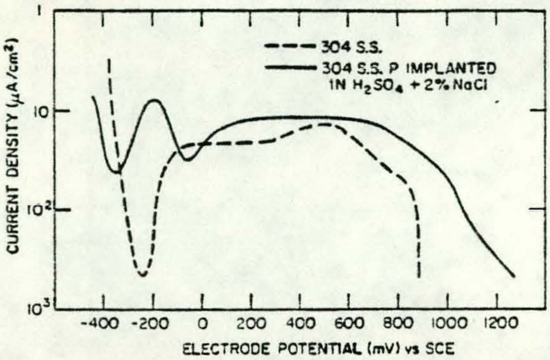

Fig. 2. Anodic polarization curves of 304 ss and P^+-implanted 304 ss in 1N H_2SO_4 + 2% NaCl solution.

PASSIVE FILM ANALYSIS

To study the nature of the passive films formed on the implanted and unimplanted steels, structural analysis was carried out using RHEED (Reflection High Energy Electron Diffraction), compositional depth profiles were obtained by AES coupled with Ar^+ ion sputtering and the chemical states of the constituents of the films was determined by XPS.

In order to prepare the passive films for analysis, samples were first cathodically pre-treated (-1000 mV, 10^3 μA cm^{-2}, 15 mins.) in deaerated 1N H_2SO_4 to remove the air formed oxide followed by potentiostating at either +250 or +550 mV (Vs. SCE) for 1 hour. Immediately following the passivation treatment samples were cleaned in doubly distilled water, dried with a jet of argon and quickly transferred to the electron microscope or electron spectrometer. Separate, freshly prepared samples were used for structural and compositional analysis.

In order to compare the effect of Cl^- ions on the passive film formed at +550 mV and +250 mV (Vs. SCE) in deaerated 1N H_2SO_4, a Cl^- ion innoculation treatment was carried out following passivation for 1 hour. The innoculation treatment consisted of the addition of a small amount of concentrated H_2SO_4 and NaCl solution in order to make up a bulk solution of 1N H_2SO_4 and 2% NaCl. The samples were then passivated for a further 10 minutes, in a solution of 1N H_2SO_4 + 2% NaCl, during which time no pitting took place. The samples were then washed and prepared for analysis as before.

RHEED ANALYSIS

All the RHEED patterns were obtained using a Phillips EM300 electron microscope. A summary of the data is given in Tables 2 and 3. The crystalline films formed on the unimplanted steel were seen to modify with increase in anodic potential (4) and with exposure to the Cl^- ions. The films formed on the implanted steel were found to be amorphous yielding halos as shown in Fig. 3. A single ring was observed between the halos in three of the samples analyzed. In order to determine the possible origin of this ring, we assumed that two other rings were superimposed on the halos. We approximated the possible position of the two other rings and determined their radii. The calculated 'd' spacings which resulted from this approximation matched those of $CrPO_4$ and $Fe(PO_3)_3$.

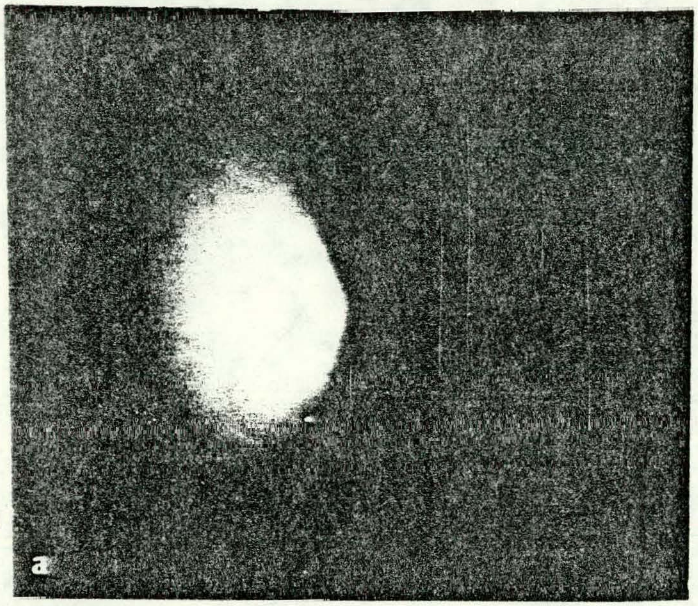

Fig. 3. RHEED halos of the anodic film formed on P^+-implanted 304ss in 1N H_2SO_4 at +550 mV SCE.

Table 2. Calculated Interplanar Spacings of the Passive Films Formed in 1N H_2SO_4 at +550 mV and +250 mV for 1 Hr.

Potential	Steel	d Spacing	Phase
+550 mV SCE	304	3.23, 2.73, 2.35, 2.18 1.88, 1.69, 1.43, 1.19	γ-FeOOH CrOOH
	304-P	2.65, 1.98, 1.44	$Fe(PO_3)_3$ $CrPO_4$
	304	3.54, 3.21, 2.85, 2.46, 2.21 1.88, 1.70, 1.60, 1.31	Green Rust II* $Fe(OH)_2$ CrOOH
+250 mV SCE	304-P	2 diffuse Rings	———

*Green Rust II (GRII): $2Fe(OH)_2\ 4Fe(OH)_3.FeSO_4.XH_2O$, Ref (5).

Table 3. Calculated Interplanar Spacings of the Passive Films Formed in 1N H_2SO_4 for 1 Hr. and continued passivation in 1N H_2SO_4 + 2% NaCl for 10 Min.

Potential	Steel	d Spacing	Phase
+550 MV	304	3.33, 3.06, 2.64, 2.20, 1.80 1.75, 1.64	γ-FeOOH $Cr(OH)_3$
	304-P	2.65, 1.98, 1.44	$Fe(PO_3)_3$ $CrPO_4$
+250 mV	304	3.91, 3.30, 2.97, 2.64, 2.40 2.03, 1.89, 1.76, 1.70, 1.57, 1.42	Green Rust I* $Cr(OH)_3$
	304-P	3 Diffuse Rings 2.70, 2.16, 1.49	$Fe(PO_3)_3$ α-$CrPO_4$

*Green Rust I (GR I): $Fe^{2+}_{3.6}\ Fe^{3+}_{0.9}\ (O,\ OH,\ Cl)_9$ Ref. (6)

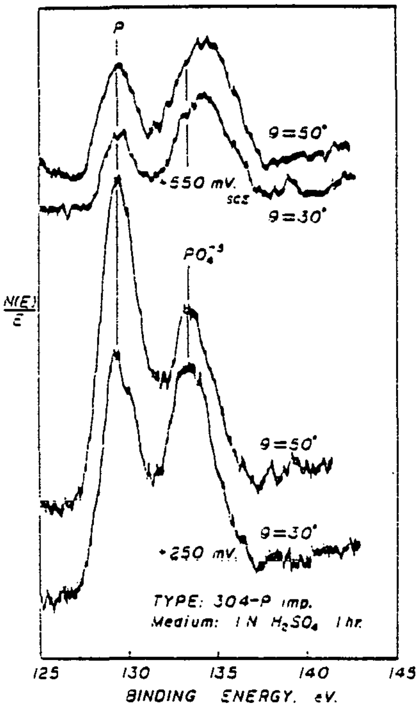

Fig. 4a

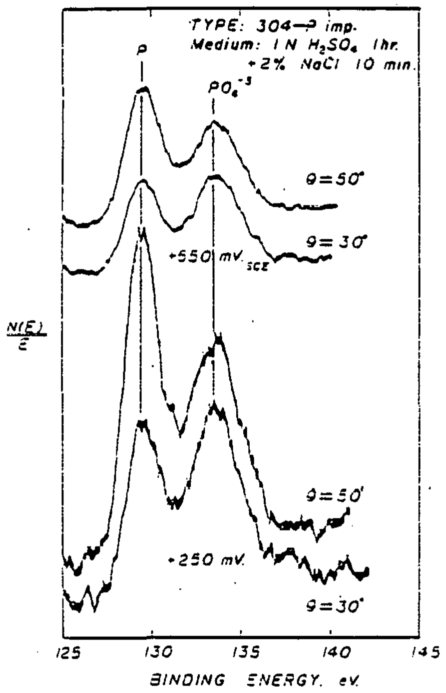

Fig. 4b

Fig. 4. The phosphorus 2P photoelectron spectra measured for anodic films formed on P^+-implanted 304 ss under various conditions.

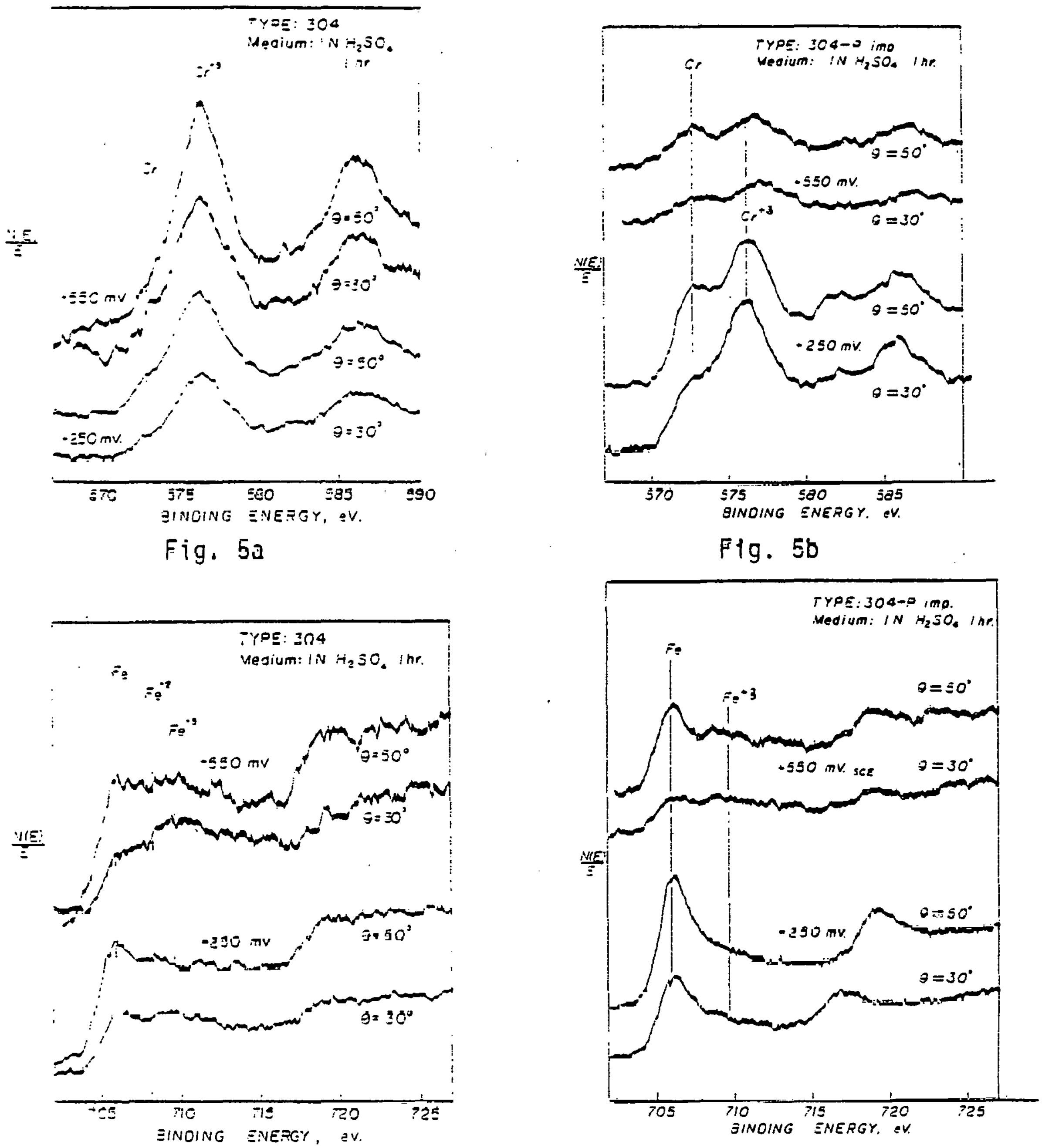

Fig. 5a

Fig. 5b

Fig. 5c

Fig. 5d

Fig. 5. Cr 2p and Fe 2p photoelectron spectra measured for anodic films formed on 304 ss and P^+ implanted 304 ss in 1N H_2SO_4 at +550 mV and +250 mV SCE.

XPS AND AES ANALYSIS

A non-destructive analysis was first carried out using XPS, varying the angle of electron take off in order to differentiate between the outer and inner layers of the passive films. XPS showed the presence of Cr^{3+}, Fe^{3+} and Ni^{2+} cations and $SO_4^{=}$ anions in all the films studied. Phosphate anions were also observed in the films formed on the surface alloy. As shown in Figs. 4 and 5 the chemically shifted peaks of the cations were lower and the metallic signals higher in the film formed on the surface alloy indicating that the surface alloy formed a thinner passive film. The phosphate peaks (P 2p) were broadened by charge shifting in the case of the film not exposed to Cl$^-$ ions. This indicates that the film is more insulating in nature.

The depth profiles obtained by AES (Figs. 6 and 7) revealed that the thickness of the films was slightly increased on exposure to Cl$^-$ ions. The passive films formed on the unimplanted samples increased from 17-22 Å while those formed on the P-implanted steel increased from 6-10 Å at +550 mV and remained almost unchanged at +250 mV. The extra film growth coincided with the depth to which Cl$^-$ ions were detected and to a plateaux in the distribution of the sulphur ($SO_4^=$) peaks. The low level of Ni^{2+} detected by XPS and AES accounts for the absence of the nickel phase in the RHEED analysis. The composition profiles also indicated a build-up of Cr^{3+} in the inner layer of the passive film in each of the cases studied.

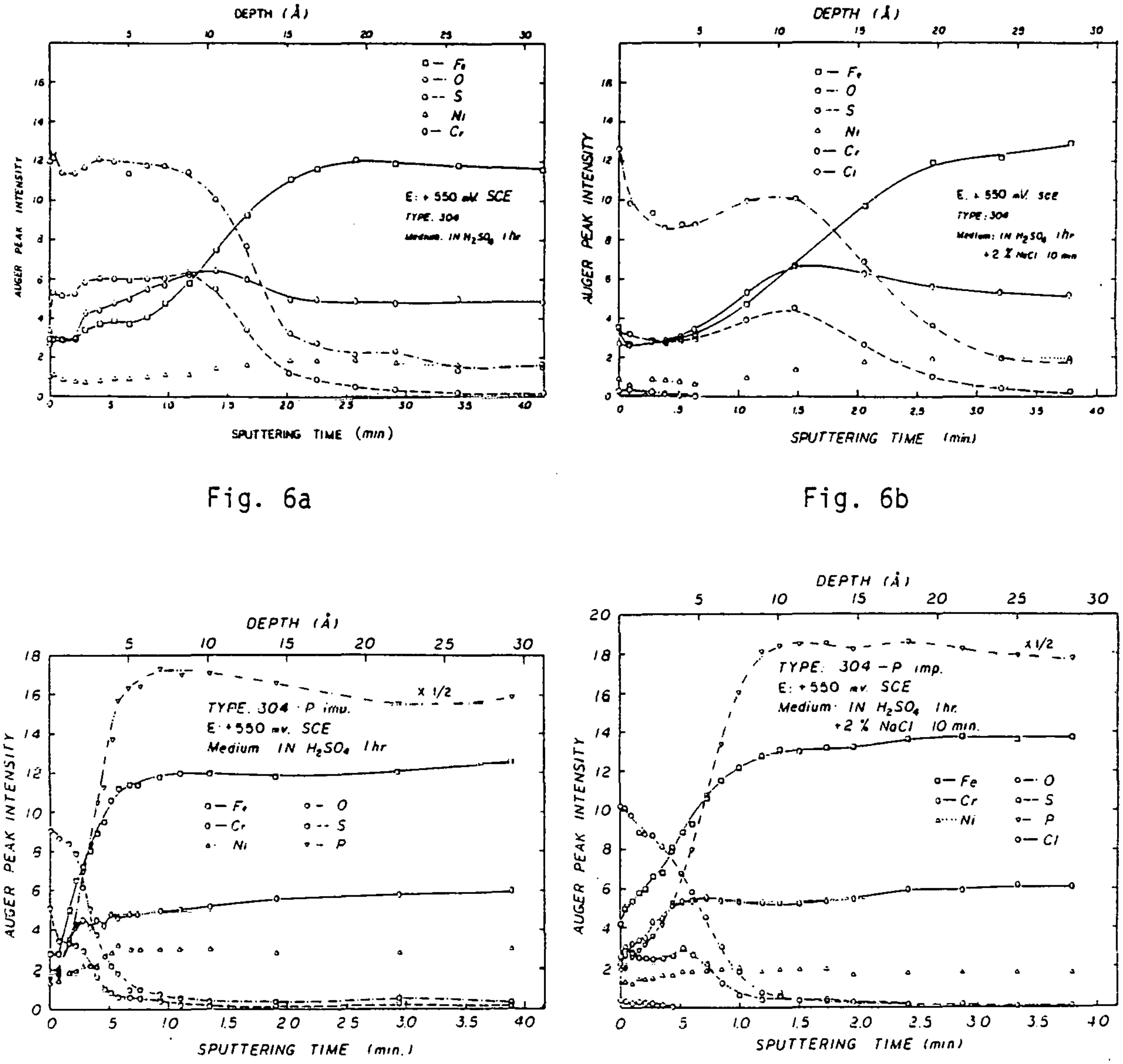

Fig. 6a

Fig. 6b

Fig. 6c

Fig. 6d

Fig. 6. AES composition profiles of the anodic films formed on 304 ss and P$^+$-implanted 304 ss in 1N H_2SO_4 at +550 mV SCE with and without the addition of Cl$^-$ ion.

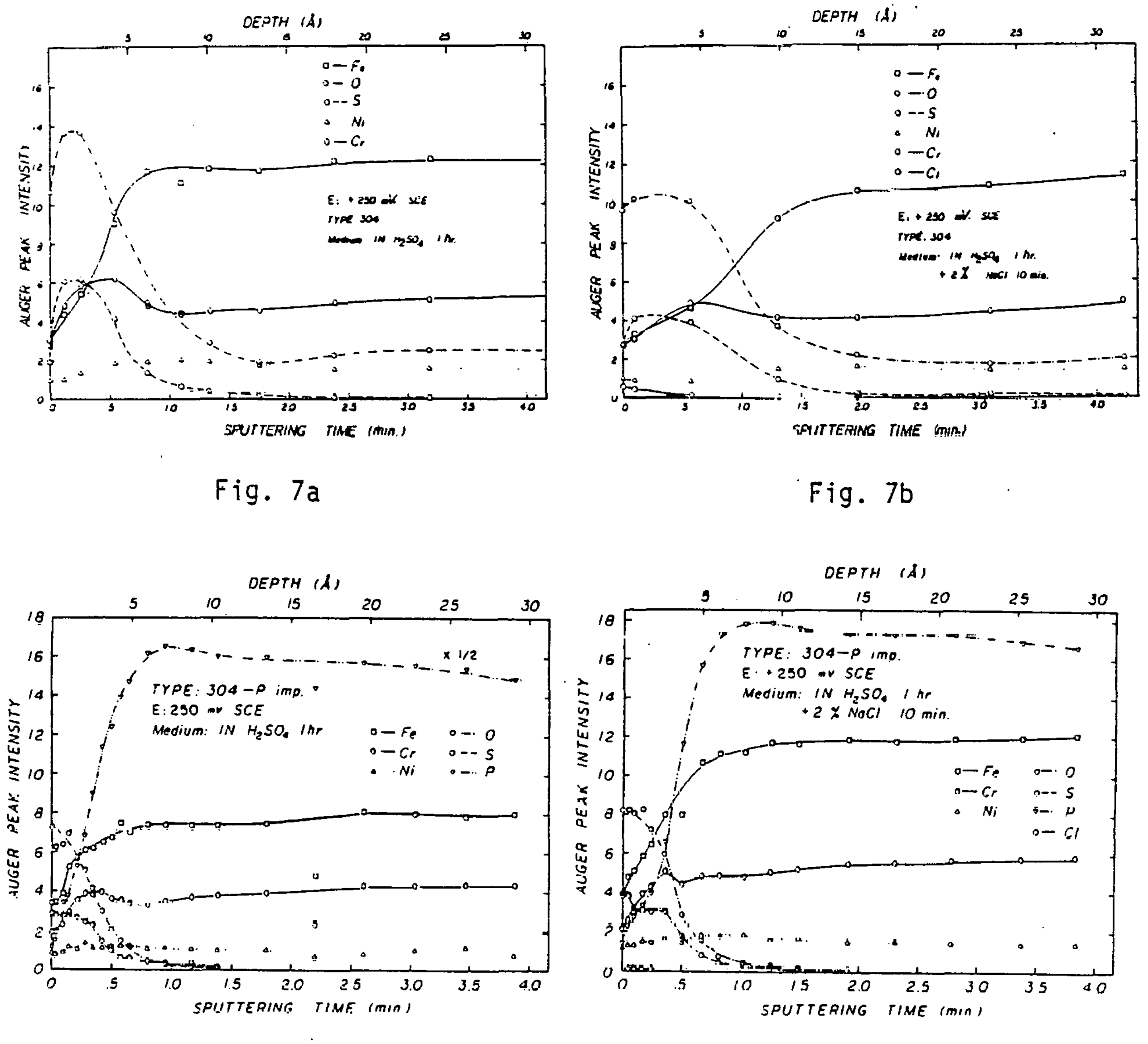

Fig. 7a

Fig. 7b

Fig. 7c

Fig. 7d

Fig. 7. AES composition profiles of the anodic films formed on 304 ss and P^+-implanted 304 ss in 1N H_2SO_4 at +250 mV SCE with and without the addition of Cl^- ion.

DISCUSSION OF RESULTS

Electrochemical analysis in deaerated acidic-chloride solution shows that the P-implanted amorphous surface alloy produces a more extensive range of passive potential accompanied by a lower passive current density. Compositional analysis indicates that the film is much thinner than is formed on unimplanted steel.

The structural modification of the passive films formed on the unimplanted 304 ss resulting from Cl^- attack has not resulted in pitting. The containment of Cl^- ions to the outer regions of the passive film appears to be due to the formation of β-FeOOH at +550 mV and G.R.I. at +250 mV which are only formed in the presence of Cl^- ions (5). Indeed G.R.I. incorporates Cl^- ions into the crystal structure. The role of $Cr(OH)_3$ is less understood, since it has been shown that the hydroxyl group of metallic hydroxides is more easily displaced by Cl^- ions than in the case of oxyhydroxides (7). An important point which must be emphasized is that the RHEED analysis carried out in this work gave no evidence of the existence of the phases formed in the passive film prior to Cl^- ion exposure. Since the AES profiles indicate that only the outer portions of the passive films are modified by Cl^- ion exposure it is reasonable to assume that the new phases which are formed are only present in the outer region of the passive film. It is, therefore, thought that the diffraction patterns from the inner portions of the passive film are too weak to be detected.

The ability of the amorphous passive film to resist Cl^- ion penetration and structural modification is probably due to (a) the difficulty with which diffusion may take place in the passive film and (b) the inhibitive action of the phosphate anions. It is apparent from the AES composition depth profiles that the phosphate anions are generally incorporated into the amor phous passive film. However, the trace of crystalline phosphates detected by RHEED in the high potential film may have resulted from precipitation from the solution.

The effectiveness of phosphates to resist Cl^- ion attack may be indicated by the ease with which phosphate anions may be displaced. Some evidence of the displacement of phosphate anions by Cl^- is seen in the high potential passive film. It is evident from the 30° P 2p spectra from +550 mV film (Figs. 4a and 4b) that the elemental P 2p peak from the surface alloy and the phosphate P.2p peak from the film are of approximately equal height following 10 minutes exposure to Cl^- ions. However, before exposure to the Cl^- ions, the 30° spectra show that the peaks from the phosphate anions are higher than for the elemental P. Since exposure to the acidic-chloride solution leads to film thickening one would normally expect the phosphate peak to be higher than the elemental peak due to (a) increased attenuation of the elemental P peak from the alloy and (b) the increase in the total number of phosphate ions in the film. It is, therefore, possible that Cl^- ions may have begun to displace phosphate ions incorporated in the outer regions of the original passive film. In contrast to this observation, the films formed at +250 mV did not show any significant change in the relative heights of the elemental P and phosphate 2p peaks resulting from Cl^- ion exposure. This is consistent with the limited penetration of Cl^- as indicated by Fig. 7d and the undetectable level of film growth resulting from Cl^- ion exposure.

CONCLUSIONS

Ion implantation may be used to produce an amorphous surface alloy on a commercial stainless steel, and, thereby, enhance considerably the corrosion resistance of that steel. The removal of grain boundaries and other imperfections in the substrate is expected to improve the general and localized corrosion resistance of the steel, because such defects disrupt the coverage of the passive film at these active sites in the crystalline substrate. A further effect of the amorphous structure of the surface alloy is to promote the formation of an amorphous passive film having superior resistance to Cl^- ion attack in acidic media. The stability of the passive films in acidic-chloride solution is probably due to (a) the effectiveness of an amorphous film to act as a diffusion barrier, (b) the corrosion inhibitor properties both of the phosphates contained within the amorphous passive film, and, the layer of crystalline phosphates which are assumed to have been deposited from solution on to the outer surface of the passive film.

ACKNOWLEDGEMENTS

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