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Pitting corrosion inhibition of 316 stainless steel in phosphoric acid-chloride solutions

Part II *AES investigation*

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The application of Auger Electron Spectroscopy (AES) to the study of the composition and thickness of the passive film formed on the surface of 316 Stainless steel in H_3PO_4-Cl^- solutions containing nitrate, dichromate, molybdate and tungstate as inhibitors is discussed. Data are presented which explain the effectiveness of the additives on the properties of the passive films of the alloy. It is concluded that much higher corrosion resistance of the alloy is observed in nitrate additives due to marked nitrogen enrichment underneath the passive film which enhances the repassivation ability of this alloy. The results could also explain the effectiveness of the dichromate, molybdate and tungstate anions due to improved film repair conditions. *© 1999 Kluwer Academic Publishers*

1. Introduction

Anodic films on the surface of steels containing Mo (e.g. austenitic stainless steel 316) are not yet sufficiently characterised with respect to their composition, structure, and properties [1–3]. All hypotheses are unsatisfactory and do not permit precise interpretation of the variety of effects observed. A conclusion was drawn elswhere [4] that film thickness plays an important role in determining the pitting resistance of 316 stainless steel.

Surface-analytical techniques provide a unique insight into the mechanism of corrosion inhibition, because they probe the top 10 A° of the surface [5]. Auger Electron spectroscopy (AES) is a surface analytical technique that has seen widespread use in the study of corrosion and inhibition.

In part I [6] of the present study, pitting corrosion inhibition of 316 stainless steel in H_3PO_4-Cl^- solutions by nitrate, dichromate, molybdate and tungstate oxyanions was examined using potentiodynamic and potentiostatic polarization techniques. The present paper has the additional aim to clarify the nature and composition of the passive films and also to determine the distribution of the elements across the depth of the films formed on the alloy in the above solutions so as to explain the mechanisms through which corrosion resistance is improved in view of the beneficial effect of the corresponding alloying elements. For this purpose, AES measurements have been made on passive films formed in H_3PO_4-Cl^- solutions in the absence and in presence of these oxyanions.

2. Experimental

Specimens measuring 10 × 10 × 2 mm, cut from commercially produced AISI 316 stainless steel were used. These were polished with emery papers, degreased in acetone, and washed with distilled water before introduction into the solution. Experiments were conducted in 30% H_3PO_4 (pH = 1.4) containing 15000 ppm NaCl with various anion additions.

The surface films were prepared by immersing the samples in the test solution for 20 h. Before introduction into the AES chamber, the samples were, thoroughly rinsed with distilled water and dried in a stream of argon. The vacuum in the analytical chamber was better than 5×10^{-9} torr (0.6 μPa). Under sputtering conditions the vacuum was better than 8×10^{-8} torr (10.6 μPa). Depth profiles were made by directing a beam of argon ions (5 μm dia.) at a specified point on the surface. Because surface films were very thin, the surface was etched at a very slow rate. This was accomplished by bombardment with argon ions at low pressure (5 mPa), rastering an area of 4 × 4 mm.

The electron beam of the spectrometer was produced under an accelerating voltage of 5 kV, with peak to peak modulation of 6. The argon gas was ionized with a voltage of 4.5 kV and an ionizing current of 25 mA. All results of surveys and profiles were produced by V005 software from Physical Electronics (USA).

3. Results and discussion

The AES spectrum and depth profile of 316 stainless steel immersed in 30% H_3PO_4 at open circuit for 20 h. Fig. 1 shows the appearance of smaller peaks of Mo, a larger O peak (Fig. 1A) and slightly more thicker film (Fig. 1B), while the results for 316 stainless steel in 30% H_3PO_4 + 15000 ppm Cl^- ions at open circuit for 20 h. Fig. 2 shows higher peaks for Mo and S in presence of Cl^- ion (Fig. 2A) which cause preferential dissolution of Fe, Cr and enrichment of both Cu and Ni

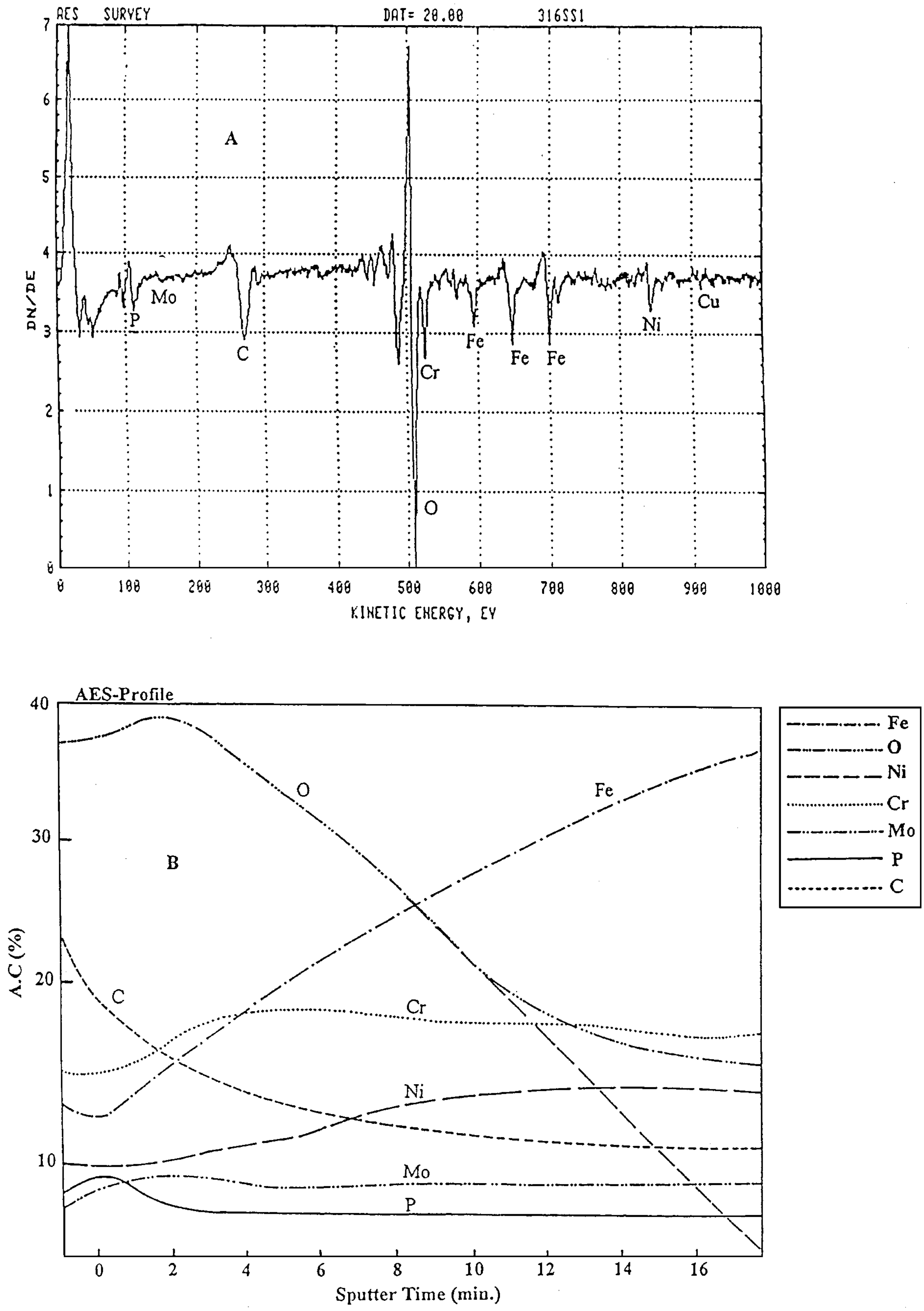

Figure 1 Surface analyses of 316 stainless steel after treatment in 30% H_3PO_4 solution. (A) AES spectrum, (B) depth profile.

in the film having slightly less thickness (Fig. 2B) than in absence of the chloride (Fig. 1B). The thickness of the film (as relative time of sputtering) may be determined by extrapolation of oxygen profile to the abscissa which approximately defines its location [7]. For pure acid, the interface determined by this method was 18 min; while the presence of chloride ions etching of the film required less than 11 min sputtering.

From Fig. 2B the chloride ions are not significantly incorporated into the film, the ion signal being confined

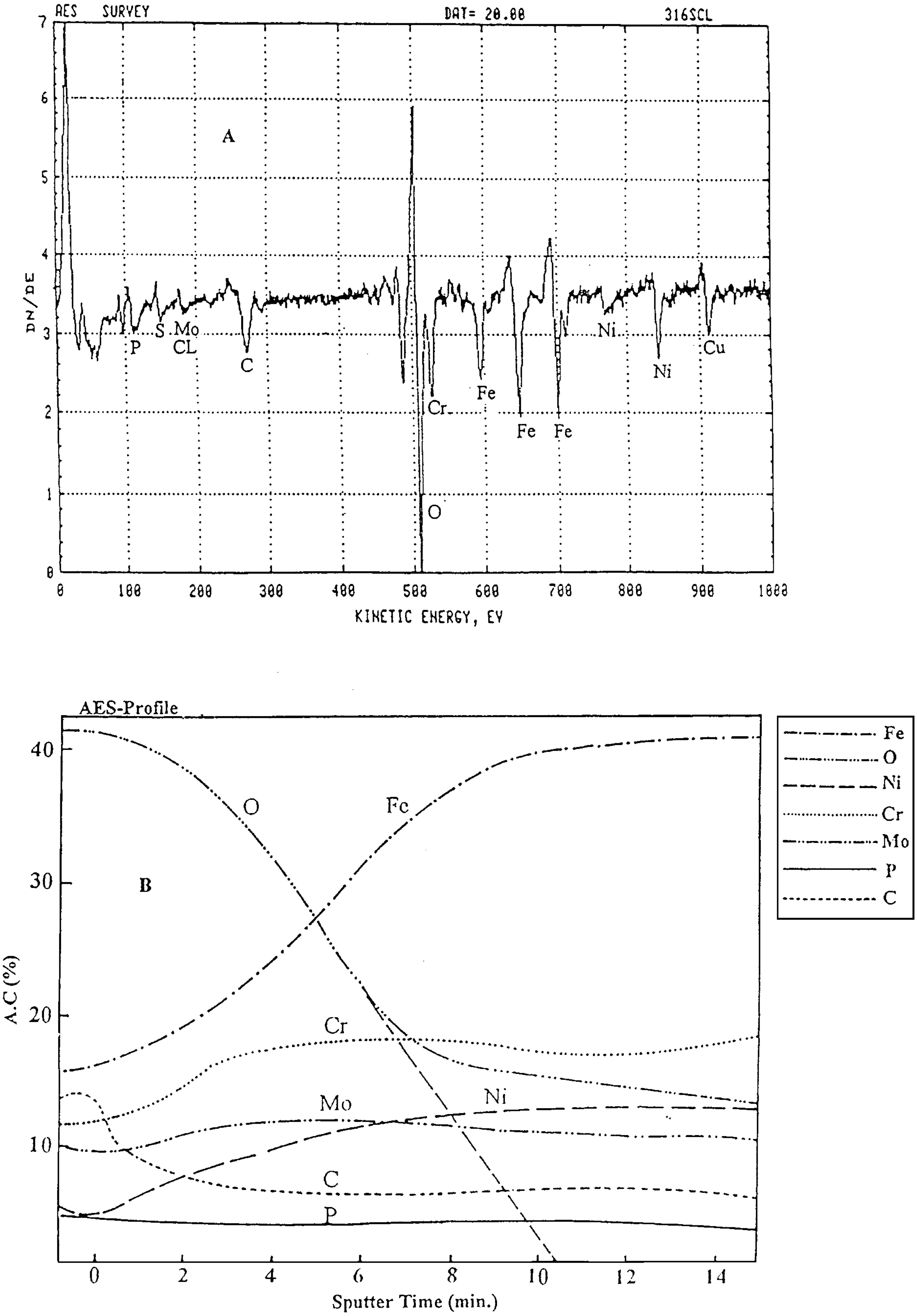

Figure 2 Surface analyses of 316 stainless steel after treatment in 30% $H_3PO_4 + 15000$ ppm Cl^- solution. (A) AES spectrum, (B) depth profile.

to the overlying region of surface contamination. Similar results were found by Cieslak and Dequette [8] who suggested that the role of halides is to interact with weak points of the film at the solution film interface.

The effect of various inhibitors on the composition and relative thickness of the film formed on the steel samples in 30% H_3PO_4-Cl^- solutions have been determined by AES. The optimum concentrations of

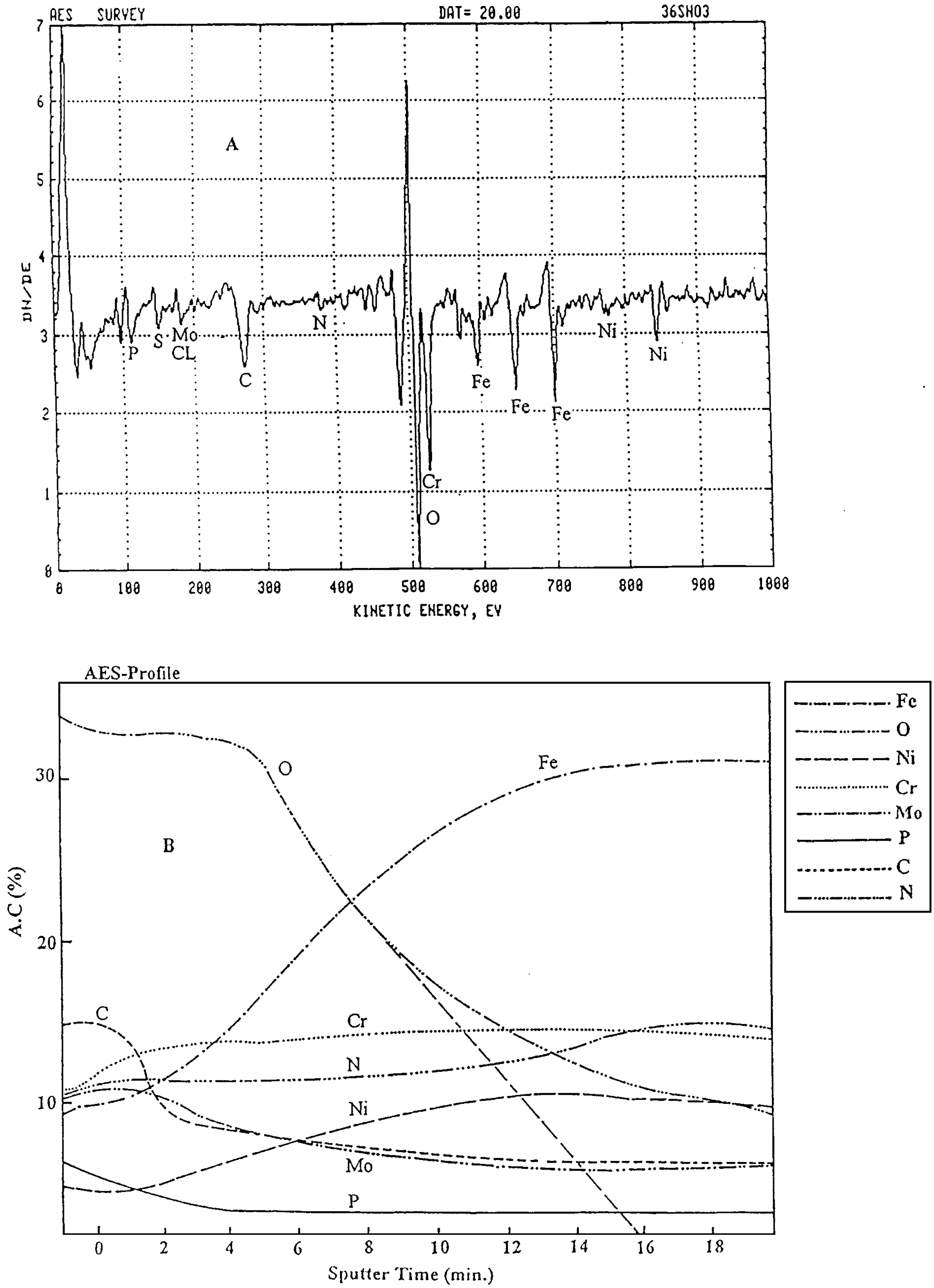

Figure 3 Surface analyses of 316 stainless steel after treatment in 30% H_3PO_4 + 15000 ppm Cl^- solution containing 1500 ppm $NaNO_3$. (A) AES spectrum, (B) depth profile.

inhibitors according to electrochemical results (part I) were 1500 ppm NO_3^-, 5700 ppm $Cr_2O_7^{2-}$, 5800 ppm MoO_4^{2-} and 5500 ppm WO_4^{2-} anions. Auger spectra and depth profiles of the specimens prepared in these solutions are shown in Figs 3–6 respectively. Also the role of these inhibitors (oxyanions) will be discussed in relation to the effects of corresponding alloying elements: N, Cr, Mo and W.

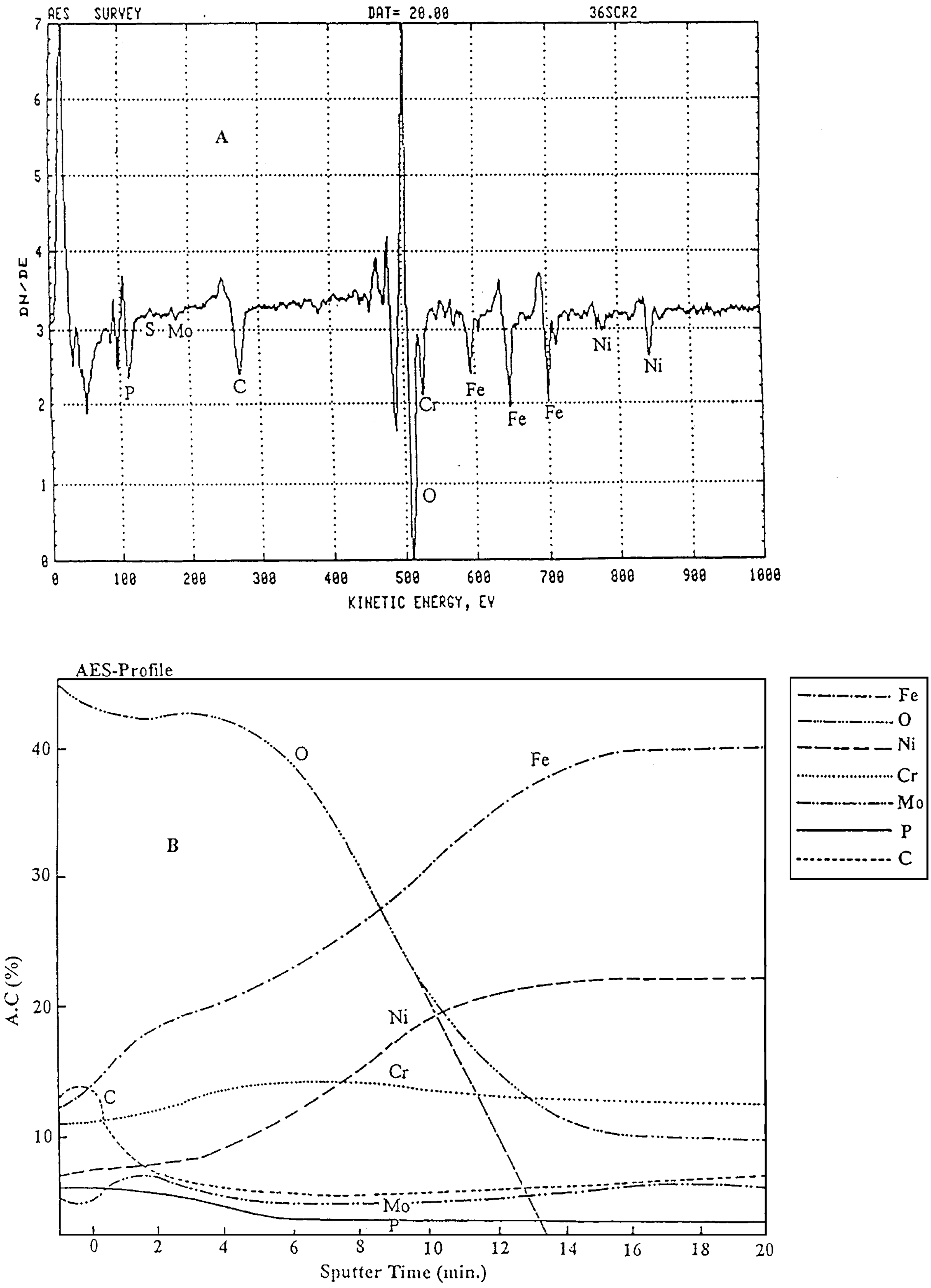

Figure 4 Surface analyses of 316 stainless steel after treatment in 30% H_3PO_4 + 15000 ppm Cl^- solution containing 5700 ppm $K_2Cr_2O_7$. (A) AES spectrum, (B) depth profile.

The major distinguishing feature of the AES spectrum and depth profile for the film formed in the presence of nitrate ions (Fig. 3) in comparison with the case when the additive is absent (Fig. 2) is the appearance of significant peak of nitrogen (Fig. 3A) and the increase in nitrogen concentration with depth into the film (Fig. 3B). It can also be seen from both figures that the film formed in the absence of nitrate ions is not as thick

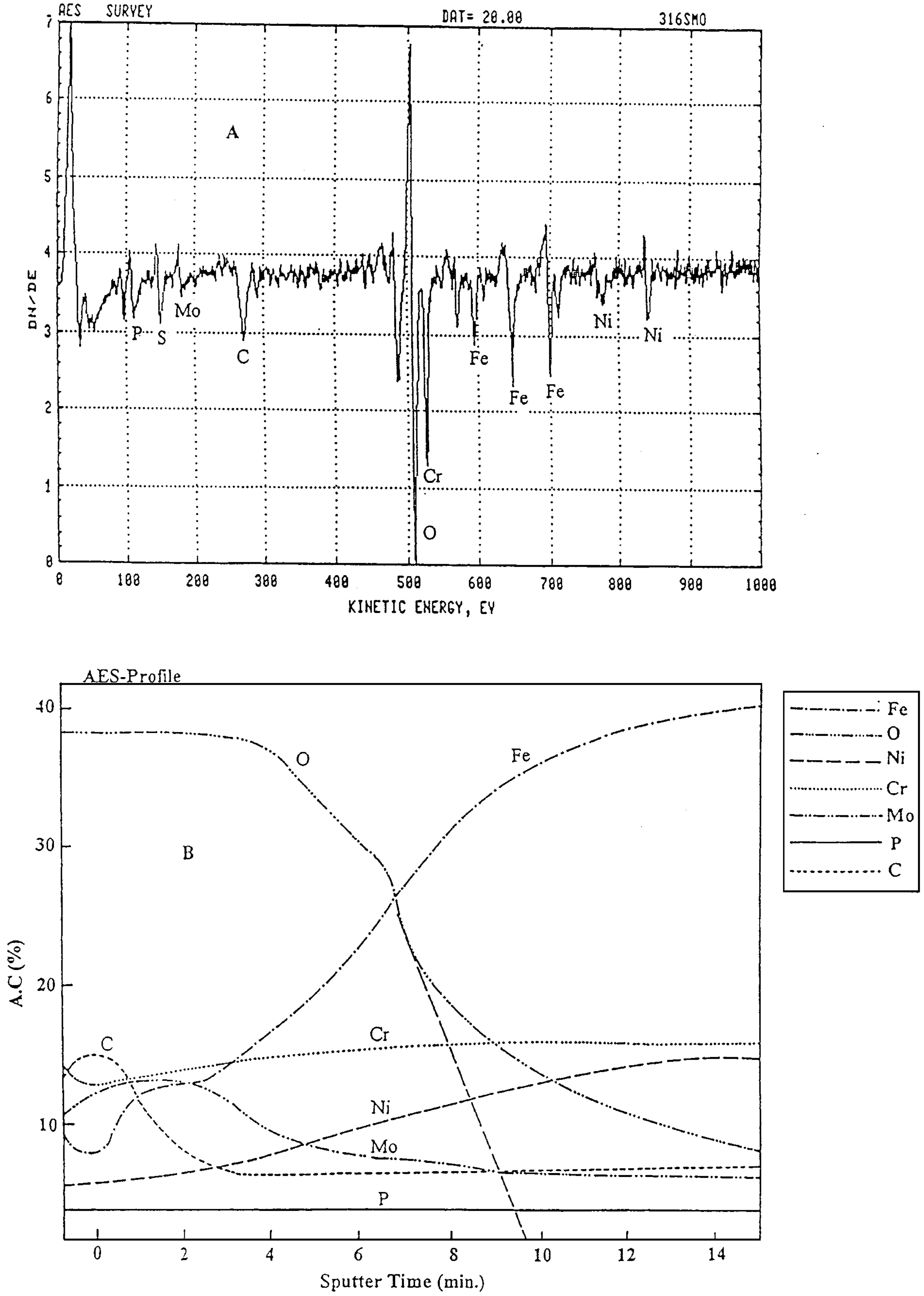

Figure 5 Surface analyses of 316 stainless steel after treatment in 30% $H_3PO_4 + 15000$ ppm Cl^- solution containing 5800 ppm Na_2MoO_4. (A) AES spectrum, (B) depth profile.

as that formed in the presence of the additive. This can be seen from the rapid decrease in oxygen content (Fig. 2B).

The above results indicate that, in the absence of inhibitor, the three main constituents of the alloy are all subject to attack; with preferential dissolution of iron, nickel and Mo. Enrichment of chromium on the film surface being also observed in this case. Addition of inhibitor prevents attack of the alloy and the film formed normally contains high concentrations of iron oxide,

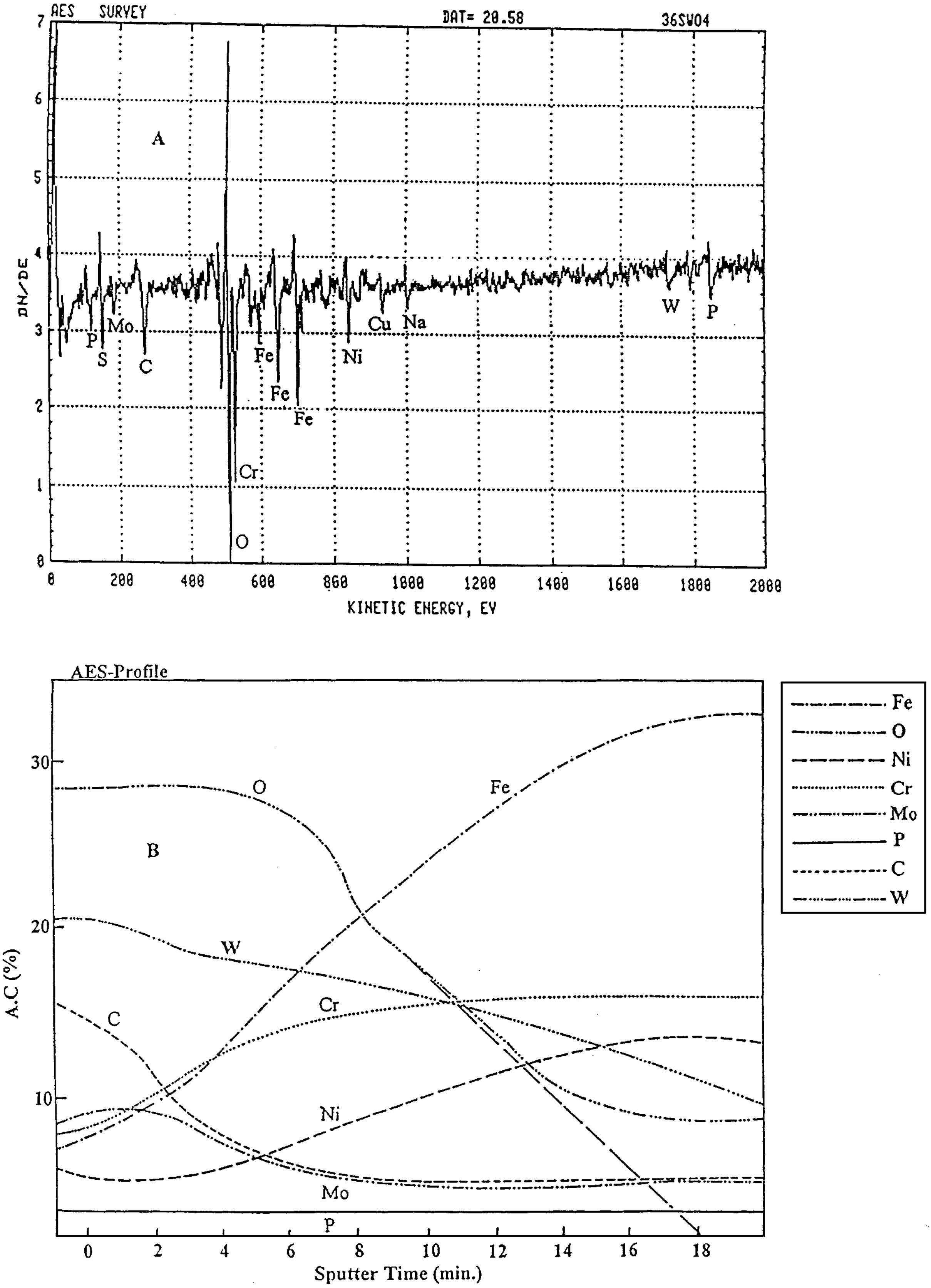

Figure 6 Surface analyses of 316 stainless steel after treatment in 30% $H_3PO_4 + 15000$ ppm Cl^- solution containing 5500 ppm Na_2WO_4. (A) AES spectrum, (B) depth profile.

with approximately equal amounts of chromium and adsorbed nitrogen compounds, in addition to nickel.

New alloys containing increasing amounts of alloyed nitrogen have led to improvements in passivation and pitting resistance [9–11]. The greatest effect of nitrogen has been observed in molybdenum-bearing steels suggesting a possible synergism between molybdenum and nitrogen [12–14].

Various opinions exist on the mechanism by which nitrogen improves localized corrosion resistance.

Tomashov *et al*. [15] suggested that nitrogen structurally homogenizes the alloy. From pitting solution analysis, Osozawa and Okato [10] proposed that nitrogen buffers the local pH through the formation of ammonium ions. Newman and Shahrabi [16] suggested that due to the sluggish reaction of nitrogen with protons during anodic dissolution, elemental nitrogen enriches the surface; which inhibits the anodic dissolution at less than monolayer coverage by blocking the kinks and steps in the surface.

For austenitic stainless steels, AES has shown that the surface concentration of nitrogen can be enriched as such by seven times the bulk concentration. At such concentrations, relatively, stable interstitial nitrides are possible [17]. This is consistent with Auger results of Lu *et al*. [18] which suggest that when passivity of stainless steel breaks down, nitrogen inhibits the anodic dissolution by enhancing the surface enrichment of beneficial elements; principally chromium [19, 20]. The significance of this observation is that it may explain the synergistic effect between nitrogen and chromium in improving pitting resistance.

In acidic solutions, chromium nitrides are more stable than in neutral solution [19]. This pH dependence of the anodic kinetics of the nitrides may accelerate the anodic segregation of beneficial elements, such as chromium during localized corrosion; therefore, building up a more resistive surface at the pit site. In conformity with this finding Sadough *et al*. [21] attributed the effect of nitrogen on the passive film formed on the austenitic stainless steel in acidic solution (0.5 M H_2SO_4) to three chemical states of nitrogen; one of them corresponding to nitrogen bonded essentially to chromium in the form of incorporated nitride. This hypothesis is in agreement with results obtained here using NO_3^- anion as inhibitor. By correlation between the data obtained form the present surface study (Fig. 3B) with the above conclusions, we find from Table I, that the Cr/N, Mo/N ratios calculated are identical; namely, 0.95 at the film surface, and 1.20, 0.52 at the film/alloy interface respectively, for 1500 ppm nitrate solutions. The higher ratio for Cr/N than Mo/N may explain why the nitrate inhibitor is effective. However, the improved pitting corrosion resistance induced by the addition of NO_3^- ion to an acidic chloride environment supports the hypothesis of an adsorped layer of chromium nitride on the oxide film [13, 21].

The AES spectrum and depth profile for samples treated with the solution containing 5700 ppm $K_2Cr_2O_7$ are shown in Fig. 4. The spectrum (Fig. 4A) exhibits small peaks for Cr and Fe compared with the spectrum from the film formed in the absence of additive (Fig. 2A). It is evident from the depth profile (Fig. 4B) that chromium, which was considered by Rozenfeld and Maksimchuk [22] as the most effective alloying element for preventing pitting, is the major constituent of the film surface plus Ni. The film in this case is more thick than that formed in the absence of chromate (Fig. 2B). Above a limited thickness (about 4 min sputtering), the iron content rapidly increases and attains, with Cr and Ni, the bulk alloy concentration after 13 min.

In other work [23], in acid chloride solutions, the presence of a certain amount of Cr is essential if Mo alloying is used to improve the pitting resistance of steels. In the absence of Cr, the addition of Mo to the alloy has no beneficial effect.

Moreover, Sugimoto and Sawada [24], found that 20Cr-25Ni-5Mo stainless steel was resistant to pitting in HCl solutions at room temperature. They presumed that tightly adherent surface films composed of Cr(III) oxyhydrated with large amounts of Fe(III) were formed. A Mo(VI) oxide was thought to be present in the form of solid solution with Cr(III) oxyhydroxide in the passive film and thus to contribute to pitting resistance of steel in HCl. Also, they showed that the thickness of anodic passive films formed on the surface of Cr-Ni stainless steels in HCl increased with steel's Mo content. This is consistent with our results plotted in Fig. 4B.

The data obtained by the above author [24] on steels resemble the data obtained by Augustynski [25] who found that the films formed on aluminium immersed in chromate solutions were composed of Cr(III) and AL(III) oxides, together with a significant degree of adsorbed Cr(VI) species. A similar conclusion was reached by Abd Rabbo *et al*. [26] from SIMS data who attributed the uptake of chromium from solution to the reduction of $CrO_4^{2-}/Cr_2O_7^{2-}$ at flaws in the surface film; while a more gradual uptake was associated with penetration of $CrO_4^{2-}/Cr^2O_7^{2-}$ anions through the outer layer of the film.

In agreement with Horvath and Uhlig [27] who found that for Fe-Cr-Ni alloys, pitting resistance was noticed when the Ni content was increased, we found that the Ni/Cr, Mo/Cr ratios calculated at Table II are 0.57, 0.30 at the film surface and 1.18, 0.18 at the film/alloy interface respectively, for 5700 ppm $K_2Cr_2O_7$ solutions. The ratios are clearly higher for Ni/Cr than Mo/Cr which may support the improved pitting corrosion resistance by the addition of $K_2Cr_2O_7$ ions.

The AES spectrum and depth profile for samples treated with solution containing 5800 ppm Na_2MoO_4 are shown in Fig. 5. The spectrum (Fig. 5A) exhibits larger peaks for Cr, Mo and a smaller peak for iron and nickel compared with the spectrum from the film formed in the absence of additive (Fig. 2A). It is evident

TABLE I Cr/N, Mo/N ratios of surface film of 316 stainless steel formed in 30% $H_3PO_4 + 15000$ ppm $Cl^- + NaNO_3$

	Atomic concentration ratios	
	Cr/N	Mo/N
At surface	0.95	0.95
At Fe-interface	1.20	0.52

TABLE II Ni/Cr, Mo/Cr ratios of surface film of 316 stainless steel formed in 30% $H_3PO_4 + 15000$ ppm $Cl^- + K_2Cr_2O_7$

	Atomic concentration ratios	
	Ni/Cr	Mo/Cr
At surface	0.57	0.30
At Fe-interface	1.18	0.18

TABLE III Ni/Cr, Mo/Cr ratios of surface film of 316 stainless steel formed in 30% $H_3PO_4 + 15000$ ppm $Cl^- + Na_2MoO_4$

	Atomic concentration ratios	
	Ni/Cr	Mo/Cr
At surface	0.36	0.79
At Fe-interface	0.65	0.44

from the depth profile (Fig. 5B) that chromium is the major constituent of the film surface and that its profile is relatively flat. Enrichment of Mo is present in the oxide film but is depleted. The film is less thick than that formed in the absence of molybdate (Fig. 2B). These results are in agreement with surface analysis of the passive film on stainless steels reported by others [28, 29].

In view of many investigations carried out [30–33] concerning the beneficial effect of Mo as alloying element and the nature of the molybdate as inhibitor [7, 34, 35], it is intended to try to explain the mechanism of the inhibition effect in the present results.

Charbonnier and others [24, 36, 37] shows that the favourable effect of Mo as alloying element on the pitting resistance of stainless steels has been attributed to the formation of a protective passive surface films containing MoO_4^{2-} ions produced on dissolution of the molybdenum in the early stages of attack. This assumption has been confirmed by work in which the addition of MoO_4^{2-} to the corrosive medium was shown to inhibit pitting of austenitic alloys with and without molybdenum [36, 37]. Also, the passive film formed on Mo-containing steels in acid media have been studied [4, 38–40] by surface analysis. The results of these studies have shown that the resistance of these alloys to localized attack is associated with elimination of active spots on the metal surface through one of these:

(a) formation of hydrated chromium oxyhydroxide
(b) formation of a protective salt layer probably containing $FeMoO_4$
(c) adsorption of bulky polymeric Mo anions at anodic sites.

In another view, some authors [7, 28, 34, 35, 41] suggested that the resistance of stainless steels to localized attack by using molybdate anions as inhibitor are probably associated with the complexity of compounds that Mo can form depending on the experimental conditions. Upon acidification of a molybdate solution, isopolymolybdate may form, for example at pH values (more acidic solutions) ranging between $0.9 < \text{pH} < 1.5$, the easily adsorbed polymeric anion $Mo_{12}O_{41}^{10-}$ becomes the dominant species [41].

Based on the shape of survey analysis shown in Fig. 5A, it is expected that the film formed on the surface of 316 steel in presence of molybdate anions will be enriched in Cr and impoverished in Mo. Depth profile (Fig. 5B) have confirmed this observation. Therefore, the external layers of oxide films of our study and of others [2, 42–45] are depleted of Mo, and this element can be detected only in the internal oxide layers close to the alloy surface.

Recently, the Mo/Cr ratio on the surface of stainless steels has been extensively discussed in the literature [7, 13], where the Mo/Cr ratio has been shown to be of great importance to pitting resistance of these alloys. In conformity with this finding the Mo/Cr ratios calculated in our results (Table III) are 0.79 at the film surface and 0.44 at the film alloy interface for 5800 ppm Na_2MoO_4 solutions. The ratio are clearly higher for molybdate additive concentration, than in the case of dichromate which may explain why the molybdate additive is effective.

From all these facts, we can conclude that the molybdate additive produces a film containing a higher concentration ratios of Mo/Cr, due to better penetration of the easily adsorbed molybdate species ($Mo_{12}O_{41}^{10-}$).

The results of samples treated with solutions containing tungstate are shown in Fig. 6. The relative intensities detected at the surface before sputtering (Fig. 6A) are not the same as those recorded in the depth profiles at the commencement of the sputtering (Fig. 6B). This difference is related to the relative elemental sensitivity factors, to which the atomic concentrations are inversely proportionl. This is quite clear in the case of tungsten, the sensitivity factor for which is 0.08, compared with 0.22 for nitrogen, 0.45 for phosphorous, and 1.0 for chloride. Tungsten, therefore, appears as a very weak signal (Fig. 6A), although it constitutes the most plentiful element on the surface and the second (after iron) within the film (Fig. 6B).

From the results in Fig. 6B which illustrate the presence of a high concentration of tungsten in the film, and knowing that tungstate ions have a clear protective action, it can be concluded that the presence of 5500 ppm concentration of WO_4^{2-} addition is an optimum condition in determining the corrosion resistance of the film. This property must therefore be directly affected by the composition of the film and the relative concentrations of the various species. By comparing the spectrum obtained before sputtering (Fig. 6A) with the spectrum produced after profiling, the latter spectrum exhibits larger peaks for iron and chromium. No significant change is visible in the tungsten signal [7].

With respect to Na_2WO_4, in comparison on the relatively large number of publications describing tungstate as inhibitors for corrosion of various metals, very little basic work was devoted to the understanding of the exact mechanism of its location. Even so, the available information is not always in agreement. Similarly, there is no unity in opinion regarding the oxidizing character of WO_4^{2-} ion. Robertson [46] concluded that the WO_4^{2-} ion is non-oxidizing.

Corrosion inhibition by WO_4^{2-} was attributed to formation of insoluble iron tungstate on the surface of corroding metal. Prior to salt formation, the WO_4^{2-} was assumed to adsorb on the surface [46]. On the other hand, some authors [47, 48] gave results suggesting the partial reduction of the WO_4^{2-} ion. Lower valent W oxides were considered to be incorporated into the corroding metal oxides to yield a passive film [49].

Specific adsorption of the WO_4^{2-} ion on the metal surface was suggested by some authors [50, 51]. In the presence of aggressive anions (e.g. Cl^-) competitive adsorption on active sites was assumed to occur. Similarly the same behavior may be occur when added WO_4^{2-} ions as inhibitor to improve the corrosion resistance of stainless steel 316 in H_3PO_4-Cl^- solutions.

4. Conclusion

1. The composition, structure, properties, and thickness of the passive film formed on the alloy surface plays an important role in determining the pitting resistance of 316 stainless steel in 30% H_3PO_4-Cl^- solutions in the absence and presence of oxyanions $NaNO_3$, $K_2Cr_2O_7$, Na_2MoO_4 and Na_2WO_4

2. Results of the correlation between the nature of these oxyanions as inhibitors and the beneficial effect of its alloying elements e.g. N, Cr, Mo and W can clarify the inhibitive mechanism of these additives.

3. Nitrate seems to be a good pitting inhibitor when compared to other oxyanions. N-metal (essentially Cr) bonds in the form of nitride are present in the passive film formed.

4. Dichromate also improve the pitting resistance when the Ni content was increased on the surface of the alloy. The Ni/Cr ratio has to be of great importance.

5. Molybdate and tungstate competitively adsorbed with Cl^- and block Cl^- adsorption. Molybdate additive produces a film containing a higher concentration ratios of Mo/Cr, due to better penetration of the easily adsorbed molybdate species ($Mo_{12}O_{41}^{10-}$).

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