ON THE ROLE OF TUNGSTEN OR MOLYBDENUM IN IMPROVED PASSIVATION TO AUSTENITIC STAINLESS STEEL IN PHOPSPHORIC ACID POLLUTED BY SULFIDES

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Abstract

The study passive state behavior of 18Cr-10Ni, 16Cr-14Ni-4W and 18Cr-10Ni-1.5Mo austenitic stainless steels has been performed in -phosphoric acid polluted by sulfides ions using electrochemical techniques, X ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS).
The addition of W or Mo. to austenitic SS induced a decrease of dissolution of rate and affects the nature of passive film. The passive film formed in an overlap of two layers with the external layer rich in W (VI), Mo (VI) and non-metallic elements (O and P). The improved resistance of SS alloys with W is related to formation the film rich in oxide of chromium and tungsten with a little concentration of sulfide. The role of Mo is attributed to formation the film of oxide chrome and molybdenum sulfide. It assumed that Mo prevents the formation of ferrous sulfide.

Intoduction

The corrosive effect of sulfide ions occurs in various industrial installations. Recently the exploitation of black phosphates (new mines in south Morocco) containing sulfides induced degradation in the plant used for the production of phosphoric acid by a wet process.[1-6]

Several studies have shown the aggressive character of sulfide ions towards metal and alloys in different media. In previous paper, we showed that sulfide ion increase the corrosion rate of stainless steel[1-2] and nickel[3] and this harmful effect is attributed to adsorption of sulfide ions on the material surface. Similar results were obtained in other sulfuric acid for nickel and nickel based alloys.[7-8] The effect of sulfide ions is linked to formation of a monolayer that presents passivity,[7-8] or to the formation of ferrous sulfide (FeS) with the specific adsorption of SH^-.[9-11]

To improve the corrosion resistance of stainless steels in various media, elements are frequently added to the alloy. In phosphoric acid without sulfide ions, the beneficial effect of molybdenum addition has been demonstrated;[12-15] this element promotes the establishment of passivity. Tungsten additions also improve the corrosion resistance of stainless steel, particularly in the presence of abrasive.[14-15]

Our purpose in this paper is to study the influence of additions of molybdenum or tungsten to austenitic stainless steel on their behavior in phosphoric acid polluted by sulfide ions. With this in view, films grown in the passive state were analyzed using XPS and SIMS techniques.

Experimental Methods

The experimental stainless steels investigated in the present study were prepared in a vacuum furnace. Solution treatment was performed by heating in nitrogen at 1150 °C for 30 min followed by water quenching. Their chemical compositions are given in Table 1.

Table 1. Chemical composition (wt %) of the stainless steels tested.

Alloy	C	Mn	Si	Ni	Cr	Mo	W	S
18-10	0.021	1.78	0.58	9.60	18.59	–	–	0.0034
16-14-4	0.005	0.30	0.41	14.10	16.50	–	4.81	0.002
18-10-1.5	0.023	1.77	0.63	9.56	18.72	1.52	–	0.0032

Stainless steels have a fully austenitic structure and contain above 0.2% ferrite. The material was shaped as a thin, cylindrical disk with a section of 1 cm^2. Prior to polarization, the specimen surfaces were polished mechanically with wet silicon carbide (SiC) paper to 1000 grade, digressed with ethyl alcohol, washed in distilled water, and dried with blowing warn air.

This study was carried out in 40% wt H_3PO_4 containing impurities: 500 ppm Cl^- and 5 ppm S^{2-} at 60 °C. Sulfides were added to the solution using sodium sulfide of high purity.

To accelerate the formation of passive film, potentiostatic curves were obtained by applying a potential step of +600 mV/S.C.E, and registering the resulting current intensity for testing time of 2 h, with an AMEL electrochemical set. Potentials were measured with respect to a saturated calomel electrode (S.C.E).

Valence of the alloy elements in the passive film was investigated by means of XPS spectroscopy. The instrument was an ESCA LAB MK2 (V. G. Scientific). The samples were irradiated with a Mg K_α radiation. Successive sputtering by means of argon ion bombardment did analysis at different depths. The photoelectron spectra on the $2p_{1/2}$ and $2p_{3/2}$ levels for Fe, Cr, Ni, P, and $3d_{5/2}$ levels for Mo, W, and 1s level for O and C were measured. The distribution profiles of elements in the passive films were obtained by SIMS using an IMS 300 Camera analyzer. The diameter of the circular zone analyzed was 25 μm. Profiles of non metallic elements were obtained in an inert atmosphere by bombardment with an argon ion gun. Metal signals were maximized by keeping the oxygen in the analysis chamber under ultrahigh vacuum (The system was evacuated to the 10^{-9} torr range).

Results and discussion

1. Electrochemical behavior on the passive

Passive films were grown by polarization at +600 mV/ S.C.E for immersion of samples in 40 wt % H_3PO_4 + 500 ppm Cl^- + 5 ppm S^{2-}. Figure 1 shows the current-time curves of the three steels studied. The curves have approximately the same features: current densities decrease quickly and take low values after a length of time, which depends on the steel composition.
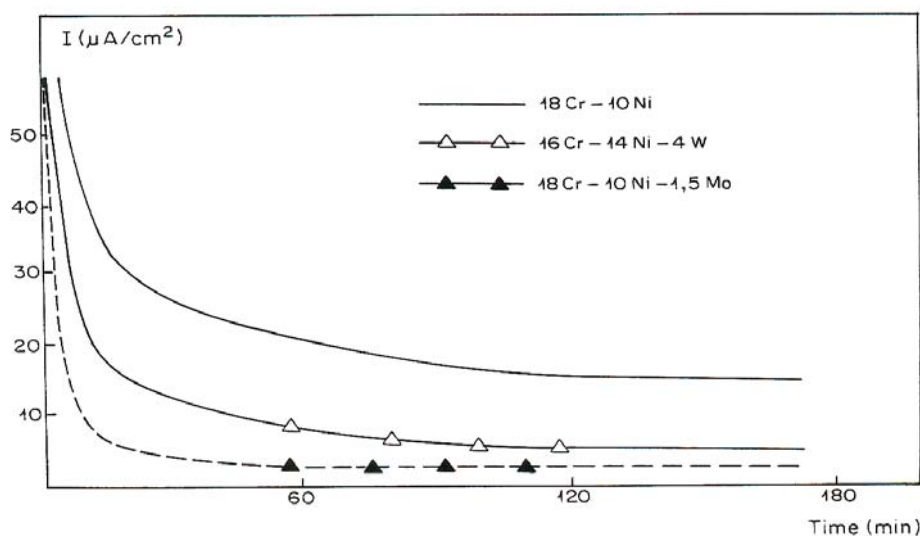
Figure 1. Plot of current against immersion time in phosphoric medium for different alloys; applied potential +600mV/S.C.E.

The presence of molybdenum in the steel accelerates a great deal the establishment of the stationary state, achieved after 50 min for 18-10-Mo steel, 120 min for 16-14-W steel, and 130 min for 18-10 steel. In addition Mo and W decrease the dissolution rate at the stationary passive state: 2.8 µA/cm^2 for 18-10-Mo steel, 5 µA/cm^2 for 16-14-W steel and 14.4 µA/cm^2 for 18-10 steel. It can be seen that alloying with molybdenum is much efficient that alloying with tungsten in improved passivation. The results are in good agreement with previous measurement obtained in corrosion-abrasion condition.[14-15] So, in this very corrosive medium, where sulfide ions enter into competition with hydroxyl groups, which usually induce passivity, and lead to a structure with defects, the presence of tungsten and especially of molybdenum in the alloy facilitates the establishment of passivity and induces layers which are more protective.

2. Spectroscopy study

Passive films grown after 4 hours at +600 mV/S.C.E on the three stainless steels were analyzed using XPS and SIMS. The layer was analyzed at various depths after bombardment with argon ions.

### Composition of the passive film: 18Cr-10Ni SS

The XPS spectra thus obtained are shown in the same figure to make comparison easier (figure 2). The Cr 2p peaks (figure 2a) observed at 577 eV (Cr 2p$_{3/2}$), and 587 eV (Cr 2p$_{1/2}$) in the passive film are generally attributed to Cr$_2$O$_3$. In the deep zone peaks appears at 574 eV corresponding to the metallic chromium of the substrate.

Iron compounds are minor constituents of the passive film. In the superficial zone the intensity of the Fe 2p peaks is too weak to be analyzed accurately (figure 2b); nevertheless the wide peaks observed about 707-709 eV (Fe 2p$_{3/2}$) and 722-724 eV (Fe 2p$_{1/2}$) can be attributed to sulfide and probably sulfate of iron rather than oxides which has peaks at higher energies. In the deep zone the spectrum of iron 2p presents two main peaks at 711 eV (Fe 2p$_{3/2}$) and 725 eV (Fe 2p$_{1/2}$) characteristic of Fe^{3+} probably in the form of Fe$_2$O$_3$, Fe$_3$O$_4$ [3,16] could also be present in the layer; these peaks coexist with two others at 707 eV and 721 eV attributed, in the superficial zone, to ferrous sulfide.[3-5,16,19]

The XPS signal of nickel was too weak to be analyzed exactly; the nickel content of the film is very low, less than a few percent in the superficial zone. The oxygen 1s

spectrum (figure 2c) presents two broad peaks at 531 eV and 532.5 eV. The second one is preponderant on the surface, and may be attributed to the oxygen of adsorbed molecules such as CO (532 eV) and H_2O (533 eV) because of contamination, or to the OH group (531.9 eV) in hydroxides.[16-18] The first one is representative of oxygen bound to a metal in an oxide,[3-5,18-19] in the deep zone the intensity of the peak at 532.5 eV decreases and only that corresponding to oxides exists.

The spectrum of S 2p (figure 2d) in the surface zone exhibits two peaks: the main one at 169 eV indicates the presence of sulfates and the other at 162.2 eV sulfides[4-5,16,19] in small quantities. In the deep zone the sulfate form disappears and sulfur is present only as sulfide.

(a)

(b)

(c)

(d)
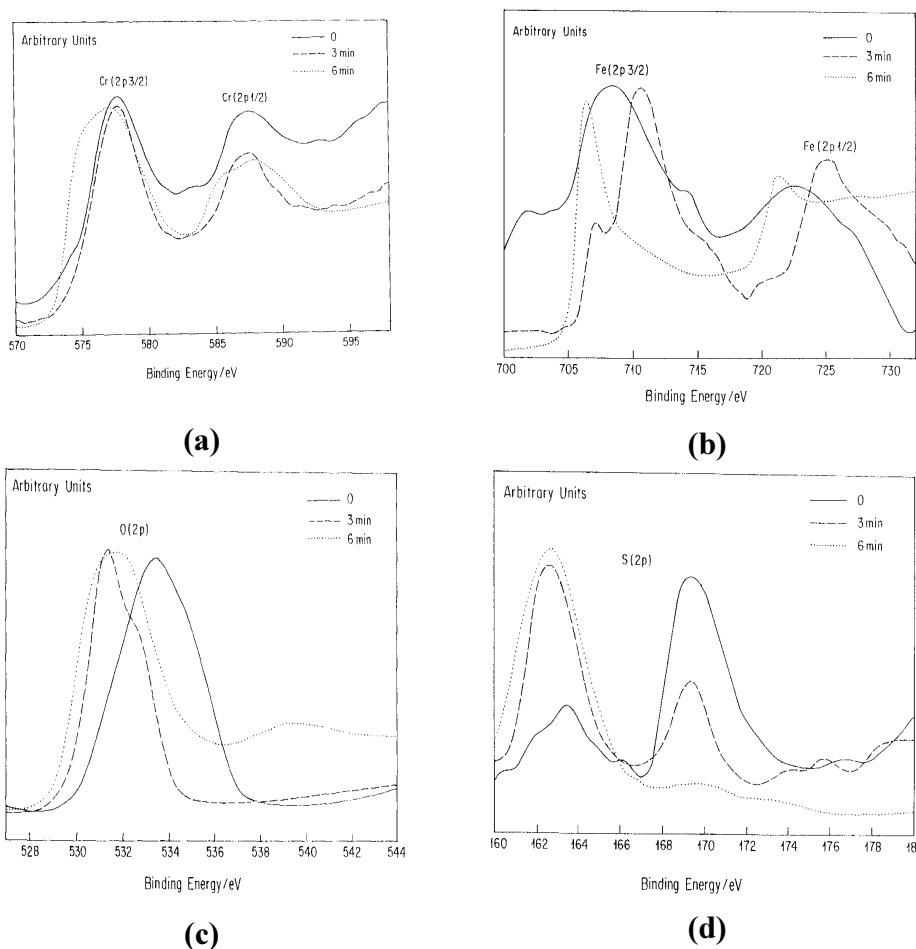
Figure 2. ESCA spectra at various depths of film grown on 18Cr-10Ni alloy in phosphoric acid polluted by sulfides; at the surface (o), after bombardment with argon for 3 min and 6 min. (a) Chromium spectrum. (b) Iron spectrum. (c) Oxygen spectrum. (d) Sulfur spectrum.

So, the passive film grown on the 18Cr-10Ni steel, in this very corrosive medium, is mainly constituted by Cr_2O_3 with a little iron sulfide in the superficial zone.

SIMS analysis (figure 3) shows that the profiles iron, chromium and nickel have approximately the same features: the signal intensity of these elements is low at the surface and increases in the deep zone.
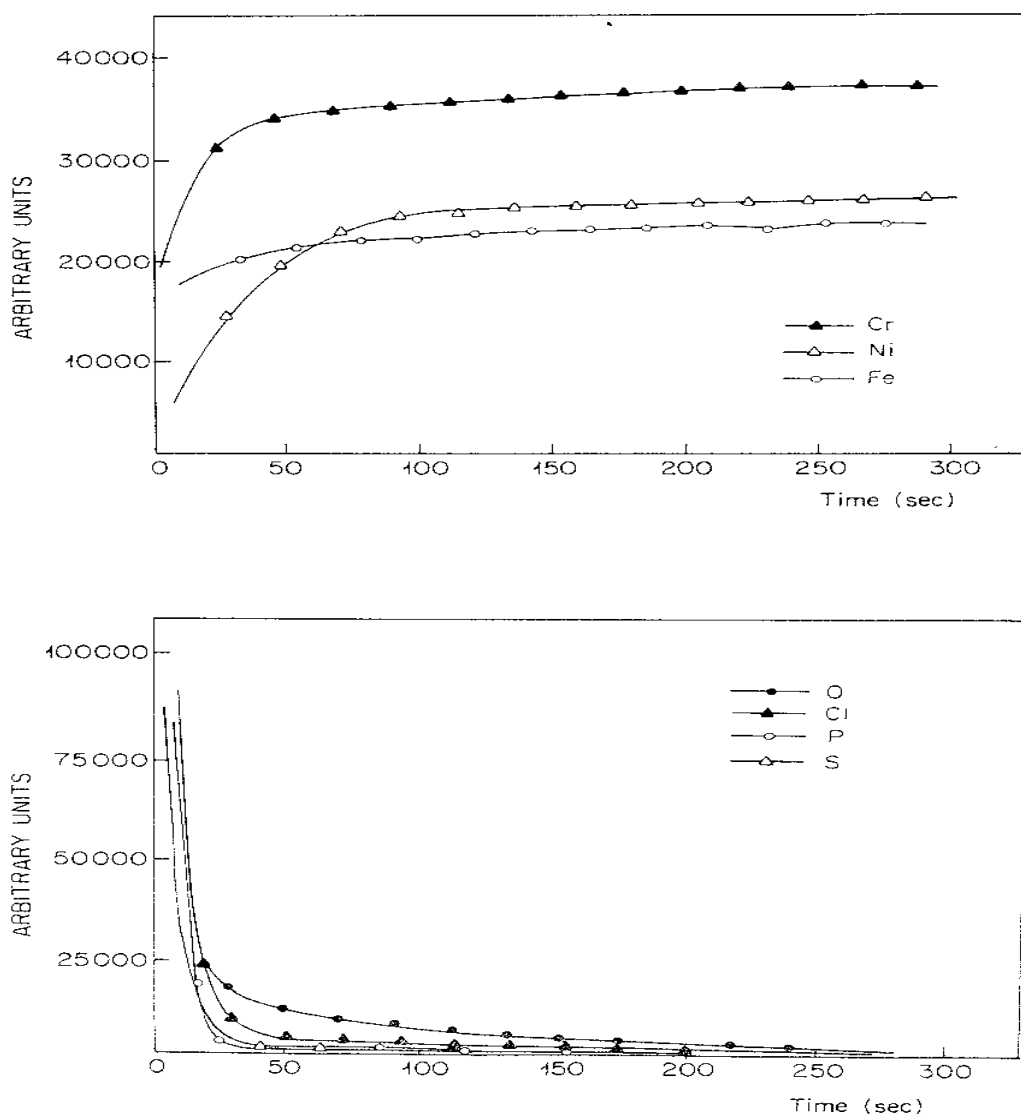
Figure 3. SIMS distribution profiles of film grown on 18Cr-10Ni stainless steel after 4 h in phosphoric acid medium with sulfide as impurity.

The superficial (external) layer is rich in non-metallic elements and particularly in oxygen whose concentration decreases from the surface to the film/metal interface (figure3). Sulfur is also present in the layer; which indicates the formation of sulfides, oxysulphides or sulfates as well as metallic oxides. Likewise the superficial layer contains chlorides and phosphates. This analysis confirms that, the nickel is not present at a significant level in the passive film.

These results suggest that the passive film consist of a mixture of Cr and Fe oxide, iron sulfide and to a small extent metallic phosphate. The high corrosion rate observed for 18Cr13Ni can be associated with the amount of ferrous sulfide.[9,20-21] The presence of iron sulfide in the passive layer mixed with chromium oxide, leads to a structure with defects because of the non-stoichiometric character of this sulfide.[20-21]

Role of tungsten: 16Cr-16Ni-4W S S

No change is observed in the spectra of chromium and oxygen by comparison to those presented for 18Cr-10Ni steel.

The spectrum of iron (figure 4a) presents, in the surface zone, peaks characteristic of oxide form (711 eV and 725 eV) and these attributed previously to Fe_2O_3 and Fe_3O_4 form with a possible contribution of metallic iron (substrate) at 707 eV and 721 eV.

The tungsten $4d_{5/2}$ spectrum (figure 4b) shows the peaks at 250 eV and 263.5 eV characteristic of W^{6+} probably in WO_3[15,23,24] at the surface.

So, the presence of tungsten in the alloy leads to WO_3 in the passive layer in addition to the constituents observed in the case of the 18Cr-10Ni stainless steel. The presence of WO_3 reinforces the stability of passive oxide.

Figure 5 shows the depth-composition profile (SIMS analysis) of the film grown on the 16Cr-14Ni-4W: the external layer is enriched in tungsten and chromium, with very low nickel content. The most interesting feature of profile constituent from stainless steel containing W is the existence of the very low amount of sulfur.

In addition, the chromium profile suggests that the chromium content of the superficial layer is high. It is well that for given chromium content in SS, the addition of W has strongly beneficial influence of passivity. Tungsten addition to stainless steel, causes the presence of WO_3 in the superficial zone of the passive layer; this compound, insoluble in acid medium, reinforces the protection of Cr_2O_3.
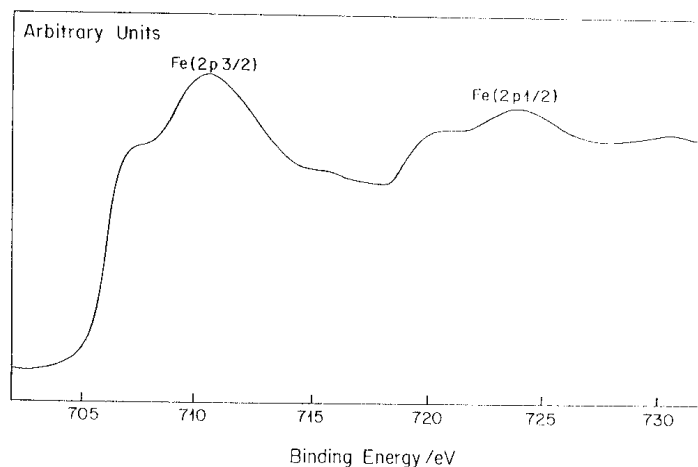
(a)
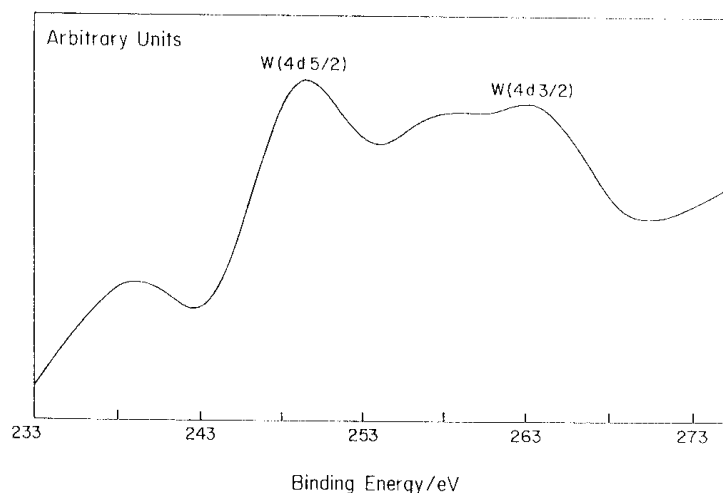
(b)

Figure 4. ESCA spectrum of film grown on 16Cr-14Ni-4W alloy in phosphoric medium polluted by sulfides: (a) Iron spectrum. (b) Tungsten spectrum.

Role of molybdenum: 18Cr-10Ni-1.5Mo S S

The spectrum of $Cr2p_{3/2}$ is the same as that observed for 18Cr-10Ni steel: Cr_2O_3 is the main component of the passive film. In the superficial zone, the spectrum of iron (figure 6a) is different from that described for the stainless steel without molybdenum; it does not present peaks attributed to iron sulfide, only peaks at 711 eV (Fe $2p_{3/2}$) and 725 eV (Fe $2p_{3/2}$) characteristics of Fe_2O_3.

The S 2p spectrum (figure 6b) shows a single peak at 162.2 eV attributed to sulfide form MoS_2.[23,24]
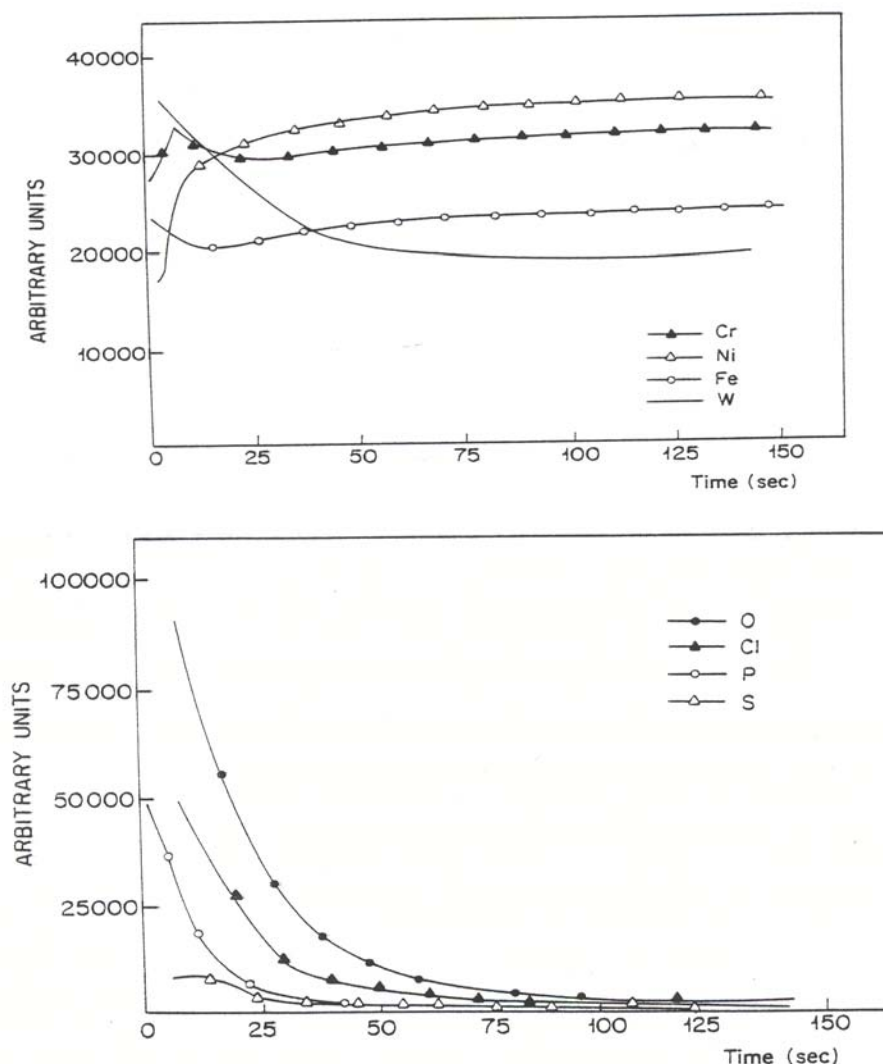
Figure 5. SIMS distribution profiles of film grown on 16Cr-14Ni-4W stainless steel after 4 h in phosphoric acid medium with sulfide as impurity.

Several molybdenum compounds are present in the layer. The different peaks of Mo3$d_{5/2}$ and 3$d_{3/2}$ (figure 6c) can be attributed: 232 eV and 235 eV to MoO_3,[25,26] 228.5 eV and 232 eV to MoO_2[27-28] and /or to MoS_2[23-24] in keeping with that of sulfides shown by the S 2p spectrum.

Thus, the passive film grown on the 18Cr-10Ni-1.5Mo steel is constituted mainly by Cr_2O_3 with minor constituents like iron oxide, and of molybdenum oxide or sulfide.
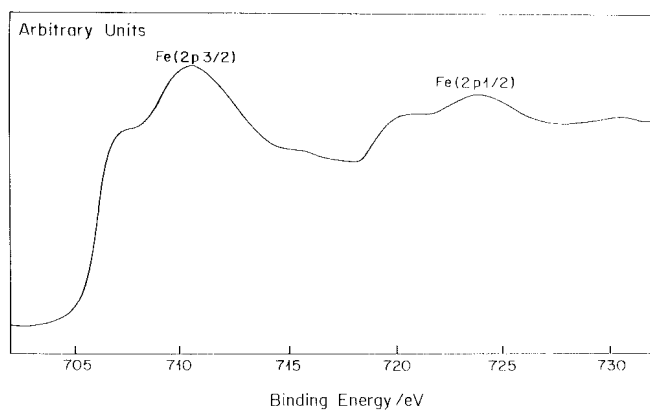
(a)
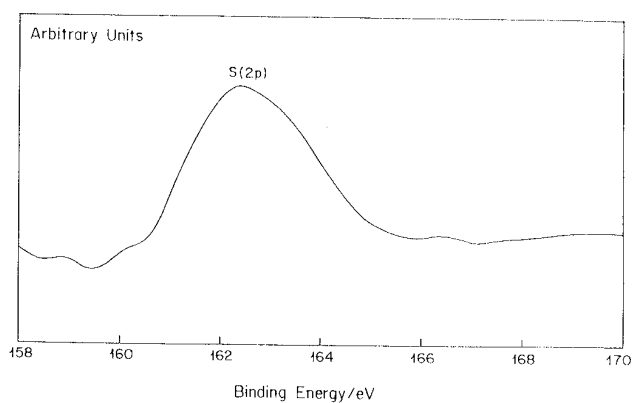
(b)
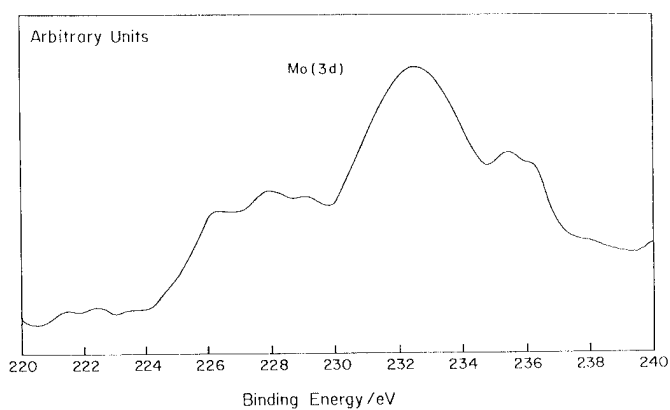
(c)

Figure 6. ESCA spectrum of film grown on 18Cr-10Ni-1.5Mo alloy in phosphoric medium polluted by sulfides a) Iron spectrum. b) Sulfur spectrum. c) Molybdenum.
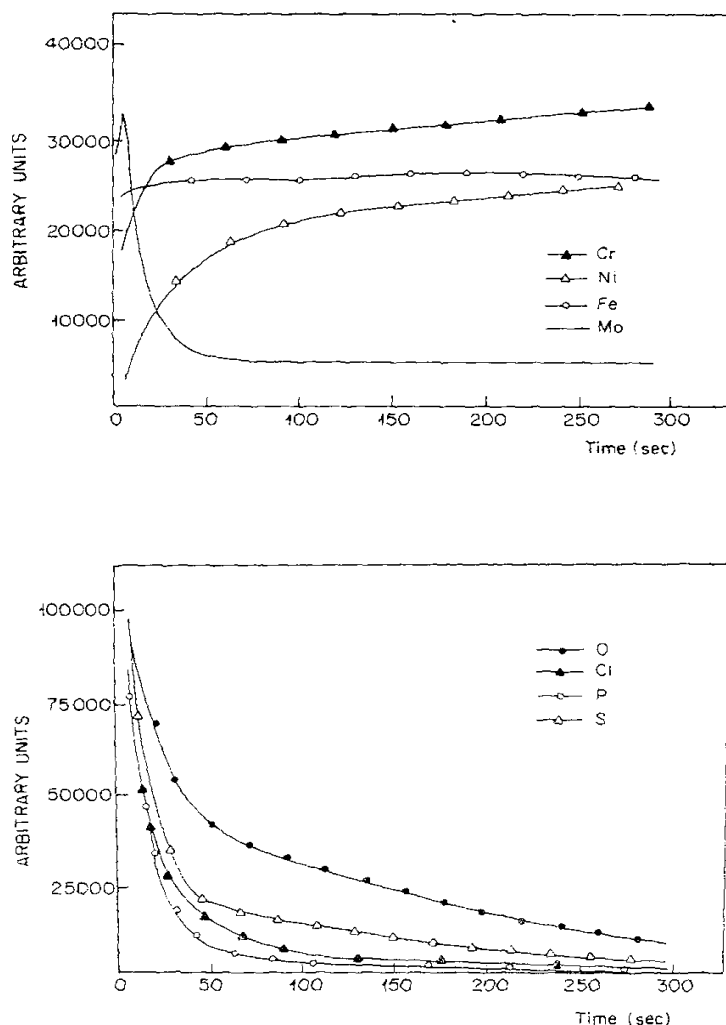
Figure 7. SIMS distribution profiles of film grown on 18Cr-10Ni-1.5Mo stainless steel after 4h in phosphoric acid medium with sulfide as impurity.

The element profiles of the 18Cr-10Ni-1.5Mo passive film (figure 7) are not very different from those observed on the stainless steel without molybdenum. However, the oxygen content is height in the internal layer of the passive film and that external layer is enriched in molybdenum and the nickel content is practically equal to zero.

This alloyed element induces the formation of molybdenum oxides, which are very protective as well as insoluble molybdenum sulfide rather than iron sulfide.

The thickness of the passive films was estimated from the abrasion time by sputtering the surface with argon ions (SIMS analysis) assuming that the erosion rate was constant. Films are very thin, their thickness are of the order of 10 nm, and are

difficult to measure with precision; it seems that the one formed on the 18Cr-10Ni-1.5Mo is a little thicker than the two others.

Conclusion

In order to explain the effect of improved passivation by added W or Mo to austenitic stainless steel in phosphoric acid, electrochemical measurement, SIMS and XPS analysis were performed:

-Passivity is improved by addition of W or Mo in steel. Molybdenum addition to stainless steel appears to be more efficient than tungsten addition in reducing the steel dissolution rate.

-The presence in the solution of sulfides appreciably modifies the composition of passive layers. A superficial layer rich in iron sulfide characterizes the passive film.

-The alloyed elements affects to nature and composition of passive film: the passive film formed is an overlap of two layer with the external layer rich in Mo (VI) or W (VI) and metallic phosphate (probably iron phosphate)

-The protective role of the film formed on W alloyed SS may be results from the formation of mixed oxide of chrome and tungsten with very little amount of sulfur The addition of W have strongly effect on sulfur content in passive film

-The role of molybdenum it is attributed to formation of oxide chrome and molybdenum sulfide. This alloyed element induces the formation of molybdenum oxides, which are very protective as well as insoluble molybdenum sulfide rather than iron sulfide.

Acknowledgements

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Povzetek

Opravljene so bile raziskave o obnašanju 18Cr-10Ni, 16Cr-14Ni-4W in 18Cr-10Ni-1.5Mo pasiviziranih austenitnih jekel v fosforjevi(V) kislini onesnaženi s sulfidnimi ioni. Dodatek volframa in molibdena povzroči počasnejše raztapljanje in vpliva na naravo pasivnega sloja. Izboljšano odpornost povzroča nastanek sloja, bogatega s kromovim(VI) in volframovim(VI) oksidom. Molibden povzroča nastajanje sloja kromovega oksida in molibdenovega sulfida ter preprečuje nastanek železovega sulfida.