

Figure.6. The recorded intensities of O²⁻, OH⁻, N(1), N(2) and N(3) signals versus time of polarization for the Fe17Cr13Ni0.15N alloy.

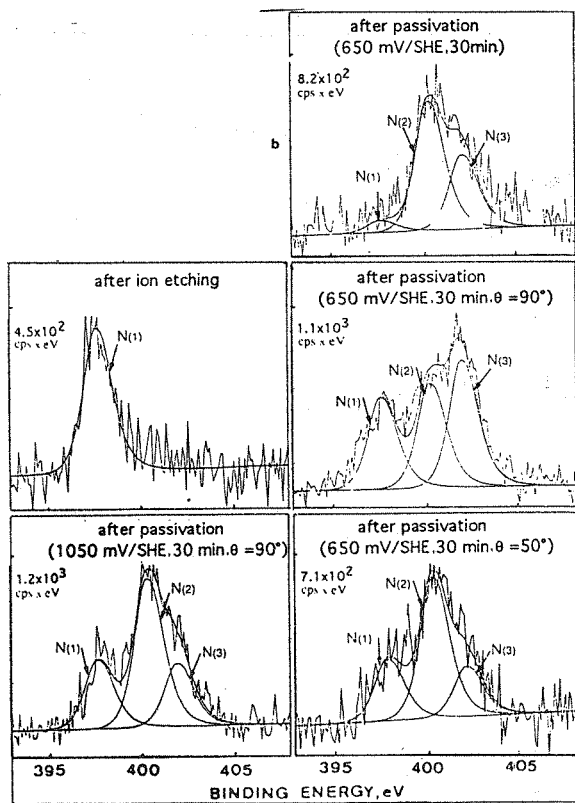


Figure. 4. continued

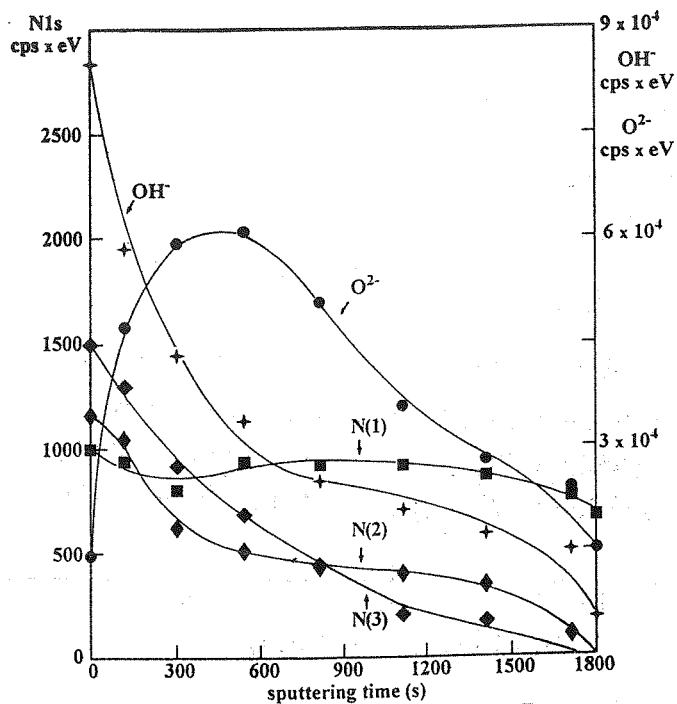


Figure.5. XPS sputter depth profile for the passive film formed at 650 mV/SHE (30 minutes) on the Fe17Cr13Ni0.15N.

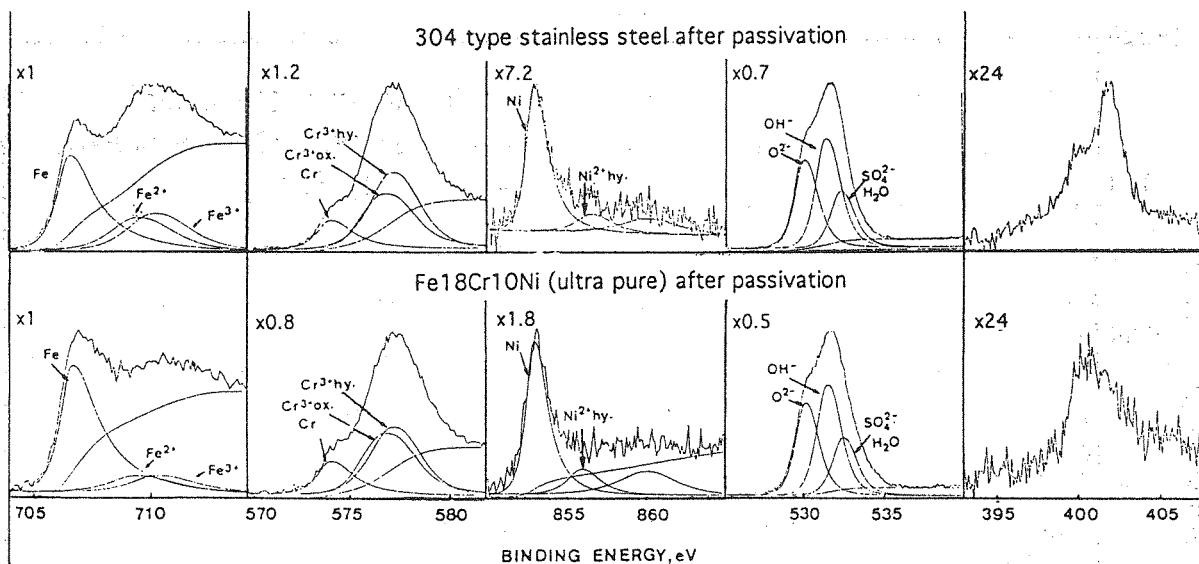


Figure. 3. continued

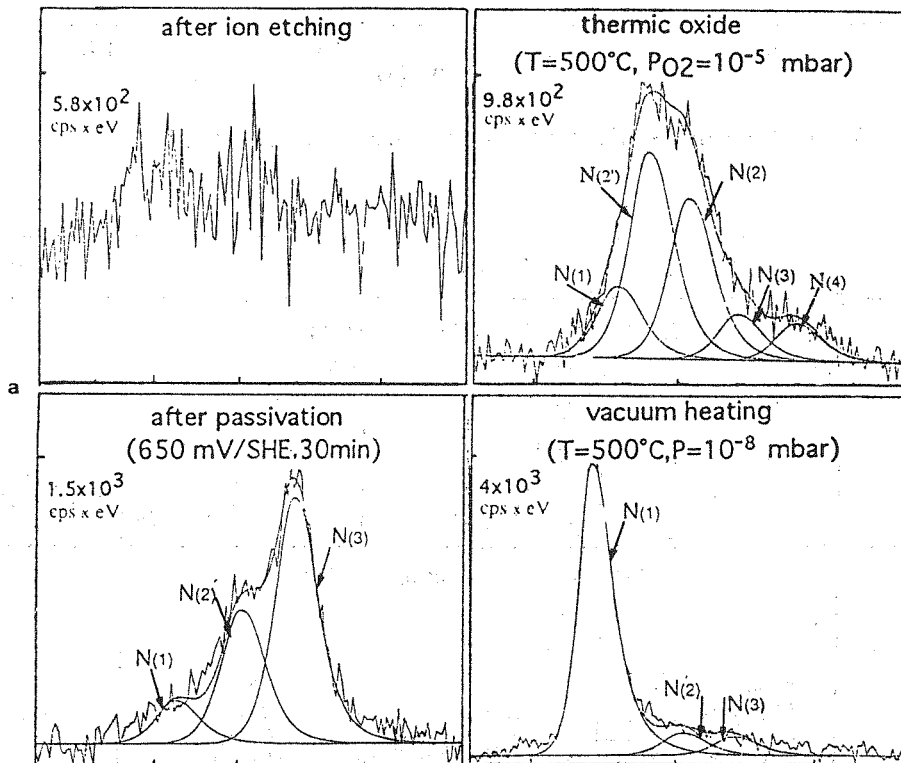


Figure. 4. Curve fitting of the N1s spectra: of (a) the 304 type alloy, (b) Fe18Cr10Ni (ultra pure) alloy, (c) Fe17Cr13Ni0.15N Alloy
 [(CPS) Counts Per Second, (θ):take- off of angle the electrons]

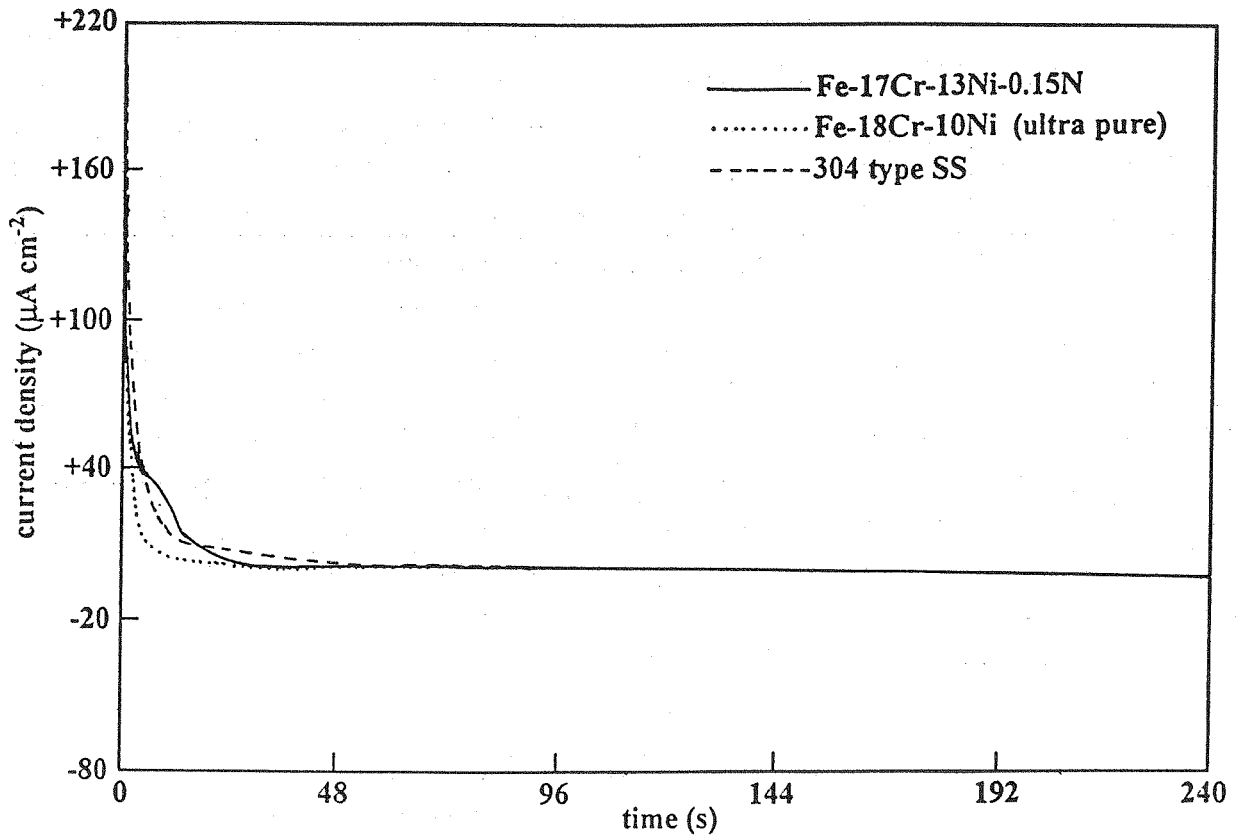


Figure. 2. Potentiostatic curves for the three alloys in 0.5M H₂SO₄

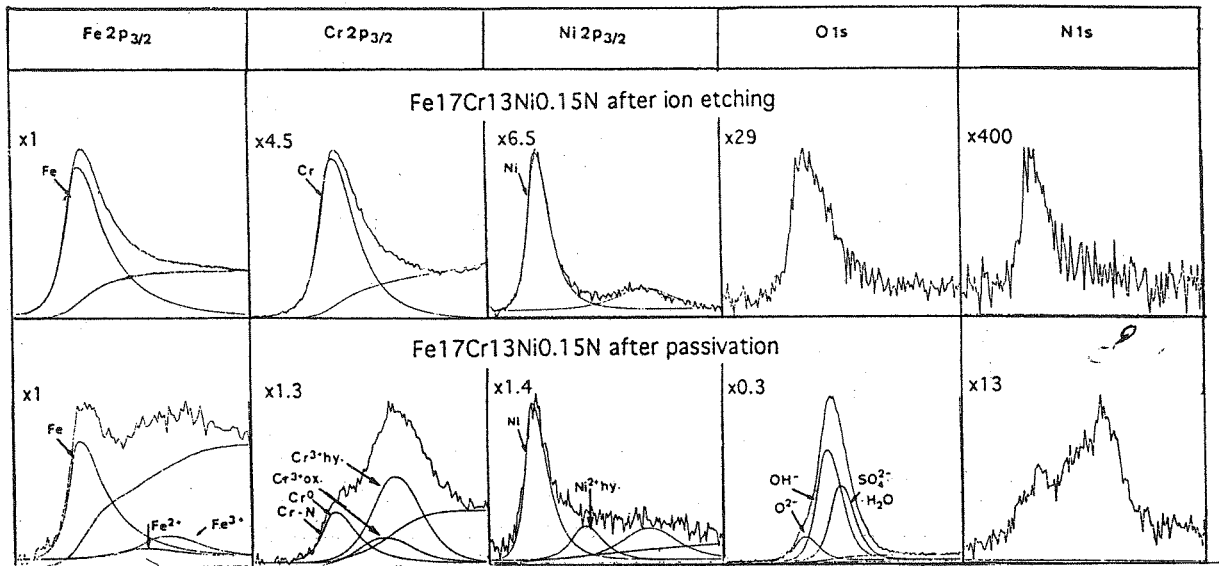


Figure. 3. XPS spectra recorded at a take-off angle of 90°
(The curve fitting of the N1s spectra is shown in Figure 4)

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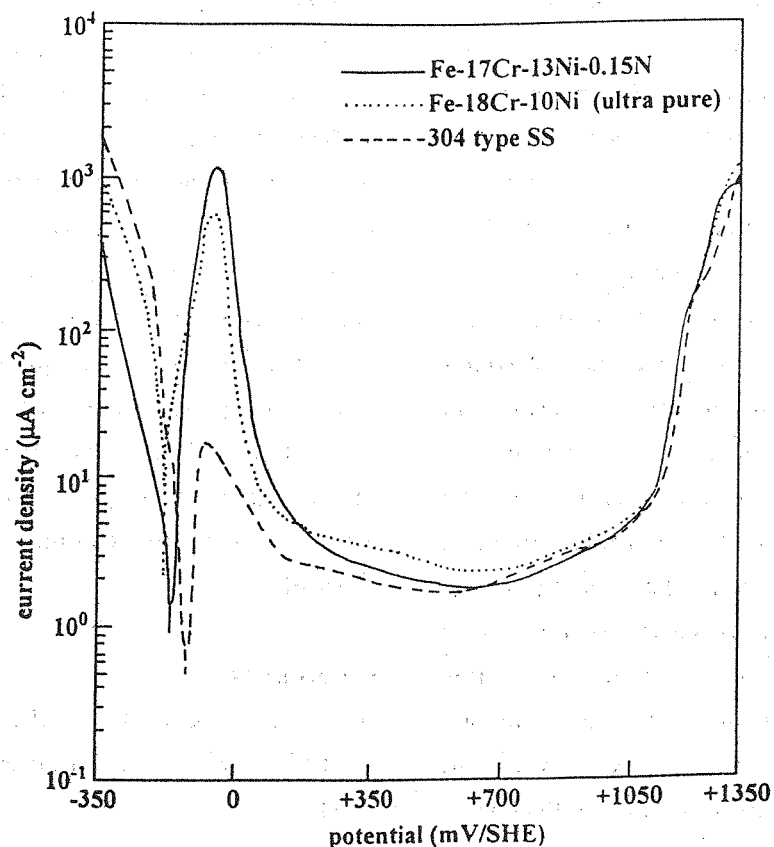


Figure. 1. Potentiodynamic curves for the three alloys in 0.5M H₂SO₄ (1mV/sec)

fig. 4c. The results suggest that the N(3) component and SO_4^{2-} are present on the passive film surface. An hydroxyde layer forms the outer layer of the passive film and contains a mixture of Fe and Cr hydroxydes, hydrated oxydes, and also the N(2) and N(3) components, while the oxide layer is located in the inner part of the film. This oxide (Fe^{3+} and Cr^{3+}) layer contains some N(2) and is located over N(1) as islands at the alloy/ passive film interface.

In order to investigate the effect of time of polarization and potential on the segregation of nitrogen in the passive film, passivation experiments were carried out for the Fe17Cr13Ni0.15N alloy at two different potentials, 650 and 1050 mV/SHE, for 1,15,30 and 120 minutes. The N1s XPS spectrum recorded after 30 minutes at 650 mV/SHE and after 30 minutes at 1050 mV/SHE are shown in fig 4c. The recorded intensities of OH, O^{2-} , N(1), N(2) and N(3) versus time of polarization are plotted in fig 6. Inspection of the curves reveals that the intensity of the N(1) signal decreases with the time of polarization for the first ~ 15 minutes and then becomes constant. The O^{2-} signal first increases, and becomes constant after ~ 15 minutes of passivation. These results are consistent with the view that N(1) is associated to nitride forming at the alloy/ passive film interface during passive film growth and that the growth of the passive film covering the nitride causes the attenuation of the signal emitted by N(1) at the interface. The N(1) signal becomes constant when the passive film has reached a stationary thickness.

The intensity of N(2) increases with the time of polarization for the first ~ 15 minutes and then decreases for 30 minutes and then becomes

constant; the variation of N(3) is similar to N(2) for 650 mV/SHE but for 1050 mV/SHE N(3) increases with the time of polarization until thirty minutes and then decreases. The large scatter in the N(3) intensity suggest that contamination of the solution by a nitrogen containing species may be, at least in part, responsible for the presence of N(3) on the passive film surface.

4. Conclusions

The electrochemical behaviour and surface composition of Fe17Cr13Ni0.15N stainless steel have been investigated with special emphasis on the role of nitrogen. Nitrogen contained in the alloy does not influence markedly on the polarization of the alloy.

After passivation of the alloy three chemical states of nitrogen are detected: the high and intermediate binding energy peaks are assigned to nitrogen species located at the surface of the passive film, and are produced via reaction with the electrolyte. The peak at low binding energy corresponds to N-metal (essentially Cr) bonds under the form of nitride, present in the inner part of the passive film near the passive film/ alloy interface. This nitride phase is formed by anodic segregation of the nitrogen contained in the alloy, during the dissolution stage preceding passivation.

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detected on the three alloys after passivation (fig 4). The fact that they are detected even on the ultra-pure alloy with a nominal nitrogen content less than 10 ppm indicates that these species may come not only from the bulk nitrogen but also from nitrogen containing species present at trace level in the solution.

Complementary experiments have revealed that N(2) and N(3) are also formed when the nitrogen atmosphere in the glove box is replaced by argon, showing that these species do not come from reaction with gaseous nitrogen or nitrogen dissolved in the electrolyte.

For comparison between wet and dry oxidation an oxide was formed on the 304 type stainless steel in pure oxygen at 500°C ($P_{O_2}=10^{-5}$ mbar) in the preparation chamber of the XPS spectrometer. The spectrum shows (fig 4a) that the intensity of the N(3) peak on the oxide layer is much lower than the intensity observed after the passivation experiments which supports the view that this species is formed by reaction with the electrolyte. It is noted that two new peaks were detected after dry oxidation: one at 399.2 which may correspond to nitrogen bonded to H (9,12,13) and the other at 404eV which may correspond to nitrogen bonded to oxygen (9). The chemical state of nitrogen segregated on the alloy surface during high temperature annealing in UHV was also investigated on the 304 alloy. After cleaning the surface by argon ion sputtering, the alloy was heated during 60

minutes in ultrahigh vacuum in the preparation chamber of the XPS system at $T=500^\circ\text{C}$. The N1s spectrum is shown in fig 4a. An intense N1s signal at the position of N(1) is observed. It corresponds clearly to N-metal bonds formed by surface segregation of bulk nitrogen.

To aid in locating the positions of the different nitrogen species in the passive film, composition depth profiles were recorded by ion sputtering and XPS analysis. The results are shown in fig. 5 for the N-bearing alloy. The XPS signal emitted by O^{2-} in the passive film is shown as an indicator of the depth scale during argon sputtering. For the three alloys, the OH/O^{2-} intensity ratio decreases with sputtering time, confirming that the hydroxide layer constitutes the outer part of the film. The slow decrease of the intensity of the N1 peak at low binding energy (397.7eV) corresponding to N-metal bonds, indicates that the nitride is present in the inner part of the passive film near the passive film/ alloy interface.

The results for N(2) and N(3) at different depths in the passive film show the high binding energy nitrogen species to be mainly at the passive film surface, confirming that it is produced at least in part via reaction with the electrolyte.

Angle dependent XPS measurements of the N1s region were carried out in order to obtain additional information on the location of N(1), N(2) and N(3) in the passive film. The spectra for two take off angles, 90° and 50° , are shown in

for the Fe17Cr13Ni0.15N alloy as well as for the ultra pure and the 304 type alloys. The chromium signal was resolved into chromium oxide Cr^{3+}ox (Cr_2O_3 type) and chromium hydroxide Cr^{3+}hyd ($\text{Cr}(\text{OH})_3$ type) (7). Nickel oxide is not detected in the passive films of the three alloys, in agreement with other reported results (7,8).

The oxygen (O1s) region clearly shows the presence of the oxide (O^{2-}) and hydroxide (OH^-) states. A third peak is present corresponding to oxygen in H_2O and SO_4^{2-} ions. These results are in agreement with XPS analysis of the passive film on austenitic stainless steels reported by others (8). It is observed here that the O^{2-} signal is lower on the alloy with nitrogen.

For the clean, unpassivated Fe17Cr13Ni0.15N alloy the N1s spectrum, recorded after 10 minutes of ion etching, shows a N1s signal at 397.6 eV. After passivation the nitrogen XPS signal is considerably more intense. This result indicates that nitrogen is enriched at the surface and incorporated in the passive film and the previous observation of the lower O^{2-} signal is an indication that the nitrogen enrichment in the film takes place at the expense of the oxide content.

In the $\text{Cr}2p_{3/2}$ spectrum of the nitrogen containing alloy a broad intense peak at low binding energy is believed to be associated with chromium in the underlying alloy and chromium located in the film and bonded to nitrogen (6). The intensity of this peak is lower for the ultra

pure and 304 type alloys.

In an attempt to obtain a clearer picture of the chemical states of nitrogen in the passive film, the N1s spectra were fitted by three peaks. The fitted spectra are shown in fig 4. On the basis of previously reported results (6) the peak located at low binding energy (N(1) at 397.7 ± 0.1) is associated to nitride incorporated in the passive film. A significant N(1) peak is detected only on the alloys with bulk nitrogen (i.e. the Fe17Cr13Ni0.15N and the 304 type stainless steel which contains 0.04% of nitrogen). The intensity of N(1) is higher for the alloy with higher N content. This observation confirms that N(1) originate from bulk nitrogen. The peak located at a higher binding energy (N(2) at $400.2 \pm 0.1 \text{eV}$) may originate from N-H or N-O (9). The third peak located at an even higher binding energy (N(3) at $402 \pm 0.1 \text{eV}$), originates from nitrogen which may be under the form of NH_4^+ (9). Similar N1s binding energy (399.9 and 402.5eV) have been reported for the molecular adsorption of inhibitors ($-\text{NR}_3$ and $-\text{N}+\text{R}_4$) on the gold surfaces (10) and for N_2H_4 on Fe(111) (11). The results for the N1s XPS spectra at different depths in the passive film on the alloy show that the high binding energy species disappear very rapidly upon ion sputtering. This confirms the location of these species to be at the passive film surface and supports the view that they are produced by reaction with the electrolyte. The peaks N(2) and N(3) were

3. Results and discussion

3.1. Electrochemical behaviour

Figure 1 shows the potentiodynamic (i-E) curves for the Fe17Cr13Ni0.15N alloy, the ultra pure alloy (Fe 18Cr 10Ni) and the 304-type stainless steel in 0.5M H₂SO₄ solution. The potential scan (1mV/s) was carried out from -350 to 1350 mV/SHE. The salient electrochemical features are reported in table 2. The current at the peak maximum varies in the following order: alloy with 0.15%N > alloy without N >> 304 type stainless steel. The major difference is mainly associated with the presence of a small amount of molybdenum (0.14%) in the 304 type stainless steel. The residual currents in the passive state are similar for the three alloys.

Table 2: Electrochemical data.

Alloys	Corrosion potential (mV/SHE)	Potential at the Peak maximum (mV/SHE)	Current at the peak maximum (μ A/cm ²)	Current in the passive state (μ A/cm ²)
Fe17Cr13Ni0.15N	-159	-40	1225	2
Fe18Cr10Ni	-180	-40	600	2.7
SS type 304	-130	-70	18	1.8

3.2. XPS analysis of the passive films

The spectra recorded after argon ion sputter cleaning of the Fe17Cr13Ni0.15 alloy and after passivation of the three alloys are shown in fig. 3 for the take-off angle of 90° (angle of the sample surface with the direction in which the electrons are analysed). The observation of XPS signals emitted by the alloy elements (Fe,Cr,Ni)

For the XPS analysis of passive films; the passivation was carried out by stepping the potential from the corrosion potential to the passivation potential at 650 mV/SHE. The recorded current versus time plots are shown in fig 2. Inspection of the curves reveals that the three alloys exhibit similar behaviours in potentiostatic experiments.

If the results of the potentiodynamic and potentiostatic experiments are compared for the Fe17Cr13Ni0.15N and the ultra pure alloy, nitrogen added to the alloy does not apparently influence markedly on the response of the material to anodic polarization.

indicates that the passive film is very thin. The curve fitting of the spectra, in fig.3 was done in the way described in a previous paper, using reference spectra recorded with reference materials (7).

The Fe2P_{3/2} signal has been resolved into Fe²⁺ and Fe³⁺. The Cr2P_{3/2} region indicates a marked enrichment of Cr³⁺ in the passive film

de St-Etienne (France) and a type 304 stainless steel supplied by UGINE (France) The chemical analysis of the alloys is reported in table 1. The alloys were mechanically polished with 0.5 μm diamond paste, giving them a mirror-like finish.

The electrochemical experiments were carried out in an inert gas glove box by using a 0.5M H_2SO_4 solution which was de aerated by purging with N_2 . Sample disks of 10 mm diameter were mounted in the electrochemical glass cell equipped with a platinum counter electrode and a mercurous sulfate reference electrode. The electrode potentials reported in this work are referenced to the standard hydrogen electrode (SHE). Following insertion of the samples into the electrochemical cell, they were cathodically reduced (-1V, 300s) prior to measurement of the anodic polarization curve. Polarization curves were recorded using a voltage sweep rate of 1 mV/s while sample passivation prior to surface analysis was carried out by a potential step to 650 or 1050mV (SHE) for different times of passivation (1,15,30 and 120 minutes). The passivated electrodes were removed from solution under applied potential, rinsed immediately in ultra pure water, dried in nitrogen gas and then transferred to the surface analysis system using the transfer vessel and the fast entry

port located on the preparation chamber of the spectrometer. A survey XPS spectrum of each sample was immediately recorded to determine its surface cleanliness. The presence of a C1s signal reveals the existence of a contamination layer; the only metallic elements detected were the constituting elements of the alloy. High resolution XPS spectra were acquired for seven energy regions corresponding to the core levels: $\text{Fe}2p_{3/2}$, $\text{Cr}2p_{3/2}$, $\text{Ni}2p_{3/2}$, $\text{O}1s_{1/2}$, $\text{N}1s_{1/2}$, $\text{S}2p_{3/2,1/2}$ and $\text{C}1s_{1/2}$. The data processing was carried out using curve fitting procedures based on reference spectra obtained for the clean and oxidized Stainless Steels. XPS measurements were obtained using an Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV) and a hemispherical analyser, with a pass energy of 20 eV for the high resolution spectra. The spectrometer (VG ESCALAB MK II) was calibrated using the $\text{Au}4f_{7/2}$ (binding energy (BE)= 84.0 eV) and $\text{Cu}2p_{3/2}$ (BE= 932.7 eV) peaks.

Composition depth profiles of passive films on the stainless steels were obtained by ion sputtering the surface, using a VG AG60 ion gun mounted in the analysis chamber, under the following conditions: an ion beam voltage of 4kV and a current density of $0.5 \mu\text{A cm}^{-2}$

Table 1: Elemental composition of the alloys (wt %)

	Fe	Cr	Ni	N	Mo	Mn	Si	Cu	B,C,AL,P,S
Fe17Cr13Ni0.15N	69.8	17	13	0.157	-	-	-	-	-
Fe18Cr10Ni (ultra pure)	72	18	10	<10ppm	-	-	-	-	-
304 type SS	72.01	17.38	8.28	0.04	0.14	1.43	0.49	0.15	<0.1

Surface Enrichment of Nitrogen during Passivation of Austenitic Stainless Steels

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ABSTRACT:

Three austenitic stainless steels (a Fe 17Cr 13Ni 0.15N alloy, an ultra pure Fe 18Cr 10 Ni alloy and a 304 type stainless steel) were used in this study in order to investigate the effect of nitrogen on the electrochemical behaviour and on the nature of the passive film formed on the steels in acidic solution ($0.5M H_2SO_4$). The presence of nitrogen in the alloy does not apparently influence significantly on the response of the material to anodic polarization in the acid electrolyte. Surface analysis of the alloys by XPS after passivation shows that nitrogen is enriched at the surface by anodic segregation during dissolution and passivation of the nitrogen bearing alloys. After passivation of the alloys three chemical states of nitrogen are detected in the N1s spectrum. The peak at low binding energy ($397.7 \pm 0.1 eV$) corresponds to nitrogen bonded essentially to chromium under the form of a nitride which is incorporated in the passive film. The N1s peaks observed at higher binding energy ($400.2 \pm 0.1 eV$ and $402 \pm 0.1 eV$) correspond to nitrogen species located on the surface of the passivated alloys, which are produced by reaction of the alloys with the solution.

1. Introduction

In the presence of both nitrogen and molybdenum, significant improvements in the resistance of stainless steels to general and localized corrosion have been reported (1-5). However, it remains unclear if nitrogen alone (i.e. in the absence of molybdenum) is capable of improving the corrosion resistance. It has been shown in a recent work that nitrogen implanted into a 304 type stainless steel does not improve the dissolution and passivation behaviour in acid solution (6). Nitrogen can be added to stainless steel in order to stabilize the austenite phase, and thus it is important to elucidate the role of this element in the passivity of the alloy. The aim of

this work is to investigate, by electrochemical and surface analytical measurements, the effect of nitrogen on the dissolution and passivation of austenitic stainless steel without molybdenum. In order to clearly identify the effect of nitrogen, two synthetic alloys, were studied, one without and the other with nitrogen. A 304 type stainless steel was also studied for comparison.

2. Experimental

The Fe 17Cr 13Ni 0.15N alloy used in this work was provided by IRSID Uuieux (France). As reference materials we used an ultra pure Fe 18Cr 10Ni alloy with less than 10 ppm of nitrogen in the bulk prepared at Ecole des Mines