The involvement of alloyed nitrogen in the corrosion of stainless steels

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Synopsis

The effects of nitrogen alloying on the corrosion properties of austenitic stainless steels were investigated by a combination of potentio-dynamic and surface-analysis techniques. The results indicate that nitrogen undergoes the phenomenon of anodic segregation, affecting both general and localized corrosion resistance. Nitrogen alloying is found to be beneficial to general corrosion resistance in a de-aerated sulphuric acid solution, but to be detrimental in an aerated solution of sulphuric acid. This phenomenon is explained in terms of an ammonium-ion polarization effect. Localized corrosion resistance is found to improve dramatically as a result of nitrogen alloying, the nitrogen improving the formation,
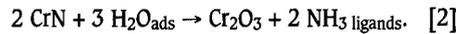
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Introduction

Effects of nitrogen alloying

Nitrogen, although typically alloyed in small quantities, has a profound influence on the corrosion behaviour of stainless steels. However, consensus has not been reached with regard to the effect of nitrogen alloying on the corrosion behaviour of stainless steels, and a number of mechanisms have been proposed to account for the various observations.

Sedricks[1] and Eckenrod and Kovach[2] have noted that nitrogen alloying appears to stabilize the passive film, while other authors, among whom are Hooper and Hones[3], have noticed a large increase in corrosion rate as a result of nitrogen alloying. Pickering[4] concluded that, as nitrogen is an interstitial element, it can form precipitates along grain boundaries, resulting in chromium-depleted zones and leading to apparently larger corrosion rates as a result of intergranular corrosion and grain dropping; but, should the nitrogen contents be below the solubility limit, nitrogen alloying is always expected to be beneficial to general corrosion resistance. Truman[5], however, in compiling corrosion data from other authors[6] for a large range of commercial austenitic alloys exposed to sulphuric, hydrochloric, nitric, phosphoric, and acetic acids, concluded that nitrogen has a slightly adverse effect upon general corrosion resistance. Bandy, Clayton, et al.[7-11], when testing in predominantly de-aerated sulphuric acid, found that nitrogen alloying is beneficial, although the number of alloys that they tested were from a smaller pool than Truman's. Other authors[12-16] have also noted that nitrogen improves general corrosion resistance, especially for duplex stainless steels[16,17].

It has generally been accepted that nitrogen improves the resistance to pitting corrosion and the passivity of stainless steels. The pitting-resistance equivalent (PRE) as described in equation [1] gives an indication of the relative effectiveness of chromium, molybdenum, and nitrogen in improving resistance to pitting corrosion. An examination of equation [1] shows that nitrogen is viewed as most beneficial in reducing the susceptibility of a stainless steel to pitting corrosion.

$$PRE = \% \, Cr + 3{,}3\% \, Mo + x\%N, \qquad [1]$$

where x varies[16,18-24] from 10 to 30.

Proposed mechanisms

Osozawa and Okato[25], after conducting an immersion test on a nitrogen-alloyed stainless steel in 20 per cent $FeCl_3$, found that the test solution contained ammonia, and proposed that the role of nitrogen is to form ammonia in newly formed pits. This would then locally raise the pH value and would prevent the pit from becoming a steadily growing pit. This theory was proposed to account for the improved resistance to pitting corrosion.

With the use of Auger techniques, Lu et al.[10] found that a seven-fold enrichment of nitrogen occurs on the interface between the oxide film and the metal for a passivated nitrogen-containing alloy. Using X-ray photoelectron spectroscopy (XPS), they claimed that the nitrogen in the nitrogen-rich layer is chemically unbonded. Bandy and Van Rooyen[7,11] proposed that the nitrogen-rich zone is the primary cause of the improved resistance to pitting corrosion. The nitrogen build-up at the metal–oxide interface has since not been confirmed or reported by any other author.

Clayton and Martin[8] also found the surface of a corroded, nitrogen-alloyed stainless steel to be enriched in nitrogen. However, instead of being chemically unbonded, the nitrogen was found to exist in the form of nitrides, ammonia, and ammonium ions. The process of surface enrichment as a result of a period of anodic activity was termed *anodic segregation*, and the authors found nitrogen to undergo anodic segregation under all conditions of corrosion, irrespective of the potential applied to the steel. No build-up of nitrogen behind the oxide film was reported, and the authors were vague as to the exact location of the anodically segregated nitrogen.

Willenbruch et al.[9] investigated the role of the surface nitrides observed by Clayton and Martin[8] and proposed that the surface nitrides, assumed to be chromium nitrides, aided the formation of a passive film by supplying Cr^{3+} ions by their decomposition reaction, outlined in equation [2]. A possible shortcoming of this theory is discussed later.

Corrosion of stainless steels

maintenance, and stability of the passive film in environments that promote pitting. Various theories that have been proposed to account for these phenomena are discussed.

$$2\ CrN + 3\ H_2O_{ads} \rightarrow Cr_2O_3 + 2\ NH_{3\ ligands}. \quad [2]$$

Pawel et al.[17] examined the role of nitrogen in improving the pitting-corrosion resistance of duplex stainless steels, and concluded that nitrogen aids the selective dissolution of iron from the surface. Consequently, he stated that a corrosion-modified surface of nitrogen-alloyed duplex stainless steel would be enriched in chromium and that the corrosion properties would subsequently be improved. However, to maintain the correct phase balance in the duplex series of alloys over the full range of nitrogen contents that they used, Pawel et al. adjusted the nickel content to vary by 4,5 per cent. His explanation of the mechanism behind the phenomenon is not valid since it was built upon effects that have been documented to be due to nickel depletion, and not necessarily nitrogen enrichment. Clayton and Martin[8] and Willenbruch et al.[9] have, however, also reported that a process of chromium enrichment and iron depletion occurs in austenitic stainless steels. Kim et al.[26], in discussing this effect, proposed that the accelerated rate of dissolution of iron may be due to the formation of some soluble complex of iron and ammonia. Hultquist et al.[27] have also reported a similar phenomenon, but for ferritic stainless steels that were essentially free of nitrogen. Hultquist et al. concluded that the relative order of the dissolution rates for the alloy constituents was generally the same as for their pure metallic counterparts. It is thus possible that the phenomenon of chromium enrichment and iron depletion may not occur solely as a consequence of nitrogen alloying, but nitrogen may aid the process.

Song et al.[28] conducted electrochemical impedance spectroscopy scans on a type 304 stainless steel that had been implanted with nitrogen ions, and reported that the density and thickness of the oxide film had been increased as a result of the ion-implantation process. They proposed that this was the reason for the observed improvement in the resistance to pitting corrosion of nitrogen-alloyed stainless steels. Despite the large number of depth-profiling experiments that have been conducted on corroded nitrogen-alloyed stainless steels, this has not yet been confirmed.

The findings of various authors and the proposed mechanisms are summarized in Table I. A more complete description of these effects and mechanisms has been given elsewhere[29].

As can be concluded from the preceding discussion, consensus regarding the effects and the mechanism of nitrogen alloying has not yet been achieved. The present study attempts to clarify the mechanism by which nitrogen alloying modifies the corrosion properties of stainless steels. If the involvement of nitrogen in the corrosion of stainless steels were better understood, nitrogen alloying could be used to greater effect in the development of new alloys and in the implementation of nitrogen-alloyed stainless steels in industry.

Experimental procedure

The following series of alloys was used in the investigation: a series of solid-state nitrided type 304 stainless steels, and a high-nitrogen, high-manganese austenitic alloy*. The type 304 steels were used in the potentiodynamic work and, as their nitrogen contents were below the detection limit of the equipment, the high-nitrogen experimental alloy was used in the surface analysis. The compositions of the steels are listed in Table II. The nitrogen-solubility limit was not exceeded in any of the alloys, and no nitrides could be detected by the use of optical metallography.

Table I

A summary of the findings of various authors on the composition of the passive film after nitrogen alloying, and the theories proposed to account for the observations

Author	Oxide film	Interface	Comments
Osozawa and Okato[25], 1976	Not mentioned	Not mentioned	NH₃ production improves pit re-passivation
Bandy and Van Rooyen[7], 1985 Lu et al.[10], 1983	Fe, Cr, Ni. Contains no Mo or N	Fe, Cr, Ni 7-fold [N] enrichment. Depleted in Mo	No evidence of charged species of N, NH₃, NH₄⁺, or nitrides
Clayton and Martin[8], 1989	Contains NH₃, nitrides. Cr-, Mo-enriched. Ni-, Fe-depleted	No mention of N, and Ni was depleted	NH₃, NH₄⁺, and nitrides are prominent
Pawel et al.[17], 1989	Cr-enriched	Not mentioned	N aids selective iron dissolution
Willenbruch et al.[9], 1990	As for Clayton et al.[8]	As for Clayton et al.[9]	Nitrides support passive film
Song et al.[28], 1990	Thickness and density increased	Not mentioned	N improves passivity
Kim et al.[26], 1994	Contains NH₃, NH₄⁺, and nitrides.	Not mentioned	Nitrogen alloying similar to nitrate and nitrite inhibition

*Alloy courtesy of C. Rennhard and Columbus Stainless

Corrosion of stainless steels

Alloy	Cr	Mn	Mo	Ni	V	Si	C	Cu	N
304, 0	17,13	1,5	0,14	9,46	0,01	0,98	0,032	–	0,028
304, 1	17,13	1,5	0,14	9,46	0,01	0,98	0,032	–	0,102
304, 2	17,13	1,5	0,14	9,46	0,01	0,98	0,032	–	0,140
304, 3	17,13	1,5	0,14	9,46	0,01	0,98	0,032	–	0,303
Exper.	25	18,2	2,1	1,97	0,17	0,19	0,02	0,5	1,25

Corrosion tests

All of the potentiodynamic tests were conducted at 25°C (± 1°C) in a de-aerated solution using a Princeton Potentiostat model 273, and a Schlumberger Solartron 1286 or a Schlumberger SI 1280, depending on the various functions that each potentiostat could offer. For all the tests, the scan rate was maintained at 1 mV per second, and all the potentials were measured relative to the SCE. Potentiodynamic scans were performed on the nitrided type 304 series of alloys in 0,05 M H_2SO_4. Another series of scans was conducted in an acid-and-salt mixture of 0,5 M H_2SO_4 + 0,5 M NaCl. The cyclic polarization scans were conducted in a solution of 0,5 M NaCl (pH 7).

Surface analysis

XPS and secondary-ion mass spectroscopy (SIMS) were conducted in a VG ESCALAB MkII spectrometer fitted with a VG SIMSLAB. For the XPS data, linear background subtraction and a least-squares fitting procedure were used in the determination of the peak positions, line widths, and peak areas. The carbon 1s peak with a binding energy of 284,60 eV was used in the correction of all the data for surface charging. The charging correction was fairly large, varying between 7,3 and 9,4 eV. All the SIMS data were recorded with a beam current of 5 nA and a beam energy of 10 keV, with rastered areas of 56 × 67 μm, or 27 × 32 μm if a better depth resolution was required, and an electronic gating of 15 per cent.

Preparation of the specimens

It was discovered in a preliminary series of tests that, after the samples had been prepared, precautions had to be taken to prevent them from coming into contact with oxygen since the film of atmospheric oxide formed on the stainless-steel surfaces masked the effects of aqueous corrosion.

Three specimens, of nominal dimensions 3 × 10 × 10 mm, were sectioned from a steel bar, and one face of each plate was polished to a 1 μm diamond finish. The samples were degreased in acetone, and two of the samples were then placed in sealed glass vials filled with de-aerated 2 N H_2SO_4, while the third sample was placed in a vial containing aerated 70 per cent HNO_3. After 18 hours, one of the samples in the 2 N H_2SO_4 was removed and was placed in a separate vial containing 70 per cent HNO_3 for a further 6 hours. The choice of these acids is explained in more detail later. After a total of 24 hours of exposure to the various acids, all the specimens were removed from the vials under an argon atmosphere, and, after they had been rinsed with distilled water, they were blown dry, mounted, and placed in an argon-flushed XPS–SIMS analysis chamber. The distilled water used for rinsing was not de-aerated, but this did not appear to interfere with the results, possibly owing to the short exposure time. At no time were the specimens exposed to the atmosphere after the surfaces had been prepared. The specimens were left in the chamber for 12 hours prior to testing to allow the chamber to be pumped down to a pressure of 10^{-10} torr. The specimen surfaces were not ion-sputtered prior to testing since this would have removed the top surface layer, which would supply the information relevant to this study.

Results and discussion

Surface analysis

Choice of acid

Sulphuric acid is a strongly reducing acid, and the stainless steel would have corroded freely in this medium, with a corrosion potential of approximately –500 mV (SCE). Nitric acid is a strongly oxidizing acid, and the stainless steel exposed to that medium would have been passivated and would have developed an oxide film. The expected potential for the surface would have been approximately +400 mV (SCE). The sample that was moved from the sulphuric to the nitric acid would have experienced an active-to-passive transition, and the oxide film formed on the surface of the specimen would thus have developed from a corrosion-modified substrate.
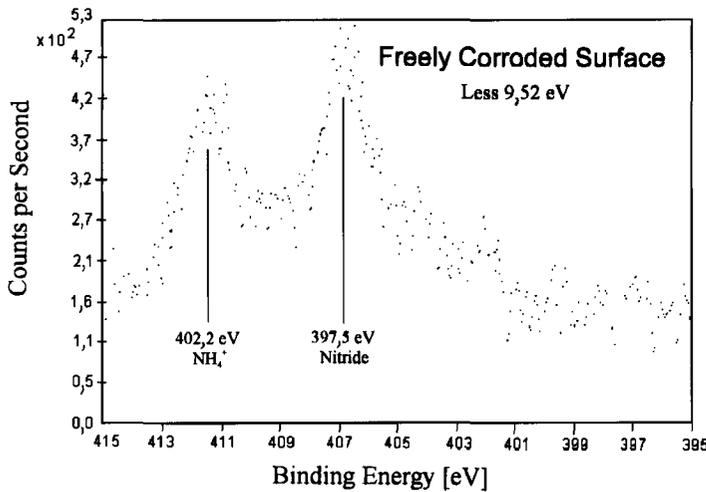
Corrosion of stainless steels

Figure 1—XPS scan, showing the nitrogen peaks for the freely corroded specimen (2N H₂SO₄ for 24 h)
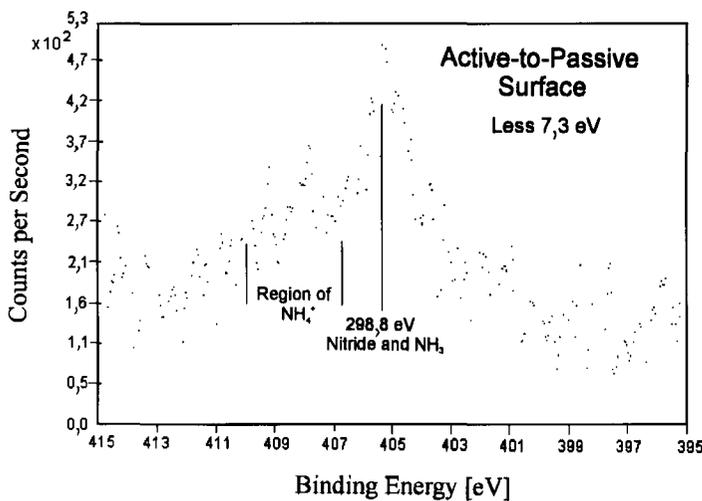

Figure 2—XPS scan, showing the nitrogen peaks for the specimen that underwent an active-to-passive transition (2N H₂SO₄ for 18 h, 70% HNO₃ for 6 h)
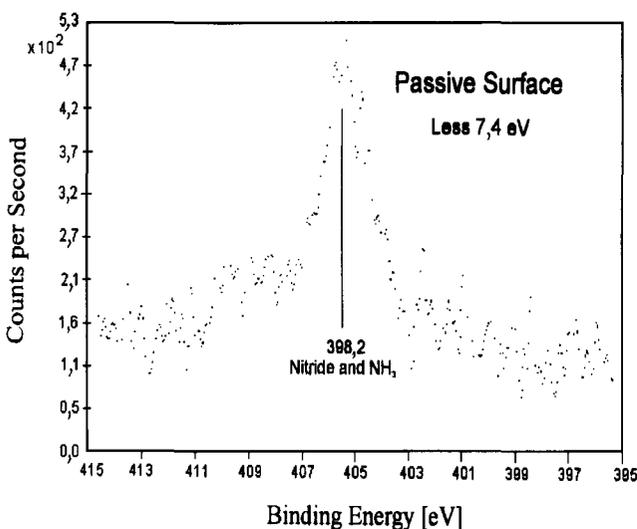

Figure 3—XPS scan, showing the nitrogen peaks for the passivated specimen (70% HNO₃ for 24 h)

Figure 4—XPS scan, showing the Cr₂O₃ doublet peaks for the freely corroded surface. (The Cr peaks should be noted)

XPS analysis

Figures 1 to 3 show the effect of acid, and hence rest potential, on the chemical nature of surface nitrogen. The correction factors for surface charging are displayed on the figures and the graph axes were not adjusted. At low potentials, as shown in Figure 1, the surface nitrogen appears to exist as a combination of nitride and NH_4^+. Figure 2 shows the spectra obtained from the alloy subjected firstly to low and then to high potentials. The surface nitrogen on this specimen is present as a mixture of nitride, NH_3, and NH_4^+. On the passivated specimen, shown in Figure 3, the nitrogen exists predominantly as a combination of nitride and NH_3, with little NH_4^+ being detected.

Figures 4 to 6 show how the same high and low potentials affected the chemical nature of the surface chromium. The surface exposed to sulphuric acid, Figure 4, shows the presence of pure chromium, which manifests itself as small shoulders superimposed on the Cr_2O_3 doublets. The presence of pure chromium peaks indicates that XPS registered the presence of metallic chromium from a sub-surface region. The chromium nitride peaks of CrN and Cr_2N occur between the peaks of pure chromium and oxide. Their possible presence is, however, being masked by the prominent oxide peaks. It is postulated that chromium nitride present as the nitrogen, from this study as well as from those of other authors[8, 9, 26], exists as a nitride on the surface. Chromium nitride is very stable and, based upon the alloy's chemical composition, this, if any, is the most likely nitride to have formed[4].
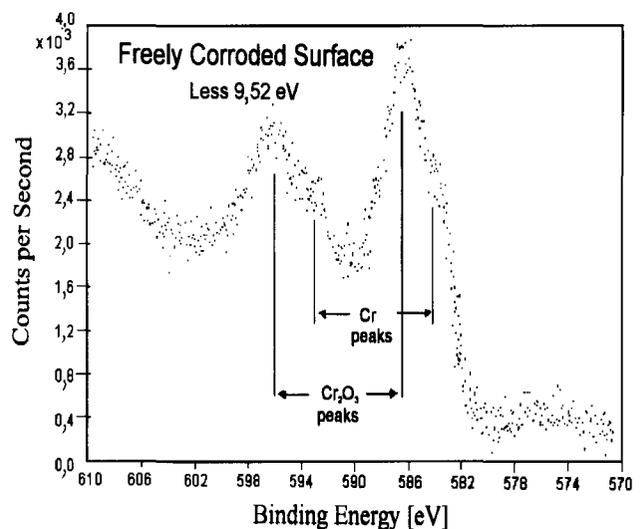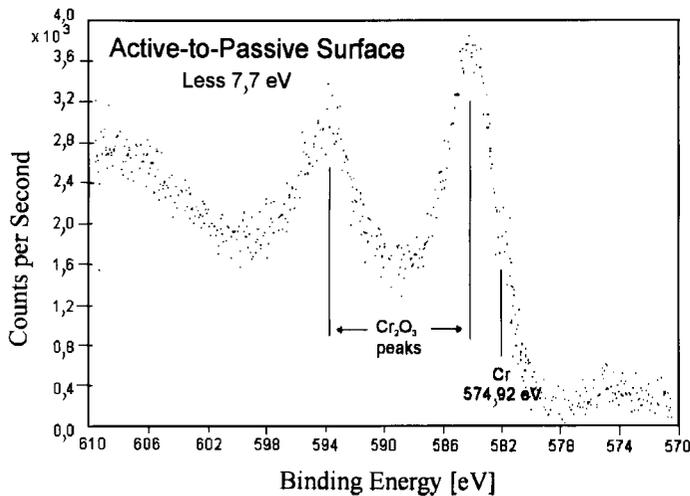
Figure 5—XPS scan, showing the Cr₂O₃ doublet peaks for the oxidized specimen. (The diminishing Cr peaks should be noted)
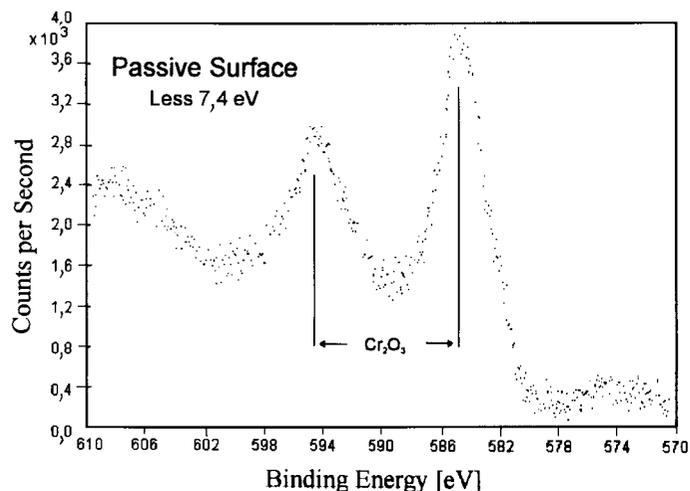

Figure 6—XPS scan, showing the Cr₂O₃ doublet peaks for the oxidized specimen. (It should be noted that the Cr peak has completely disappeared)

Figure 5 shows the XPS results for the specimen exposed firstly to sulphuric and then to nitric acid. The presence of the pure chromium shoulders can still be noted in this spectrum, despite the strongly oxidizing nature of nitric acid.

Figure 6 shows the Cr₂O₃ peaks for the surface that was exposed to nitric acid. No peaks of chromium metal can be seen, and this sample has the thickest oxide film.

SIMS analysis

Both cationic and anionic scans were conducted to produce a full elemental scan. Nitrogen, oxygen, and carbon were registered in the anionic scan, and all the metallic elements were found in the cationic scan. From the cationic scans, Figures 7 (b), (d), and (f), it might appear that chromium, iron, and manganese were enriched in the surface oxide layer. This is misleading since these metals would actually have been diluted in the oxide film owing to the presence of oxygen, but the

metal oxide emits a larger signal than the 'pure' metal, resulting in an increase in the amount of metal registered[30]. As a result of this, it is possible only to make assertions about the relative quantities of the metals present in the oxide film, and these quantities appeared to remain relatively constant for all the specimens tested.

The thickness of the oxide layer, given in the anionic scan, is related to the etching time taken to reach an oxygen value that corresponds to the average of the oxygen content for the passive film and the base material. This is illustrated in Figure 7 (a), where the oxide film of the oxidized specimen was found to have a thickness that corresponded to 335 seconds of sputtering. This was the thickest of all the films tested. From the anionic scan for the specimen exposed to both nitric and sulphuric acids, Figure 7 (c), the oxide film was found to have a thickness corresponding to 280 seconds of sputtering. The specimen exposed only to sulphuric acid had the thinnest oxide film, corresponding to 168 seconds of sputtering, as shown in Figure 7 (e).

Figure 7 (a) is the anionic depth profile of the surface of the specimen exposed to oxidizing nitric acid. Nitrogen does not experience an increase in signal strength due to the presence of oxygen[30], as in the case of the metals, and as such the trace is representative of the varying nitrogen content through the oxide film. From this figure it can thus be concluded that the oxide film is enriched with nitrogen. This enrichment must have occurred through the selective removal of the rest of the alloying elements, leaving the nitrogen to accumulate on the surface since this is the only feasible way for enrichment to occur on a surface experiencing dissolution[27]. This process, which has been termed anodic segregation, has also been reported for nitrogen by other researchers[8,9]. A full discussion of their findings has been presented elsewhere[29].

Figure 7 (c) is the anionic depth profile of the specimen exposed firstly to sulphuric and then to nitric acid. The nitrogen trace indicates that, like the oxidized surface of Figure 7 (a), the oxide film is enriched in nitrogen.

Figure 7 (e) is the anionic depth profile of the specimen exposed to sulphuric acid. Nitrogen does not appear to follow the profile of the oxide film, indicating that the oxide layer does not appear to be enriched in nitrogen. There does, however, appear to be an increase in the nitrogen content on the very surface of the specimen, and the nitrogen-concentration profile is similar to that of the curve for carbon, implying that the nitrogen layer is very thin and is located on the outermost surface. The gradual decline in the trace value of both nitrogen and carbon is due to the knock-on effect[30]. This is a phenomenon in which small amounts of surface element are nudged further into the substrate during analysis, resulting in their continued detection.
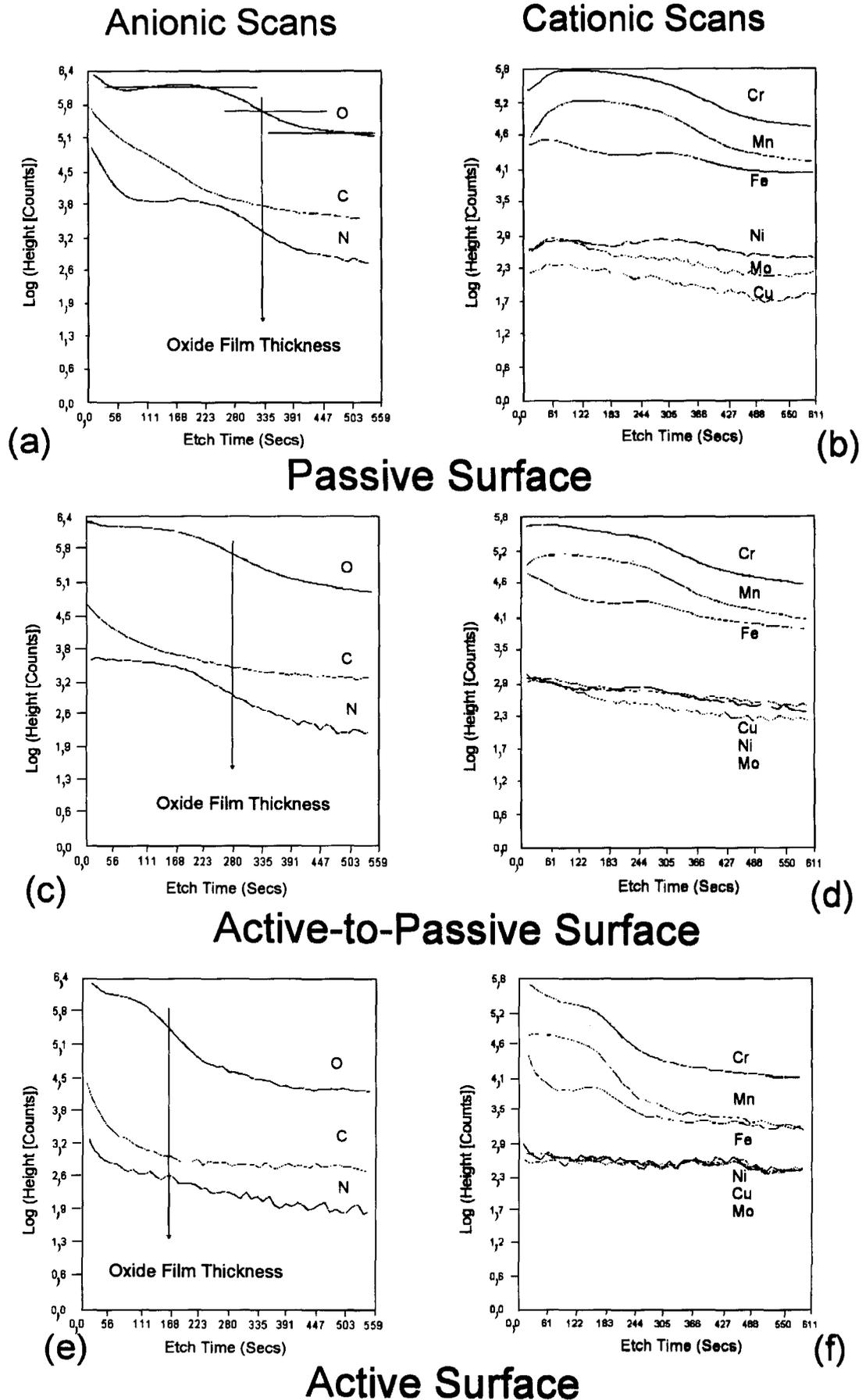
Anionic Scans

Cationic Scans

(a)

(b)

Passive Surface

(c)

(d)

Active-to-Passive Surface

(e)

(f)

Active Surface

Figure 7—SIMS depth-profiling scans, showing the cationic and anionic elements registered
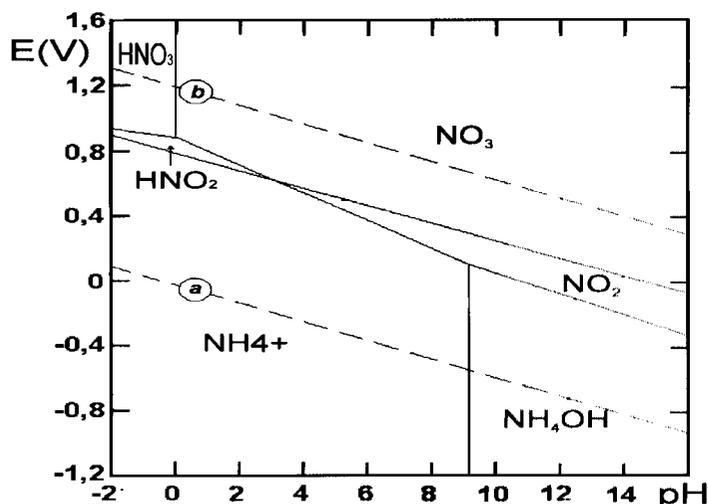
Figure 8—Simplified potential–pH (Pourbaix) diagram, showing the regions of stability for the dissolved species of nitrogen

Figure 8 shows the simplified potential–pH diagram[31] (Pourbaix diagram) for the dissolved species of nitrogen. Given the approximate potentials and the pH, it can be seen that the stable state for nitrogen is as an NH_4^+ ion. Thus, should a nitrogen-alloyed stainless steel undergo dissolution, the nitrogen forced into solution as a result of the dissolved lattice would react to form NH_4^+. The exact chemical path of nitrogen in solid solution [N] to NH_4^+ is not known, but equation [3] shows the overall process:

$$[N] + 4H^+ + 3e^- \rightarrow NH_4^+. \tag{3}$$
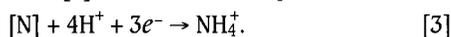
Pourbaix[31] has reported that, although the reaction $N_2 + 3\,H_2 + 2\,H_2O = 2\,NH_4OH$ is thermodynamically possible, it is an irreversible reaction and does not proceed to any appreciable extent. He has also reported that nitrides are typically sparingly soluble and, in a sense, nitrogen in solid solution would fall somewhere between these two extremes. It is thus possible
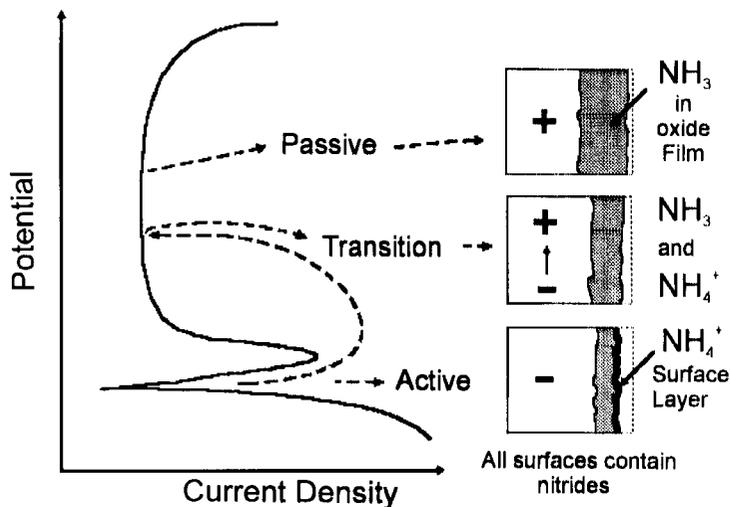
that equation [3], for which the reversible potential is not known, is somewhat 'sluggish'. This could be a possible reason for the observed accumulation of nitrogen on the steel surfaces. As equation [3] is a reduction reaction, it would proceed more strongly at reducing or cathodic potentials, as witnessed by the low amounts of retained nitrogen in the oxide film of the specimen subjected to these potentials. At more oxidizing potentials, this reduction reaction would slow down even further, as the nitrogen-rich oxide film of the passivated specimen would seem to bear out. Due to this accumulation of nitrogen, it is possible that the nitrogen solubility limit could be exceeded and the formation of nitride could become possible, as the XPS results seem to indicate.

At low potentials, with equation [3] proceeding to an appreciable extent, the positively charged NH_4^+ ions could be attracted back to the freely corroding, negatively charged surface. The XPS results confirm that the nitrogen species on this surface are predominantly NH_4^+ and nitrides, and are located on the outermost surface. The implications of this to the general corrosion resistance are discussed later.

Conversely, the passive stainless-steel surface would be more positively charged, and any NH_4^+ ions formed from a passive surface would tend to be repelled. (NH_4^+ is still the stable solute species of nitrogen at those potentials.) The XPS results indicate that the passive surface is enriched in NH_3 and, because this species is unstable at the pH value used in the experiments, the NH_3 must have separated from the electrolyte and be entrapped in the oxide film.

These results are summarized schematically in Figure 9 and are in conflict with those presented by Bandy and Van Rooyen[7,11] and by Lu et al.[10], who found no evidence of either nitrides or NH_3 and NH_4^+. In the present study, no evidence was found to confirm the existence of an enriched-nitrogen [N] zone at the metal–oxide interface. Clayton and Martin[8] detected nitrides, NH_3, and NH_4^+, and never mentioned a layer rich in nitrogen [N]; however, they also never mentioned a predominance of any species of nitrogen corresponding to any particular potential range. Kim et al.[26] and Willenbruch et al.[9] found NH_3, NH_4^+, and nitrides to be present in the oxide film irrespective of the applied potential. Also, they never stated whether a species of nitrogen was predominant at any particular potential. From the results obtained in the present investigation, it can be stated that all three of the reduced species of nitrogen were present at all potentials, but the relative percentages of the NH_3 and NH_4^+ species varied significantly as a function of the rest potential.

Figure 9—Summary of the XPS and SIMS results

Corrosion of stainless steels

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Potentiodynamic-polarization results

Free corrosion potential (FCP)

The FCP is the non-steady-state, graphically extrapolated potential at which the anodic and cathodic partial reactions are in equilibrium with each other, and there is thus zero net current[32]. According to this definition, a change in the FCP value would indicate that either the anodic or the cathodic partial reactions (or both) had been modified owing to the presence of nitrogen.

The type 304 series of alloys showed a significant shift in the FCP due to nitrogen alloying. Figure 10 (a) is a linear plot of applied potential versus current density in the region of the FCP for these alloys. From this figure, the cathodic reaction appears to have been modified by the addition of nitrogen, while the anodic reaction appears to have remained mostly unchanged. This resulted in a decrease in the FCP and an increase in the slope of the curve for E versus I in the region of the FCP. The slope of the curve at this point is the polarization resistance, and an increase in this value implies a decrease in corrosion rate.

Figure 10 (b) is the logarithmic plot of the curve for E versus I in the region of the FCP. It can be noted from this figure that the current densities at any given cathodic potential are lower with higher nitrogen contents. A possible reason for this is, either that some anodic reaction is occurring at a potential that is cathodic relative to the steel and this reaction is being summed onto the curve to produce the decrease in overall cathodic current, or that there is a cathodic reaction product that is acting to polarize the surface, resulting in a reduction in the net cathodic current. Figure 9, the summary of the SIMS and XPS work, shows the outer surface of the actively corroding specimen to be coated with NH_4^+ ions, and it is proposed that these species are polarizing the surface.

General corrosion resistance

The corrosion rates were determined from a combination of linear-polarization and harmonic analyses.

Figure 11 is a plot of the corrosion rate (in millimetres per annum) versus the nitrogen content for the type 304 alloy tested in 0,5 M H_2SO_4. From this figure it can be seen that an increase in nitrogen content results in a reduction in corrosion rate. It is interesting to note that the initial series of tests, conducted in 0,05 M H_2SO_4, showed no clear trend due to nitrogen alloying. This is a possible confirmation of the ammonium-ion polarization effect, because insufficient quantities of nitrogen would be released when the acid is too dilute, and thus the polarization effect would not be detected. It would be expected, if the corrosion rates, the nitrogen contents, or the observation time had been increased, that the polarization effect would become more pronounced.

Reactions in the Region of the FCP
Nitrided 304, 0,5M H_2SO_4

(a) *E [mV]* — Cathodic, Anodic, Increasing [N]. Note: The slope of the cathodic curve has increased with higher [N] contents. (−345 to −477; −226, µA/cm², 202)

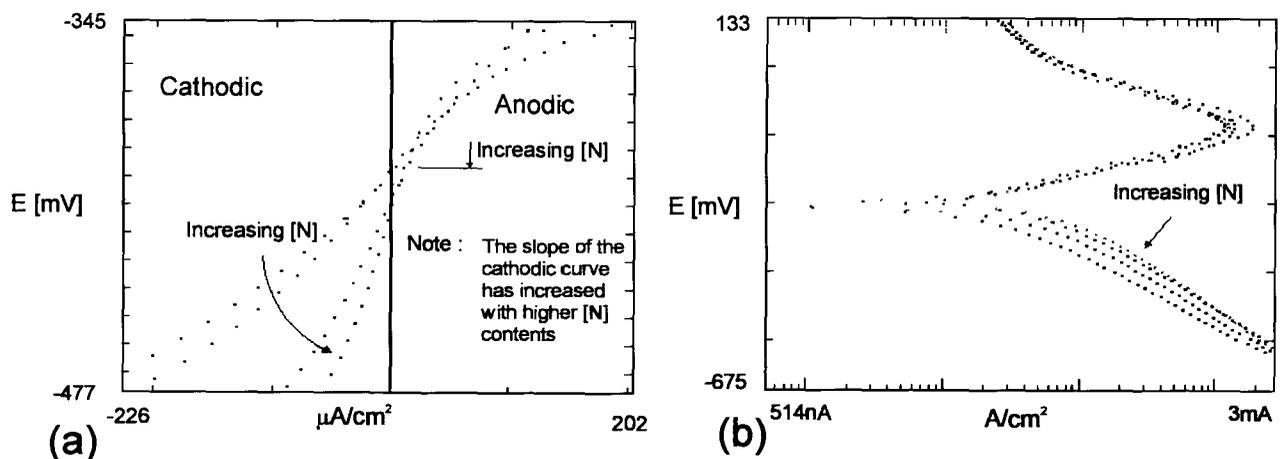**(b)** *E [mV]* — Increasing [N]. (133 to −675; 514nA, A/cm², 3mA)

Figure 10—Plots of E versus I for the nitrided austenitic alloy in the region of the FCP. (The arrows show the direction of increasing nitrogen contents)

Corrosion of stainless steels

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Corrosion Rate vs [N]
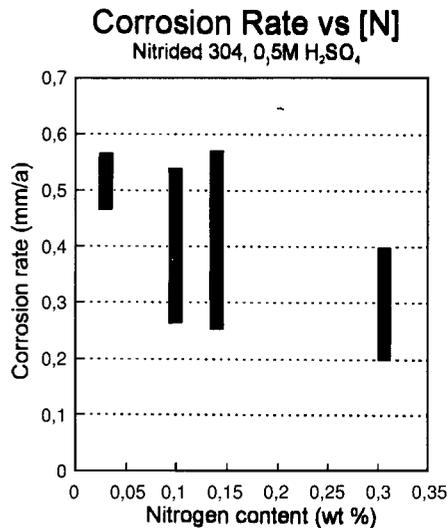Nitrided 304, 0,5M H₂SO₄

Figure 11—Plot of the corrosion rate in 0,5 M H₂SO₄ versus the nitrogen content for the nitrided austenitic alloy, as determined by linear, polarization, and harmonic analyses

Total immersion tests were conducted on a series of nitrogen-containing duplex alloys in aerated 1 M H₂SO₄. The results from these tests indicated that the presence of alloyed nitrogen was detrimental to general corrosion resistance. This can be seen to support the ammonium-ion polarization theory since a steel immersed in aerated sulphuric acid has a higher (more noble) FCP than one placed in de-aerated sulphuric acid. The ammonium ions would thus be attracted more strongly to the alloy in the de-aerated solution (with the lower FCP) than to the alloy in the aerated solution. Thus, nitrogen alloying would

be beneficial, from the point of view of general corrosion, only in environments that encourage a low FCP. The deleterious effect of nitrogen alloying found by certain authors on general corrosion resistance could possibly be due to this phenomenon. If the FCP were made more noble, say through the aeration of the corrosive medium, there is no reason why nitrogen alloying, like carbon alloying, would not be detrimental to the general corrosion resistance.

Passivation characteristics

The critical current density for passivation is the maximum current density recorded when the alloy undergoes an active-to-passive transition. The lower the critical current density, the greater the ease of passivation. The current density to maintain passivity (I_{pass}) has been defined as the lowest current density registered in the passive range, and a reduction in this value implies the presence of a more stable passive film.

From the results of the potentiodynamic tests conducted on the type 304 alloy in 0,05 M H₂SO₄, it appeared that nitrogen alloying had a negligible, or even a slightly deleterious, effect on passivation characteristics. The tests were repeated in a more aggressive solution, 0,5 M H₂SO₄, but again the variation in nitrogen content appeared to have little effect on the potentiodynamic response. The tests were repeated, but this time with a solution consisting of 0,5 M H₂SO₄ + 0,5 M NaCl. The results of these tests are shown in Figure 12 (a), and constitute a summary of the effects of nitrogen alloying on the passivity of stainless steels under sufficiently aggressive conditions.

Effect of [N] on the Passive Response of Nitrided AISI 304

(a) 0,5 M H₂SO₄ + 0,5 M NaCl
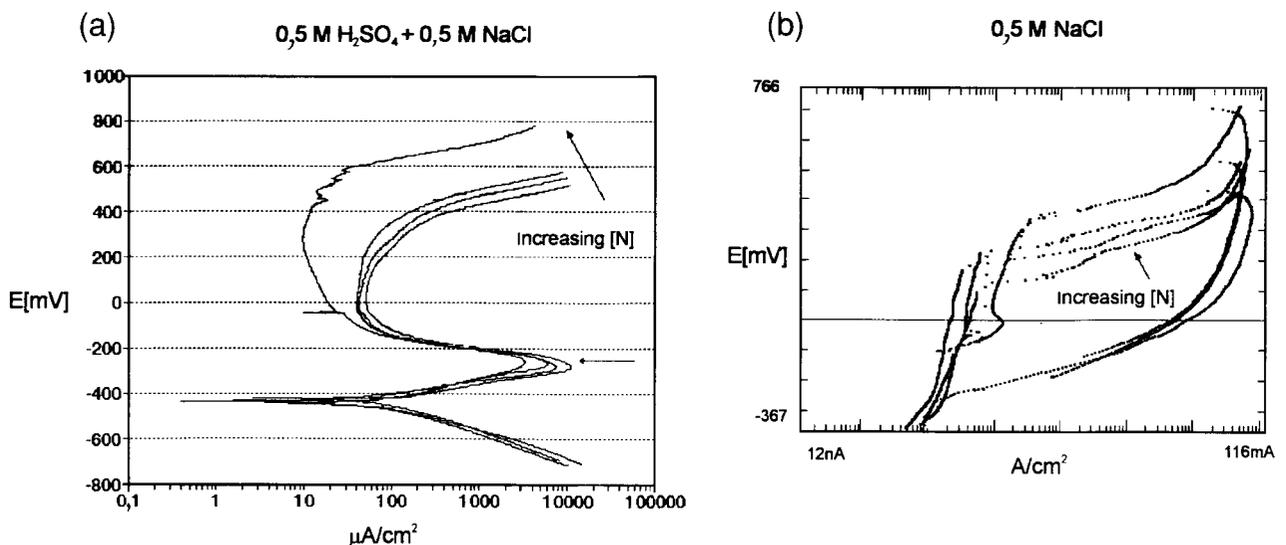

(b) 0,5 M NaCl

Figure 12—(a) Superimposed potentiodynamic responses for the nitrided austenitic alloy in 0,5 M H₂SO₄ + 0,5 M NaCl (b) Cyclic polarization scans in 0,5 M NaCl

Corrosion of stainless steels

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From this figure it can be seen that, with increasing nitrogen, the critical current density for passivation decreases, implying that nitrogen alloying improves the formation of a passive film. This is a logarithmic plot, and the difference in current densities between the high- and the low-nitrogen contents is significant. The current density at any given point within the passive range can also be seen to be lowered through the addition of nitrogen, which implies that the passive film is more stable, and that maintenance of the film requires a lower current density. The passive film can also be seen to be stable to higher oxidizing potentials with increasing nitrogen, and this implies that there would be an improvement in the resistance to pitting corrosion. This is confirmed in Figure 12 (b), which shows a superimposed plot of cyclic polarization scans conducted on the alloys in 0,5 M NaCl. This plot shows, despite the scatter, the significant effect of nitrogen alloying in improving the resistance of stainless steels to pitting corrosion.

With regard to passivity, then, nitrogen alloying can be said to improve the *formation, maintenance,* and *stability* of the passive film. Willenbruch *et al.*[9] proposed that it is the decomposition of surface nitrides that gives those properties, but Pourbaix[31] reported that nitrides are typically sparingly soluble, and it can thus be assumed that these would not participate in the dissolution process to any great extent. From the surface-analysis results, ammonia was found to be enriched in the passive film and, should it come into contact with the solution when, for example, the oxide film is ruptured, the ammonia would spontaneously hydrolyse to form an ammonium ion and would be repelled from the positively charged passive surface. This reaction consumes protons (H^+), and the pH value of the solution at that localized point would thus be raised. This could have the effect of aiding in maintenance and stability, but does not explain how nitrogen assists in the formation of the passive film. It may be possible that the chromium nitrides present on the surface encourage the dissolution of the surrounding metal due to galvanic interaction, and thus, like noble-metal

alloying, this process could force the stainless steel to reach its critical current density for passivation, resulting in a perceived improvement in the ease of passivation. This theory is possible only if the chromium nitrides are more noble than the surrounding metal and their formation does not result in a severe localized depletion of chromium.

Summary and conclusions

As stated earlier, the oxidation of nitrogen from solid solution to a nitrate or nitrite species is unlikely. As a result, nitrogen is predominantly de-alloyed from the surface as a cathodic reaction species, either when the surface is deliberately cathodically charged or when it is undergoing active corrosion. When removed from the surface as part of a cathodic reaction in an acidic medium, nitrogen is liberated in the form of ammonium ions (NH_4^+). If the surface of the metal is sufficiently negatively charged, the ammonium ions are attracted back to the surface and can potentially polarize the surface, leading to a reduction in general corrosion rate. As the polarization is strongly dependent on the potential of the surface, this effect is noticed only when the surface is sufficiently negatively charged. If the free corrosion potential is not negative enough, nitrogen alloying, like carbon alloying, appears to be detrimental to general corrosion resistance. This explanation can account for the apparent discrepancies reported in the literature on the effects of nitrogen alloying on the general corrosion resistance of stainless steels in acids.

Nitrogen alloying has been reported as being very beneficial in improving the passivity of stainless steels. This was confirmed earlier in this paper, where nitrogen alloying is reported to be beneficial in improving the formation, maintenance, and stability of the passive film. A mechanism was proposed to account for the improved stability of the passive film, but the involvement of nitrogen in the formation of the passive film is still unknown. ◆