

Influence of nitrogen addition on the crevice corrosion resistance of nitrogen-bearing austenitic stainless steels

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Crevice corrosion studies were carried out on nitrogen-bearing types 304, 316 and 317 austenitic stainless steels (SS) by a potentiodynamic anodic polarisation method in an acidic chloride medium. A special all-glass crevice assembly was used for providing reproducible crevice effects on the surface of the test specimen. The results indicated that the increase in nitrogen content improved the crevice corrosion resistance of the alloys by decreasing the active dissolution, and increasing both passive film stability and the potential at which crevice attack was stable. This was very significant for 304 and 316 SS alloys in comparison with 317 SS alloys. The combined influence of nitrogen and molybdenum was found to be very significant in providing high crevice corrosion resistance for 317 SS alloys. Optical microscopic observation revealed severe crevice attack on types 304 and 316 SS alloys compared to mild crevice attack on type 317 alloys. Based on the results of the present investigation a possible mechanism by which nitrogen addition improved the crevice corrosion resistance is discussed. © 2000 Kluwer Academic Publishers

1. Introduction

High nitrogen steels and nitrogen-bearing stainless steels are now extensively used in various industrial applications where significant corrosion resistance combined with adequate mechanical properties are in demand [1]. The addition of nitrogen has been reported to considerably increase the passive film stability, and resistance toward pitting, crevice corrosion, intergranular corrosion, corrosion fatigue, and stress corrosion cracking in some media [2–9]. Though it has been reported that the addition of nitrogen improved the crevice corrosion resistance by a few investigators [10–14], systematic investigations, and the mechanism by which crevice corrosion resistance improved are less available. Crevice corrosion is one of the most serious localised forms of corrosion attack which can occur prior to pitting attack in the presence of a suitable crevice [14].

Many investigators have reported that the addition of nitrogen widened the passive range in which crevice as well as pitting attacks were less probable [13, 14]. Sakamoto *et al.* [11] reported an improvement in the crevice corrosion resistance of 25Cr-16Ni-3Mo-2Cu austenitic steel with increasing levels of nitrogen, while the specimens were tested by immersion in a ferric chloride solution. Azuma *et al.* [12] reported that the beneficial effect of nitrogen addition in improving the crevice corrosion was by the way of delaying the crevice initiation and decreasing the propagation rate by forming ammonium ions at the crevice site. The experiments

were conducted in sea water solution by immersion tests as well as by electrochemical techniques.

In the present work an attempt was made to study the crevice corrosion behaviour of nuclear grade nitrogen-containing austenitic stainless steels in an acidic chloride medium by potentiodynamic anodic polarisation method. A specially designed all-glass crevice assembly was used for this purpose. The results of this investigation are discussed in the paper.

2. Experimental work

The chemical composition of the alloys studied in the present investigation are given in Table I. Nitrogen content varied from 0.05% to 0.16% for type 316 SS alloys, and from 0.08% to 0.14% for type 317 SS. Specimens of 10 mm × 10 mm × 3 mm were cut and solution annealed at 1050° C for 30 minutes. These specimens were mounted into an araldite resin such that no incidence of crevice attack will take place at the specimen/resin interface during the experiments, as described elsewhere [15]. After mounting, the specimens were polished up to 1 μm finish and used for the experiments.

Potentiodynamic anodic polarisation of the specimens was carried out at room temperature in a solution containing 0.5 M NaCl and 0.5 M H₂SO₄. A Wenking Potentioscan POS-73 (German make) was used in the present investigation. Prior to and during the polarisation the solution was deaerated using purified argon.

TABLE I Chemical composition of alloys (in wt%)

| Material | Cr | Ni | Mo | C | N | Mn | Si | S | P | Fe |
|----------|-------|------|------|-------|-------|------|------|-------|-------|-----|
| 304 SS | 18.39 | 9.7 | 0.03 | 0.043 | 0.086 | 1.68 | 0.31 | 0.014 | 0.026 | Bal |
| 316 SS | 16.46 | 12.4 | 2.28 | 0.049 | 0.053 | 1.69 | 0.64 | 0.006 | 0.025 | Bal |
| 316 SS | 17.90 | 12.1 | 2.45 | 0.025 | 0.068 | 1.76 | 0.98 | 0.002 | 0.026 | Bal |
| 316 SS | 17.40 | 13.2 | 2.57 | 0.021 | 0.160 | 1.60 | 0.84 | 0.003 | 0.021 | Bal |
| 317 SS | 18.22 | 14.2 | 3.04 | 0.022 | 0.088 | 1.82 | 0.30 | 0.002 | 0.025 | Bal |
| 317 SS | 18.47 | 13.2 | 3.58 | 0.014 | 0.141 | 1.09 | 0.69 | 0.001 | 0.032 | Bal |

A specially designed all-glass crevice assembly [15] with the following parameters was fixed carefully at the specimen surface: angle between glass and specimen surface— $1.2^\circ \pm 0.2^\circ$, bulk to crevice area ratio— $5.6 \pm 1.5 : 1$. The specimen with crevice assembly was kept immersed in the deaerated solution for an hour and the anodic polarisation was started from -500 mV with respect to a standard saturated calomel electrode (SCE). The applied potential was scanned at a rate of 10 mV/min in the anodic direction till a monotonic increase in the anodic current exceeding $25 \mu\text{A}$ was noticed. This potential was termed as the critical crevice potential, E_{cc} , above which significant crevice attack occurred on the surface of the specimen. Therefore, higher the critical crevice potential better would be the crevice corrosion resistance. After the polarisation experiments some specimens were examined in an optical microscope for the morphology of crevice corrosion attack.

3. Results and discussion

Fig. 1 shows the potentiodynamic anodic polarisation curves obtained for type 304 SS (0.086% N) in comparison with type 316 SS (0.053% N). It can be seen that 304 SS alloy showed equivalent critical crevice corrosion potential, though the active dissolution current density of 304 SS was higher than that of 316 SS alloy. This indicated the importance of nitrogen addition, which surpassed even the beneficial influence of

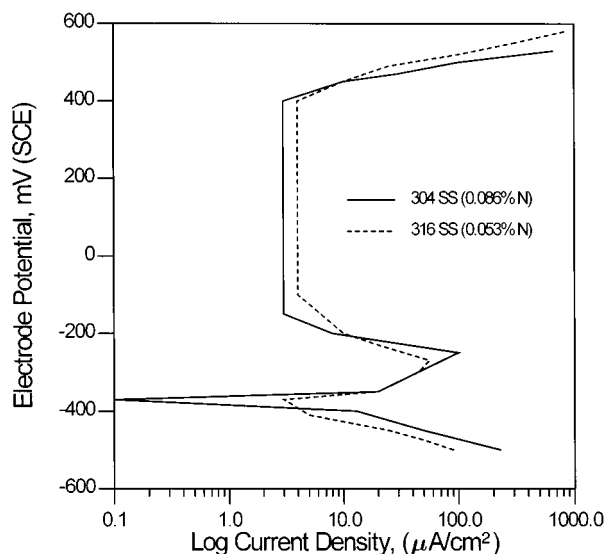


Figure 1 Potentiodynamic anodic polarisation curves of nitrogen-bearing types 304 and 316 stainless steels.

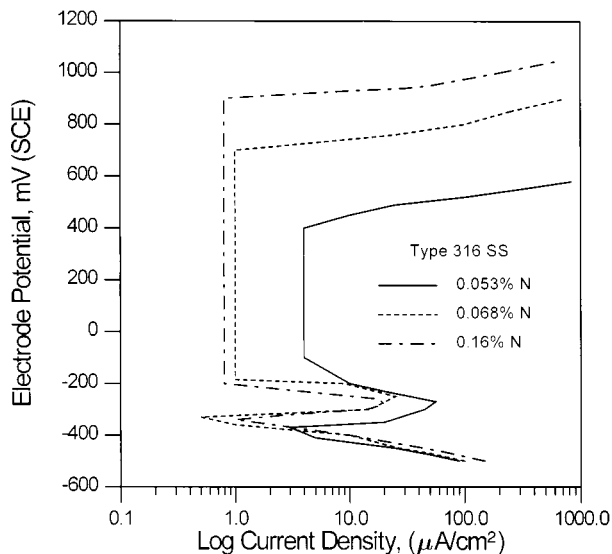


Figure 2 Potentiodynamic anodic polarisation curves of nitrogen-bearing types 316 stainless steels containing various levels of nitrogen.

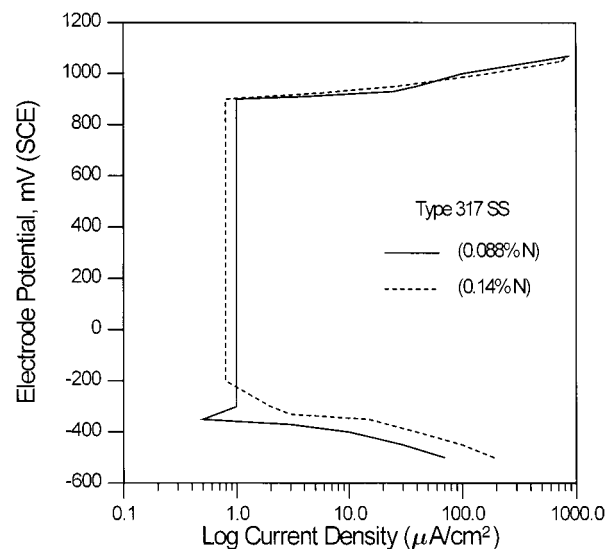


Figure 3 Potentiodynamic anodic polarisation curves of nitrogen-bearing type 317 stainless steels.

molybdenum present in type 316 SS alloy in improving the crevice corrosion resistance. Fig. 2 shows the potentiodynamic anodic polarisation curves of type 316 SS alloys containing various nitrogen contents. As the nitrogen level increased, the following points were noted: (1) the active dissolution current density decreased, and (2) the critical crevice potential increased. However, for type 317 SS alloys, (Fig. 3) no active dissolution peak was noticed irrespective of nitrogen content, and the critical crevice potential was almost similar. In addition,

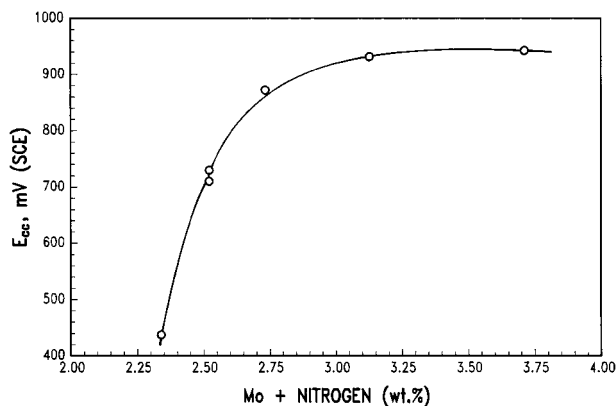


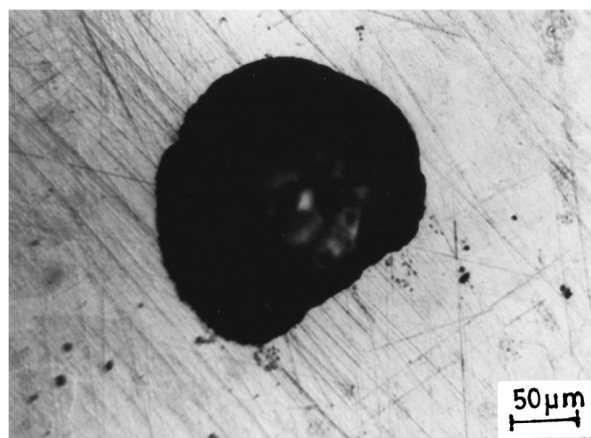
Figure 4 Influence of combined levels of nitrogen and molybdenum on critical crevice potentials.

from Figs 1 to 3, it can be seen that the increase in nitrogen addition decreased the current density in the passive region for all the alloys indicating the formation of a thin and stable passive film on the surface. Fig. 4 shows the plot of nitrogen content versus critical crevice corrosion potential for all the alloys studied in the present investigation. From the results it can be noticed that for type 317 SS alloy the E_{cc} values did not show any appreciable increase in comparison with types 304 and 316 SS alloys. Also, as the combined molybdenum and nitrogen content increased the E_{cc} values also initially increased, which later showed a tendency for saturation with respect to type 317 SS alloys.

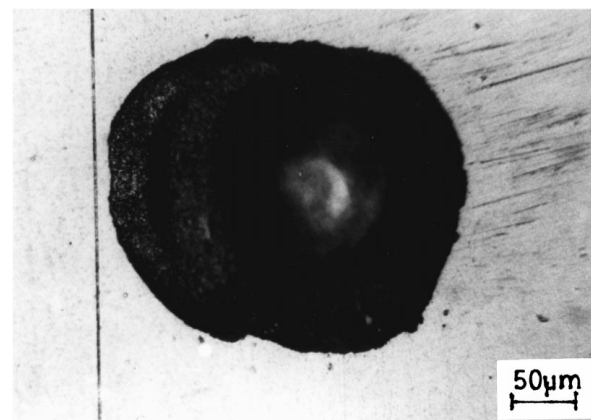
The optical micrographs of the specimens studied in the present work are shown in Fig. 5a–d. In the case of types 304 and 316 SS it can be noticed that the crevice attack was severe and well developed on the surface. However, for type 317 SS alloy, the crevice attack was mild and developed insignificantly on the surface.

3.1. Influence of nitrogen addition on crevice corrosion resistance

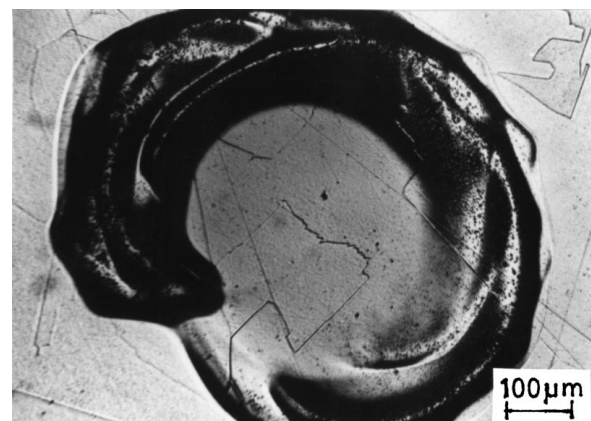
Nitrogen has been long recognised as a beneficial alloying element to localised corrosion of austenitic stainless steels, particularly for pitting and crevice corrosion resistances. The effect of nitrogen in improving the localised corrosion resistance was remarkable compared to other alloying elements, like molybdenum, silicon, nickel etc. Many investigators [2–9] reported the significant improvements in the pitting resistance in acidic and neutral chloride solution at room temperature to higher temperatures. The analysis of the solution inside a pit indicated the presence of ammonium or nitrate ions [2, 16, 17]. The presence of ammonium ions in the pit solution considerably increased the pH of the solution, and thus favoured a faster repassivation and increase in the pitting resistance. The combined effect of nitrogen and molybdenum was reported to further enhance the pitting corrosion resistance [8]. The mechanism for the improvement in the pitting resistance is still not established though there were many hypotheses [2, 6, 18–20]. Notable among them are: (1) nitrogen dissolves at the pit site to form ammonium ions



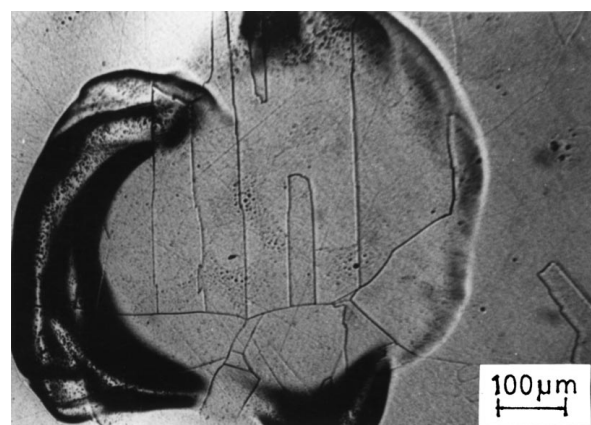
(a)



(b)



(c)



(d)

Figure 5 Optical micrographs of specimens undergone crevice attack (a) 304 SS (0.086% N), (b) 316 SS (0.16% N), (c) 317 SS (0.088% N) and (d) 317 SS (0.14% N).

and render the pit solution less aggressive for the pit to grow, (2) nitrogen segregated to the metal surface as other elements dissolve preferentially leaving a nitrogen enrichment layer providing an inactive surface for the aggressive chloride ions during pitting, (3) nitrogen is incorporated into the passive film to form a dense protective oxynitrided layer increasing the stability of the passive film against any break down, and (4) nitrogen in the steel dissolves to form nitrites or nitrates which might act as inhibitors locally at the pit site.

Investigations carried out on the crevice corrosion resistance of nitrogen-bearing austenitic stainless steels also indicated the formation of ammonium ions during the crevice attack [12]. The results of the present investigation indicate the following order of crevice corrosion resistance: 317 SS (0.088% and 0.14% N) > 316 SS (0.16% N) > 316 SS (0.068% N) > 304 SS (0.086% N) ≥ 316 SS (0.053% N). The highest resistance of type 317 SS could be attributed to the combined effect of nitrogen and molybdenum on the improvements in the localised corrosion resistance.

The beneficial effect of nitrogen in improving the crevice corrosion resistance could be similar to that of improvements in pitting resistance. The following mechanism was proposed by Fontana and Greene [21] with respect to crevice attack for austenitic stainless steels: Initially the dissolution of metal atoms and the reduction of oxygen occur uniformly over the metal surface including the crevice region. However, within a short time oxygen at the crevice region is consumed although the dissolution of metal atoms continued outside as well as inside the crevice. In order to maintain the charge balance inside the crevice with the cessation of reduction of oxygen to hydroxyl ions, migration of negatively charged chloride ions into the crevice takes place. Subsequent formation of metal chlorides, and the hydrolysing of the metal chlorides to hydroxide and free acid results in the acidification of the crevice site favouring an autocatalytic corrosion attack similar to that of pitting corrosion. Thus, the necessary condition favouring crevice corrosion is the break down of the passive film, and the migration of chloride ions

CREVICE CORROSION MECHANISM

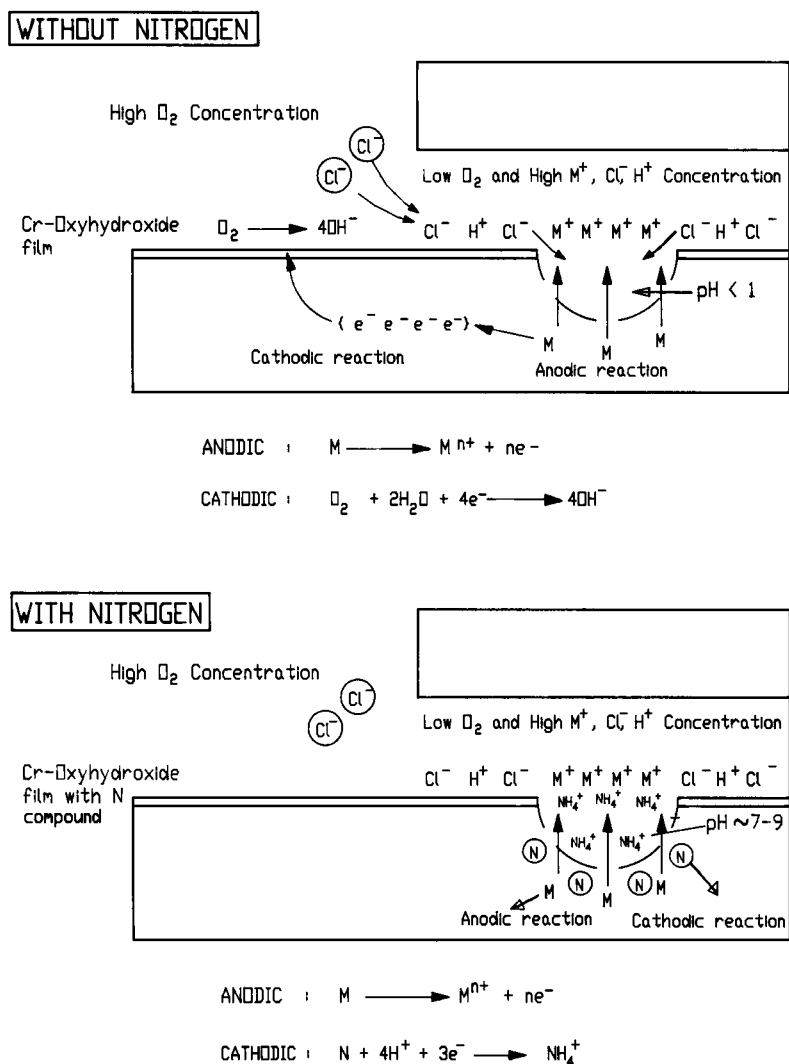


Figure 6 Schematic view of crevice corrosion mechanism of austenitic stainless steels with and without nitrogen addition.

into the crevice leading to acidification and accelerating corrosion.

In the case of nitrogen present in the alloy, the following favourable conditions could have led to the improvements in the crevice corrosion resistance (Fig. 6): During dissolution reaction at the crevice site, nitrogen dissolved along with other metal ions forms ammonium ions which significantly raise the pH inside the crevice. The electrons produced during the metal dissolution reactions are consumed in the reduction of nitrogen (N^{-3} ions) to form ammonium ions. Under this situation, the migration of negatively charged chloride ions into the crevice region is slowed down, and hence acidification process is reduced significantly compared to low-nitrogen containing alloys. Thus, nitrogen addition favoured increased crevice corrosion resistance. In addition, as discussed earlier, nitrogen addition also strengthened the passive film, and thus increased the incubation period for the stable crevice attack to initiate. The absence of crevice attack in type 317 SS alloys could be due to the increased resistance of the passive film for break down due to the combined presence of molybdenum and nitrogen.

4. Conclusions

The results of the present investigation on the crevice corrosion resistance of nitrogen-containing austenitic stainless steels are summarised below:

- Nitrogen addition increased the crevice corrosion resistance of austenitic stainless steels.
- The crevice corrosion resistance of type 304 SS with 0.086 wt% N was equivalent to that of type 316 SS with 0.053 wt% N.
- The improved crevice corrosion resistance is attributed to,
 - (i) reduction of nitrogen at the crevice in preference to oxygen,
 - (ii) formation of ammonium ions which increases the pH of the solution within the crevice, and
 - (iii) the presence of most stable passive film

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