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Segregation effects on the corrosion behaviour of a phosphorus-doped AISI type 304L stainless steel

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Abstract

The effect of grain boundary (GB) segregation on intergranular stress corrosion cracking (IGSCC) in hot water environments at 150°C and 250°C was studied in a P-doped AISI type 304L stainless steel. The extent of segregation was measured by an exposure test in boiling 5 N HNO_3 + 8g/L $K_2Cr_2O_7$ solution as well as by a potentiostatic etch test at +1325 mV (SHE) in 5 N H_2SO_4 solution. Although GB segregation was detected in all the aged specimens, IGSCC was shown by only the specimens aged for 550°C/1000 h. The results suggest that it is the GB chromium depletion, rather than the segregation of phosphorus at the GBs, that controls IGSCC of stainless steels in the hot water environments studied.

1. Introduction

Austenitic stainless steels are widely used as structural materials in applications that require excellent resistance to general corrosion in combination with good mechanical properties. However, these steels, in the sensitized condition, are susceptible to intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC). One of the mechanisms that explains this increased susceptibility to intergranular attack is the formation of Cr-depleted zones in the vicinity of grain boundaries (GBs) as a result of the precipitation of Cr-rich carbides at the GBs during thermal exposure at temperatures from 450°C to 800°C [1,2]. It is also possible that segregation of impurity elements such as phosphorus and sulphur at the GBs can facilitate intergranular attack even in the absence of Cr-depletion [3]. Although an enrichment of these elements at GBs is possible even in solution annealed steel [4], if the bulk concentration is high, thermal ageing especially in the low temperature regime (400–600°C) facilitates segregation. Besides, neutron irradiation enhance impurity segregation to the GBs [5]. Therefore, segregation effects are very pronounced in nuclear reactor core components. Since Cr carbide precipitation and segregation take place in the same temperature regime it is often difficult to study the influence of segregation alone on the corrosion behaviour of stainless steels.

The aim of the present investigation was to study the effect of GB segregation on the IGSCC susceptibility, by using a P-doped AISI type 304L stainless steel containing a very low amount of carbon. The susceptibility of the steel to IGSCC in different aged conditions was studied in hot water environments. The extent of segregation was evaluated using both chemical and electrochemical test methods.

2. Experimental procedure

2.1. Alloy preparation

A P-doped AISI type 304L stainless steel was used in this study. The chemical composition of the alloy is (wt%): 70.0 Fe, 17.8 Cr, 10.9 Ni, 1.1 Mn, 0.112 P, 0.009 S and < 0.005 C. The P concentration of the alloy was kept high when compared to the concentration in ‘normal’ 304L stainless steel (0.04% max). The alloy was

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vacuum induction melted, cast, forged, and finally drawn to 10 mm diameter rods. All samples were then given an isothermal solution anneal (SA) at 1100°C for 1 h, followed by water quenching. 100 mm long pieces of this material were subjected to various heat treatments viz., 600°C/140 h, 550°C/1000 h and 500°C/1000 h. All the heat treatments were performed either in vacuum or in an argon atmosphere.

2.2. Detection of segregation

After the heat treatment, the samples were machined to 8 mm diameter rods. 10 mm long samples for IGC tests were cut from these rods. All the samples were polished to a 600-grit surface finish, prior to corrosion testing, unless stated otherwise. Two corrosion tests were used in this study for detecting segregation: boiling HNO_3 + Cr^{+6} test, and an electrochemical etch test at +1325 mV (SHE). Besides, a copper–copper sulphate–sulphuric acid test was used for detecting Cr-depletion.

The nitric acid–dichromate test, also known as Coriou test [6] consists of exposing samples to boiling 5 N HNO_3 + 8g/L $K_2Cr_2O_7$ for 6 h. The Coriou test is sensitive to the segregation of impurities such as P [6,7]. After the exposure, the weight loss of the sample was determined. Intergranular attack in this test is indicative of segregation at the GBs.

The test conditions used for the transpassive potential exposure tests were the same as those used by Iwabuchi et al. [8], and Watanabe et al. [9]. The aim of this test was to duplicate the conditions electrochemically that exist in the HNO_3 + Cr^{6+} corrosion test. A potentiostat equipped with an interface and a personal computer were used for conducting the electrochemical etch tests at the transpassive potential. Samples of approximately 0.5 cm^2 area were mounted in resin with a wire lead attached to the back and polished to fine diamond surface finish. The experimental setup consisted of a corrosion cell with a reference electrode and a platinum counter electrode. A mercury–mercury sulphate (Hg–$HgSO_4$) electrode was used as the reference electrode to avoid electrolyte contamination by chloride ions. Tests were conducted in 5 N H_2SO_4 solution at 25°C. Specimens were polarized at +1325 mV (SHE), in the transpassive range, for 1 h and the current density was monitored as a function of testing time. The accumulated charge during the electrochemical test gives a measure of the segregation at the boundaries.

The boiling copper–6% copper sulphate–16% sulphuric acid test [10] was used to detect the presence of any Cr-depletion in the aged samples. 8 mm diameter and 10 mm long specimens were exposed to boiling copper–copper sulphate–sulphuric acid solution for 72 h. The specimens were then examined for intergranular attack.

The corrosive attack after all of the tests was studied by scanning electron microscopy.

2.3. Slow strain rate stress corrosion tests

Round tensile specimens with a gauge diameter of 4 mm and gauge length of 20 mm were used for the slow strain rate tests. The specimens were polished to a 600-grit surface finish and cleaned before the test. Tests were conducted on a screw driven machine (Instron Universal Testing Machine) in two test environments viz. 0.01 M NaCl solution at 250°C and oxygenated 0.01 M sodium sulphate solution at 150°C. The oxygenation was done by bubbling pure O_2 gas for 1/2 h through the solution at room temperature. A cross head speed of 50 μm/h which corresponds to a nominal strain rate of 7×10^{-7} s^{-1} was used for the tests. The test environments were prepared using deionised water and reagent grade chemicals. All the tests were conducted under open circuit potential conditions. A Hastelloy autoclave of 2 l capacity was used as the environment chamber. After the test, the fracture surfaces were examined under a scanning electron microscope in order to characterise the mode of fracture. The parameters such as % elongation, % reduction in area, and ultimate tensile strength (UTS) in the test environment were used for comparing the SCC susceptibility of the steel under different heat treatment conditions.

2.4. Grain boundary chemistry

Thin foils of the specimens heat treated for 550°C/1000 h and 500°C/1000 h were examined in a TEM. Energy dispersive X-ray (EDX) analysis of the GB regions were carried out to understand the distribution of various elements in and around the GB.

3. Results and discussion

3.1. Intergranular corrosion

Exposure of samples in the boiling acid dichromate test has shown maximum weight loss in the 550°C/1000 h specimen followed by 500°C/1000 h, 600°C/140 h and solution annealed (1100°C/1 h) specimens (Table 1). The scanning electron microscopic (SEM) examination of the specimen surfaces revealed GB attack in all the cases. Fig. 1 shows the surface appearance of the solution annealed and 550°C/1000 h specimens after the exposure test. GB attack was observed even in the case of the solution annealed specimens, although its matrix was free from corrosion attack. Severe corrosion of matrix sites had taken place in all the aged specimens. The extent of matrix attack was high in the case of 550°C/1000 h. This was also the heat treatment which

Table 1
Weight loss of the aged specimens after exposure to boiling 5N HNO_3 + 8g/L $K_2Cr_2O_7$ solution for 6 h

Heat treatment	Weight loss (mg/cm^2)
Solution annealed	0.4
600°C/140 h	0.9
550°C/1000 h	2.1
500°C/1000 h	1.2

gave maximum weight loss. This indicates that the weight loss in the boiling nitric acid test is not directly related to the extent of GB segregation.

Fig. 2 shows the accumulated charge versus time plots, in the transpassive potential exposure test, for specimens under different heat treatment conditions. The charge density was found to increase with time in the case of aged specimens. The responses of the 550°C/1000 h and 600°C/140 h specimens were of the same magnitude, whereas the 500°C/1000 h specimen showed lower charge density values. There was no significant change in charge density with time for the solution annealed specimen. However, SEM examination of the etch surfaces indicated GB attack in all the cases. SEM micrographs of the etched surfaces of solution annealed as well as 550°C/1000 h specimens are given in Fig. 3. There was no corrosion attack in the matrix in the solution annealed condition. But sites of preferential dissolution were observed clearly in the matrix in all the aged samples. The severity of matrix attack was more in the case of specimens which gave high charge densities. This behaviour was similar to that observed in the case of boiling nitric acid test. This is understandable as the electrochemical potential in the HNO_3 + Cr^{+6} test is almost in the same range as the transpassive potential applied in the electrochemical test. The increase in matrix attack, in both the tests, with ageing time and temperature, suggests that segregation also occurs in the high energy regions within the matrix such as inclusions, twin boundaries and dislocation loops. It should be mentioned here that the alloy used in the study had a fairly high density of oxide inclusions. Therefore, it is possible that the inclusion–matrix interfaces provide sites for segregation of phosphorus in the alloy. The absence of any matrix attack in the case of solution annealed specimen, especially in the electrochemical test, suggests a fairly uniform distribution of phosphorus in the matrix of the annealed material. The similarity in the nature of attack in both the nitric acid–dichromate test and the etch test at the transpassive potential of +1325 mV (SHE) indicates that both these tests are sensitive to the presence of segregated phosphorus.

Scanning electron microscopic examinations of the specimens after exposure to copper–copper sulphate–sulphuric acid solution indicated intergranular attack only in the case of the 550°C/1000 h heat treatment (Fig. 4). This is indicative of Cr-depletion in the material. Since there were no carbides present at the GBs, Cr-depletion might have been caused by the formation of a Cr–P phase at the boundaries as discussed in the analytic electron microscopic results.

3.2. Grain boundary composition

Line scans across GBs by scanning transmission electron microscope (STEM) showed an enrichment of P and Cr at the GBs in some places in the case of the 550°C/1000 h aged specimen. Elemental mapping in the GB regions also showed an enrichment of both P and Cr together at many GB sites and corresponding depletion of Fe and Ni at these sites (Fig. 5). An enrichment of Cr and P together at some points may exist because of the formation of some Cr–P compounds. However, specimens with other heat treatments did not show evidence for the formation of Cr–P compounds. The formation of Cr–P compounds has been reported in thermally aged

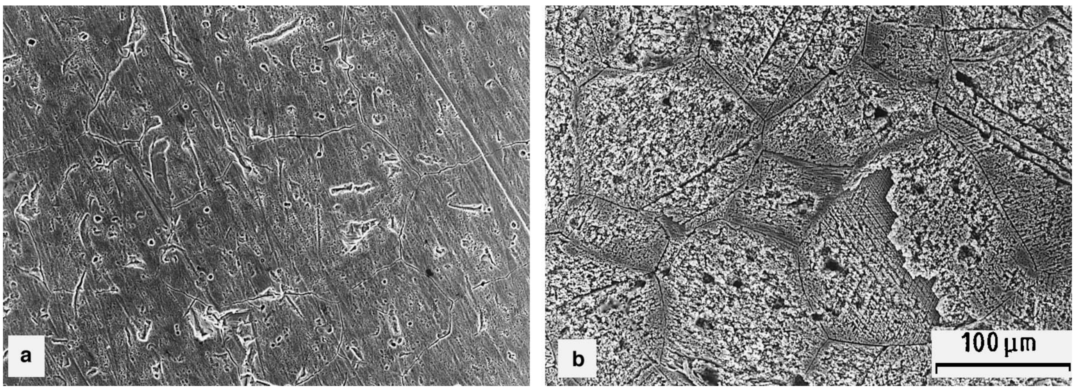

Fig. 1. SEM micrographs of the specimens after exposure to boiling 5N HNO_3 + 8g/L $K_2Cr_2O_7$ solution for 6 h. (a) solution annealed, (b) 550°C/1000 h.

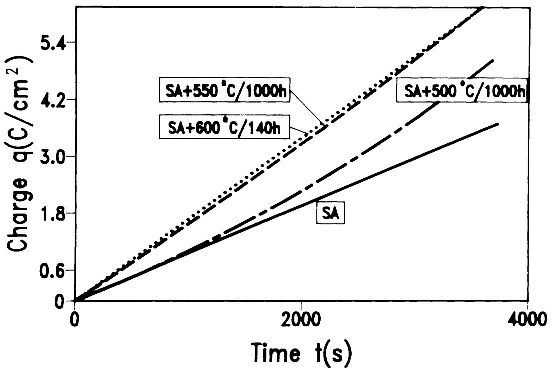

Fig. 2. Plot of total accumulated charge versus time in potentiostatic etch tests at the transpassive potential of +1325 mV (SHE) in the solution annealed AISI type 304L steel under various heat treatment conditions.

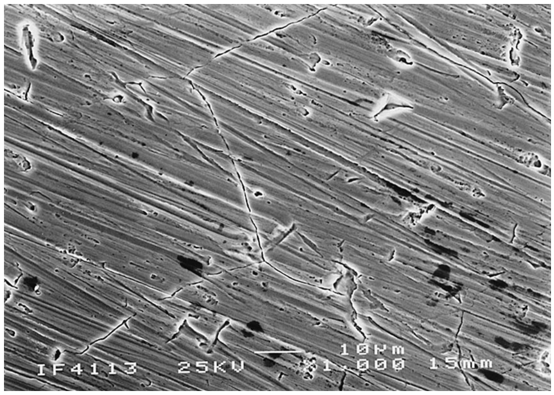

Fig. 4. SEM picture of the surface of the 550°C/1000 h specimen after exposure to Cu–6% $CuSO_4$–16% H_2SO_4 solution.

AISI type 304L stainless steel with higher P content [11]. Formation of Cr-rich P compounds can deplete the nearby region of Cr. There were also regions with Cr-enrichment but without any enrichment of phosphorus. This may be because of the formation of a sub-microscopic sigma phase at the boundaries. Intergranular attack in boiling copper–copper sulphate–sulphuric acid test confirms Cr-depletion in the 550°C/1000 h specimens.

3.3. Stress corrosion cracking

The summary of constant extension rate test results in 0.01 M NaCl solution at 250°C and 0.01 M Na_2SO_4 solution at 150°C are given in Tables 2 and 3, respectively. In the tests conducted at 250°C, there was no significant difference in the parameters such as % reduction in area, % elongation, UTS, etc., for various heat treatments. Also, the mode of fracture was transgranular stress corrosion cracking (TGSCC) for all the heat treatment conditions. However, in the tests conducted in an oxygenated environment at 150°C, % elongation, % reduction in area and UTS showed significant reduction for the 550°C/1000 h heat treatment over the other heat treatments. The mode of fracture was IGSCC. However, all the other heat treatments showed only TGSCC in the oxygenated environment at 150°C.

SEM observations of the fracture surfaces has shown typical TGSCC for all the specimens except the 550°C/1000 h specimen tested in oxygenated solution. Fig. 6 shows a typical SEM photograph of TGSCC in the 550°C/1000 h specimen, tested in 250°C water. An SEM fractograph is given in Fig. 7(a) showing IGSCC in the 550°C/1000 h specimen, after the test in oxygenated solution at 150°C. An SEM picture of the specimen surface, from an interrupted test of a specimen under the same heat treatment, showing intergranular crack initiation is given in Fig. 7(b).

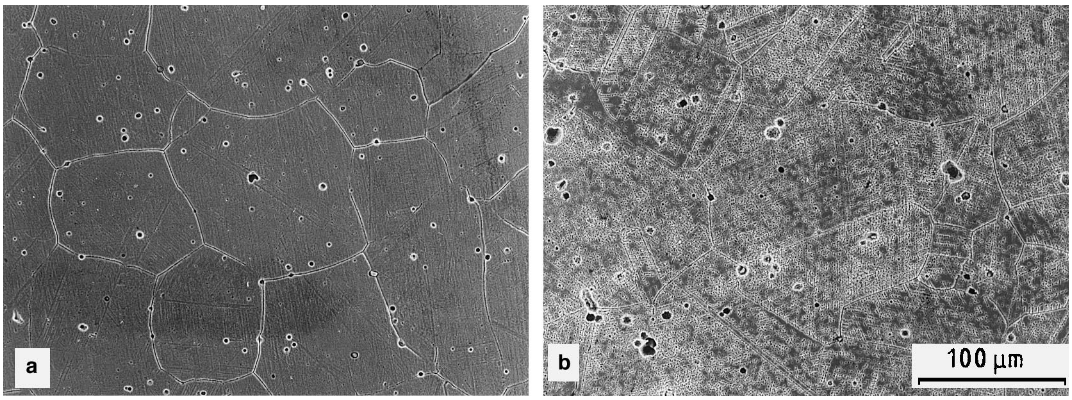

Fig. 3. SEM micrographs showing the corrosion morphology of the specimens exposed to etch test at +1325 mV (SHE). (a) solution annealed, (b) 550°C/1000 h.

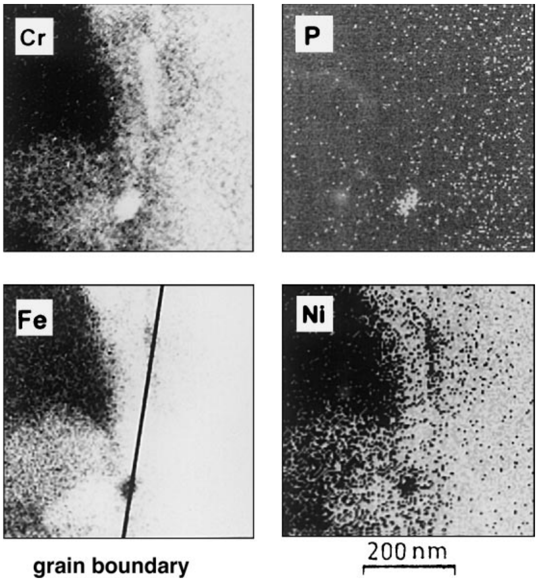

Fig. 5. Cr, P, Fe and Ni elemental distribution maps in STEM analysis of a 550°C/1000 h specimen – bright areas show enrichment and dark areas show depletion.

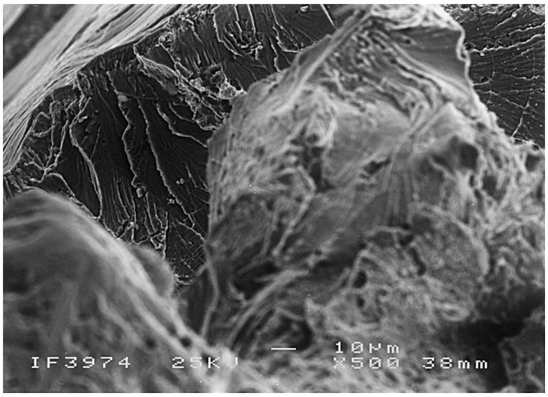

Fig. 6. SEM micrograph of a typical TGSCC region in a 550°C/1000 h specimen tested in 0.01 M NaCl solution at 250°C and at the saturated vapour pressure.

In the present study, IGSCC has been observed only in the P-doped steel aged for 550°C/1000 h, when tested in oxygenated water containing Na_2SO_4 at 150°C. It is also the only heat treatment in this study that produced both P-segregation and Cr-depletion at the GBs. It should be mentioned here that no chromium carbide precipitation is expected in this steel as the carbon content is very low (< 0.005%) and Cr-depletion can result only from the precipitation of Cr–P compounds. One possible reason for the absence of IGSCC in the solution annealed, 500°C/1000 h and 600°C/140 h specimens can be the insufficient GB segregation in these cases. It is also possible that segregation alone cannot cause IGSCC in the hot water environments studied and the effect of P-segregation is only to enhance the IGSCC susceptibility of a stainless steel with Cr-depletion near the GBs. It may be recalled that the Cu–$CuSO_4$–H_2SO_4 test showed no Cr-depletion in aged specimens except in the case of the 550°C/1000 h specimen. This view is shared by many researchers. Briant [12] and Briant and Andresen [10] have shown that P-segregation enhances corrosion in the Huey test. But P-segregation appears to have little effect on the IGSCC in high temperature water. There has been a number of studies in the literature which show that austenitic stainless steels containing P-corrode much more rapidly in the Huey test (boiling 65% HNO_3 test) than those steels that do not contain P [3,4,7,10,12]. However, it is not clear from the literature whether segregation of P or other impurity elements alone can cause IGSCC of austenitic stainless steels. Tice et al. [13] have shown that phosphorus enrichment alone cannot significantly affect the dissolution or passivation behaviour in either near neutral or low pH solutions, suggesting that segregation

Table 2
Results of slow strain rate tests at a nominal strain rate of 7×10^{-7} s^{-1} in 0.01 M NaCl solution at 250°C

Heat treatment	Reduction in area (%)	Elongation (%)	UTS (MPa)	SCC morphology
Solution annealed	24.1	40.8	377	TG
600°C/140 h	24.8	42.9	378	TG
550°C/1000 h	24.5	44.6	400	TG

Table 3
Results of slow strain rate tests at a nominal strain rate of 7×10^{-7} s^{-1} in oxygenated 0.01 M Na_2SO_4 solution at 150°C

Heat treatment	Reduction in area (%)	Elongation (%)	UTS (MPa)	SCC morphology
Solution annealed	28.9	50.0	418	TG
600°C/140 h	28.9	50.0	423	TG
550°C/1000 h	21.9	36.0	413	IG
500°C/1000 h	24.3	47.0	435	TG

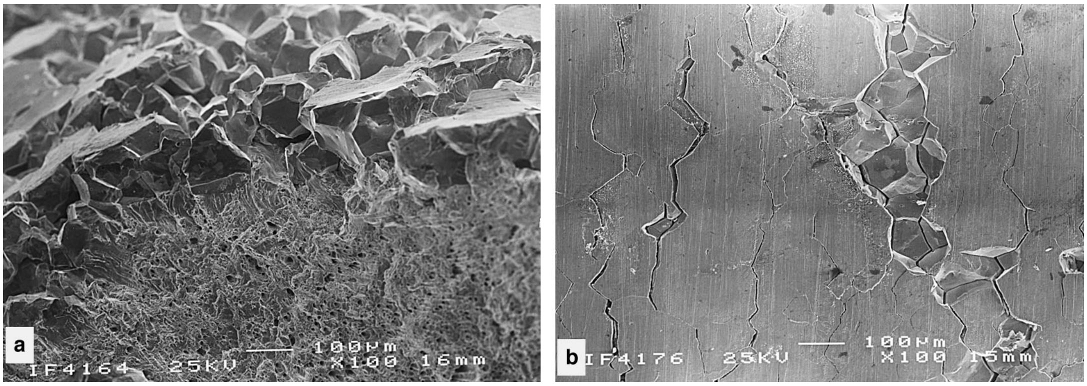

Fig. 7. SEM micrograph of IGSCC in a 550°C/1000 h specimen, tested in oxygenated 0.01 M Na_2SO_4 solution at 150°C and at saturated vapour pressure, (a) fracture surface and (b) cracks on the specimen surface.

of impurity elements alone cannot explain cracking observed in operating LWR plant. According to Kuroda et al. [14] intergranular attack in the Huey test correlated with segregation of P at the GBs. But IGSCC hardly occurred in such cases. However, in the cases where P-segregation takes place in synergy with Cr-depletion, increased susceptibility to IGSCC was observed.

In summary, the present studies have shown the usefulness of both the boiling acid–dichromate tests and potentiostatic etching tests in detecting segregation. However, more studies are necessary to quantify the extent of segregation using these tests. It was also found that P-segregation alone cannot cause IGSCC in hot water environments; but the effect of P-segregation, if any, is to enhance the IGSCC susceptibility of a stainless steel with Cr-depleted GBs.

4. Summary and conclusions

The effect of segregation on the IGSCC susceptibility of P-doped AISI type 304L specimens, solution annealed at 1100°C/1 h and then subjected to 600°C/140 h, 550°C/1000 h and 500°C/1000 h heat treatments, has been studied. A 6 h exposure test in boiling 5 N HNO_3 + 8g/L $K_2Cr_2O_7$ solution and an etch test at a transpassive potential of +1325 mV (SHE) in 5 N H_2SO_4 solution were used for detecting segregation of phosphorus. The IGSCC susceptibility was measured using a slow strain rate test at a nominal strain rate of 7×10^{-7} s^{-1} in two environments, viz., oxygenated 0.01 M Na_2SO_4 solution at 150°C and 0.01 M NaCl solution at 250°C. The following are the conclusions of the study.

1. Both the acid exposure test and the etch test at the transpassive potential of +1325 mV (SHE) are sensitive to P-segregation.
2. There was no direct correlation between the GB attack and either the weight loss in the nitric acid test or the cumulative charge in the acid etch test. This is because of the preferential attack at both the GBs and the P-segregated sites in the matrix.
3. Intergranular stress corrosion cracking was observed only in the 550°C/1000 h specimen, which showed Cr-depletion near the GBs as a result of the precipitation of Cr–P compounds at the GBs. In all other cases which showed segregation, but no Cr-depletion, only TGSCC was observed.
4. The present studies suggest that GB segregation of P alone is not sufficient to cause IGSCC in AISI type 304L stainless steel in the hot water environments studied.

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