ICF100765OR

Stress Corrosion Crack Growth Behaviour of Austenitic Stainless Steels in Hot Concentrated Chloride Solution

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ABSTRACT

The stress corrosion crack (SCC) growth behaviour of austenitic stainless steels (SS) in different metallurgical conditions was studied by the fracture mechanics (FM) approach. Threshold stress intensity parameters, K_{ISCC} and J_{ISCC}, and plateau crack growth rate (PCGR) were determined in boiling 5M NaCl+0.15M Na_2SO_4+2.5 ml/l HCl solution for AISI type 304N SS, AISI type 316 SS, and for AISI type 316 LN SS in different metallurgical conditions. Sensitisation of AISI type 304N SS and type 316 SS doubled the PCGR and decreased K_{ISCC} and J_{ISCC} to about 0.6 to 0.7 times the value of annealed material. Cold working (CW) of type 304N SS reduced K_{ISCC}, J_{ISCC}, and PCGR to less than those of sensitised SS. In type 304N SS, activation energy of 65 kJ/mol for the SCC process, crack growth in bursts, and crack arrest marks on the fracture surface indicated that hydrogen played a role in the cracking process. The values of K_{ISCC} and J_{ISCC} were about four times higher and the PCGR was nearly one order of magnitude lower for AISI type 316 LN austenitic stainless steel base metal vis-à-vis its weld metal. The higher K_{ISCC}, J_{ISCC} and lower PCGR for type 316 LN stainless steel vis-à-vis type 316 stainless steel signified the beneficial effect of nitrogen addition in improving SCC resistance. Higher K_{ISCC}, J_{ISCC} and lower PCGR for type 316 LN SS as compared to type 304 LN SS indicated the beneficial effect of Mo addition on SCC resistance.

KEYWORDS: Stress corrosion cracking, K_{ISCC}, J_{ISCC}, cold work, delta-ferrite, sensitisation, plateau crack growth rates, austenitic stainless steels

INTRODUCTION

A wide variety of industries, including the nuclear industry, employ austenitic SS as construction materials because of their excellent resistance to general corrosion, adequate high temperature mechanical properties and good fabricability. However, these SS are susceptible to localised corrosion attacks. Amongst the various microstructures encountered in an austenitic SS weldment, the sensitised heat affected zone (HAZ) has the lowest SCC resistance [1].

The resistance of these steels to sensitisation is increased, without sacrificing the strength levels, by reducing the carbon content and enhancing the nitrogen content [2]. The improved resistance to localised corrosion attacks has made nitrogen-added austenitic SS an attractive candidate material in a wide variety of industries. Information available in literature on SCC crack growth behaviour of austenitic SS with high nitrogen contents by using the fracture mechanics (FM) approach is insignificant. Most research on SCC of austenitic SS using a FM approach has been carried out in $MgCl_2$ solution [3]. However, $MgCl_2$ solution is insensitive [4]; while NaCl is sensitive [5]; to the effects of chromium depletion or impurity segregation in austenitic SS. Moreover, NaCl environment is most often encountered in nature. All the crack growth data on austenitic SS has been generated using the FM approach in conjunction with the constant load (CL) and constant strain (CS) testing techniques. Similar data can be generated in a relatively short time using the slow strain rate testing technique (SSRT).

Although the SCC behaviour of base metal of austenitic SS has been thoroughly investigated, studies on weld metal and weld joints have been few and far between. The SCC behaviour of base and weld metals differ depending on chemical composition, environment and testing techniques [6,7]. δ-ferrite alters both the SCC resistance and crack morphology of weld metal. The SCC resistance of weld metal depends on the content, distribution and solidification mode of δ-ferrite. No crack growth data has been published on weld metal of austenitic SS.

In this study, SCC crack growth data (K_{ISCC}, J_{ISCC} and PCGR) were generated in boiling 5M NaCl+0.15M Na_2SO_4+2.5 ml/l HCl solution for AISI types 316 and 304N SS, in various metallurgical conditions, using a combination of constant load and constant strain techniques, and for AISI type 316 LN SS and its weld metal, using the SSRT technique.

EXPERIMENTAL PROCEDURES

10 mm thick compact tension (CT) specimens from base metal of types 304N, 316LN and 316 SS, and 7.5 mm thick CT specimens with side grooves from weld metal of type 316N SS, were machined as per ASTM E 399. The chemical compositions of all the SS of the present study are presented in Table 1. SCC data was generated for annealed, cold worked and sensitised type 304N SS, for annealed and sensitised type 316 SS, and for annealed type 316 LN SS and its weld metal. Welding was carried out by depositing type 316N SS electrodes, using the manual metal arc welding process, in V-groove joint of type 316LN SS base metal with 20 mm root gap.

SCC tests were conducted in a boiling solution containing 5M NaCl + 0.15M Na_2SO_4 + 2.5 ml/l HCl (b.p = 381 K, pH = 1.3). SCC tests were carried out on AISI type 304N SS, in SA, 10% cold worked and sensitized conditions, at 363, 373 and 381 K. For the other two SS, the tests were carried out in boiling solution at 381.5 K. AISI type 304N and type 316 SS were tested using a combination of constant load and constant strain (wedge-loading) techniques. AISI type 316 LN SS and its weld metal were tested by SSRT technique at a constant extension rate of 10µm/hour to pre-specified values of load. The SCC-failed samples were subjected to fractographic examination in a scanning electron microscope (SEM).

TABLE 1
CHEMICAL COMPOSITIONS IN WEIGHT PERCENT OF AISI TYPE 304N, AISI TYPE 316LN AND ITS WELD METAL, AND AISI TYPE 316 STAINLESS STEELS

Weight % of Element	C	Cr	Ni	Mo	Mn	Si	N	S+P
Type 304N SS	0.04	18.3	9.2	--	1.6	0.37	0.086	0.026
Type 316 SS	0.054	16.5	11.4	2.3	1.7	0.64	--	0.031
Type 316 LN Base Metal	0.027	17.4	11.2	1.8	1.6	0.65	0.11	0.039
Type 316N Weld Metal	0.061	19.7	10.7	1.8	2.0	0.7	0.14	0.034

RESULTS AND DISCUSSIONS

The results are discussed in terms of three parameters viz. threshold stress parameters, K_{ISCC} and J_{ISCC}, and plateau crack growth rates, PCGR. The values of these parameters for the different SS studied are listed in Table 2. The maximum valid value of K_I (K_Q), calculated based on linear elastic fracture mechanics, and J_I (J_Q), calculated based on elastic-plastic fracture mechanics, has assessed the applicability of the FM approach in the range of loads of the tests.

TABLE 2
SCC GROWTH DATA FOR THE THREE STAINLESS STEELS IN DIFFERENT METALLURGICAL CONDITIONS IN 5M NaCl + 0.15M Na_2SO_4 + 2.5 ml/l HCl

Parameters	SA 304N SS	10 %CW 304N SS	20 %CW 304N SS	Sensitised 304N SS	SA 316 SS	Sensitised 316 SS	316 LN BM	316 N WM
K_{ISCC} (MPa.m$^{0.5}$)	17.0	9.0	3.0	11.0	13.0	10.5	22.38	5.79
J_{ISCC} (kPa.m)	0.9	0.45	0.15	0.5	1.0	0.6	2.601	0.233
da/dt (m/s)	1.3E-8	4.0E-9	8.0E-9	2.3E-8	4.0E-9	1.0E-8	1.75E-9	2.8E-8
K_Q (MPa.m$^{0.5}$)	18.0	32.0	42.0	17.0	11.2	13.28	18.0	24.0
J_Q (kPa.m)	240.0	220.0	275.0	230.0	74.8	84.0	112.0	122.0

SA → solution annealed; BM → base metal; WM → weld metal

Sensitisation decreased K_{ISCC} and J_{ISCC} and increased the PCGR of annealed type 304N and type 316 SS, as shown in Table 2, due to grain boundary Cr-depletion which resulted in weaker passive film in the regions along the grain boundary. The higher PCGR for sensitised material was due to the presence of pre-existing active paths coupled with lesser stress relaxation, due to lesser branching.

Cold work reduced K_{ISCC} and J_{ISCC} and also PCGR of annealed type 304N SS (Table 2). The reduction in K_{ISCC} and J_{ISCC} increased with increasing degree of CW. The decrease in K_{ISCC} and J_{ISCC} was attributed to increased density of metallurgical defects, which provided pre-existing sites for crack initiation, and increased dissolution rate due to increased strain energy. The higher strength of the CW material, vis-à-vis annealed SS, caused lower strain rates at crack-tip, leading to reduced PCGR.

Weld metal of type 316N SS showed lower K_{ISCC} and J_{ISCC} than the type 316 LN base metal it joined (Table 2 and Figure1). This was because the microstructural and microchemical heterogeneities in the weld metal, caused by the presence of δ-ferrite, and segregation of S & P at the δ-ferrite/γ interface along with the high concentration of microscopic and macroscopic defects in the weld metal, resulted in formation of uneven and weakly adherent passive film on its surface vis-a-vis base metal. The higher PCGR for the weld metal vis-à-vis the base metal was attributed to the higher yield strength (YS) and lower ductility of the former due to the presence of delta-ferrite [8] and cold work [9]. The poorer SCC resistance of high YS materials was attributed to lesser stress relaxation and, thus, reduced branching ahead of the crack-tip [4].

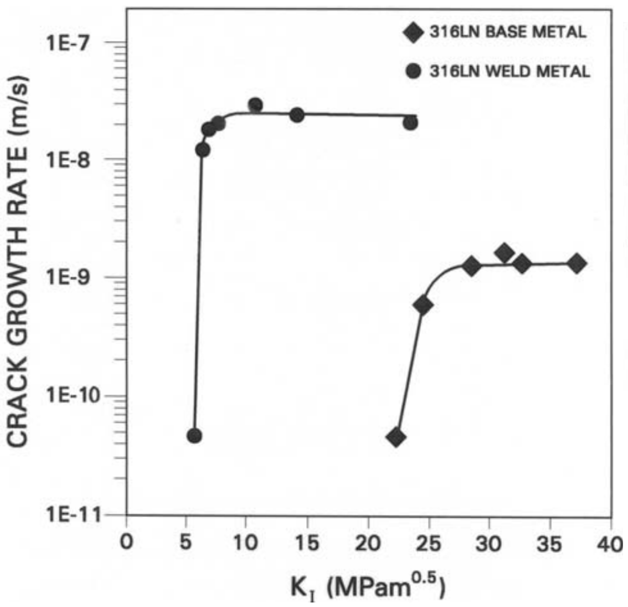

Figure 1: K_I vs. da/dt curves for type 316LN SS and its weld metal

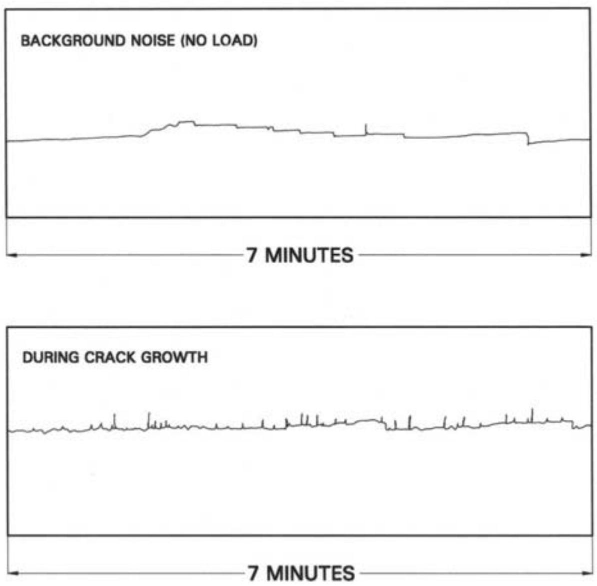

Figure 2: A typical record of acoustic events during crack growth for annealed type 304N SS

Comparison of the crack growth behaviour of types 316LN, 304N and 316 SS (Table 2), shows that type 316LN SS has higher K_{ISCC} and J_{ISCC} and lower PCGR than type 316 SS because of lower carbon and higher nitrogen contents in the former. Usually, SCC of austenitic SS in boiling acidified concentrated NaCl solution initiates through pits, which act as precursors to SCC. Thus, increase in resistance to SCC initiation is explained based on improved pitting resistance of nitrogen-added SS due to improved passive film stability, which also aids in decreasing the PCGR of type 316LN SS vis-à-vis type 316 SS. Type 304N SS had lower values of K_{ISCC} and J_{ISCC}, and higher PCGR than type 316 LN SS due to the role of Mo in improving SCC resistance through its influence on improving pitting resistance.

Comparison of crack growth data (Table 2) of types 316 and 304N SS gives an insight to the effects of Mo and N on the SCC behaviour of 18-10 austenitic SS. In this study, the Ni content was higher by 2%, Cr content was lower by 2% and carbon content was higher by 0.01% in the former. Presence of higher Ni and lower Cr would nearly neutralise any beneficial or detrimental effects of these additions on the SCC properties of 18-10 SS. Type 316 SS showed a lower PCGR and lower K_{ISCC} and J_{ISCC} than type 304N SS. This suggested that nitrogen imparted better resistance to SCC initiation, as compared to Mo, in 18-10 SS due to a more adherent passive film that it formed. However, Mo imparted better resistance to crack growth for an 18-10 SS. This was because of the effect of nitrogen in lowering the stacking fault energy, which, in turn, would promote planar slip. Planar slip accelerates SCC crack growth. However, the presence of both these elements synergistically improves the SCC resistance of austenitic SS as evidenced by better SCC properties for type 316 LN SS as compared to the other two SS.

The acoustic emission (AE) data on annealed, sensitized and 10% cold worked type 304N SS indicated that the crack growth was discontinuous, as seen in Figure 2 and Table 3. In the plateau region, crack growth per acoustic event varied from less than a micron to 15 μm. These observations and crack arrest marks on the surface (1 to 7 μm) (Figure 3), suggested that cracking occurred by discontinuous jumps of the order of a few microns. Activation energies of cracking were determined by using the PCGRs of annealed, 10% cold worked and sensitised type 304N SS at 163, 173 and 181 K, in the Arrhenius rate equation. The plot of PCGR and 1/T, shown in Figure 4, showed activation energy of the cracking process to be in the range of 50-65 kJ/mol, which corresponded to the diffusion of hydrogen in iron and steel. Table 3 also shows hydrogen diffusion distances per event time for the plateau region of the crack growth curves calculated using the equation $X=Dt^{1/2}$, where $D = 1.76 * 10^{-10}$ for hydrogen diffusion in austenitic SS [10]. It is seen that hydrogen diffuses more than the crack growth per event. This suggests that cracking occurs only when a critical concentration of hydrogen accumulates ahead of the crack-tip. From the above observations it was concluded that hydrogen played a vital role in the cracking of type 304N SS.

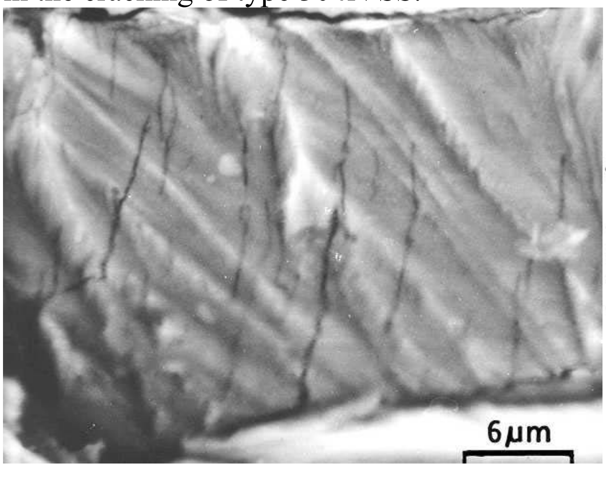

Figure 3: Fractograph showing crack arrest marks

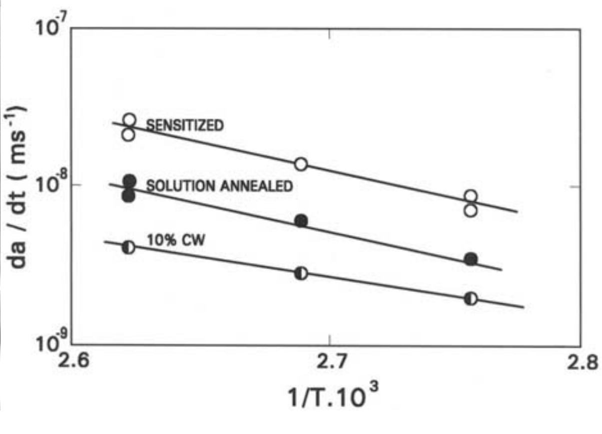

Figure 4: Dependence of da/dt on temperature for type 304N SS

TABLE 3
ACOUSTIC EMISSION DATA MEASURED DURING CRACK GROWTH

Sl. No.	Material Condition	Range of K_I ($MPa.m^{0.5}$)	da/dt (m/s)	Crack growth/event (μm/N)	Time period per event (s)	Hydrogen diffusion distance (μm/event)
1.	SA	33-46	1.1E-8	0.55	50	13
2.	SA	24-30	1.6E-8	1.15	72	159
3.	SA+sensitised	15-25	8.6E-9	2.3	375	360
4.	10% CW	18-20	7E-10	0.27	380	1000
5.	10% CW	43-80	4.8E-9	15	2870	---
6.	10% CW	24-43	3.6E-9	11	3120	1040

CONCLUSIONS

K_{ISCC} and J_{ISCC}, and PCGR were determined in boiling 5M NaCl+0.15M Na_2SO_4+2.5 ml/l HCl solution for NA types 304 and 316L SS and AISI types 316 SS in various metallurgical conditions. The following conclusions were drawn:

1. Sensitisation of annealed types 316 and NA type 304 SS lowered K_{ISCC} and J_{ISCC} by about 60 to 70 %, and increased the PCGR by 2 to 3 times.
2. K_{ISCC} and J_{ISCC} were about four times higher and PCGR was nearly one order of magnitude lower for base metal vis-à-vis the weld metal of AISI type 316 LN SS.
3. Results of AE, fractography and activation energy measurements during SCC of type 304N SS showed that hydrogen played a vital role in the cracking.
4. Comparisons of K_{ISCC} and J_{ISCC} and PCGR of base metals of types 316 LN and 316 SS, indicated the influence of nitrogen on improving the SCC properties of the former. Comparison of K_{ISCC} and J_{ISCC} and PCGR of types 304N and 316 SS indicated that nitrogen influenced to resist crack initiation while Mo functioned to resist crack growth.

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