Failure Propensity of Austenitic Stainless Steels by Chloride Induced Stress Corrosion Cracking in Air *

M. Mayuzumi **, H. Hayashibara **, J. Tani *** and T. Arai ***

** Tokyo Institute of Technology

*** Central Research Institute of Electric Power Industry

Chlorides induced stress corrosion cracking (ESCC) behavior was examined for SUS304L, SUS316L and SUS304 stainless steels (SS) after depositing synthetic sea water simulating sea salt particles at a temperature range from 333 K to 353 K with relative humidity of 35%. A stress-ESCC failure time relationship was formulated for SUS304L SS as $\log(t_f) = -A \log(\sigma) + B$, where σ : applied stress (MPa), t_f : time to failure (h), $A = 23.7T - 7020$, $B = 43.7T - 11600$, T : absolute temperature (K). Even an incipient micro-crack was not observed on the specimen surface of the SS at the applied stress level of 0.25 σ_y (σ_y : 0.2% proof stress), although SCC initiated at the applied stress level of 0.5 σ_y . Thus the threshold stress should be between 0.5 σ_y and 0.25 σ_y for these SS, and the threshold stress would rise beyond these values if the stress concentration be considered at the bottom and circumference of a pit. A statistical analysis suggested that the ESCC crack length and crack depth conformed to the double exponential distribution.

Key words : stainless steel, ESCC, chlorides, sea salt particle, relative humidity

1. Introduction

Stainless steels are widely used as structural materials for chemical plants, nuclear power plants, etc, because of the superior general corrosion resistance, mechanical properties, heat resistance, and weldability¹⁾. However, it is well known that austenitic stainless steels are susceptible to stress corrosion cracking (SCC) in certain environments under tensile stress. SCC induced by chlorides, such as sea salt particles, for example, is observed on various components in chemical plants^{2), 3)}, and also on piping of a nuclear power plant⁴⁾ built in the coastal area. This type of SCC is called as external SCC (ESCC) or atmospheric SCC since the cracking starts from out side of the equipment in air^{2), 3)}.

ESCC manifests itself as inter-granular cracking or trans-granular cracking depending on relative humidity, material condition, such as sensitized or not, and temperature. Inter-granular SCC (IGSCC) was usually observed in sensitized parts of stainless steel components at around ambient temperature. On the other hand, trans-granular SCC (TGSCC) observed regardless of the material conditions at relatively high temperature > 323 K. For the environmental condition, a certain degree of relative humidity (RH) is necessary to moisten the chlorides adhered on the stainless steel surface. The RH for ESCC easy to occur (RH_p) is dependent on the type of chlorides. Thus the RH_p of NaCl, for example, is 60% and that of MgCl₂ is 30% according to Shoji et al.⁵⁾ Another important factor of ESCC is the residual tensile stress derived from the welding or cold working processes. Hence, ESCC was usually observed at the weld joints or geometrical disconti-

nities.

To prevent premature failures of equipment caused by ESCC of stainless steels, it is necessary to clarify the stress-ESCC failure time relationships after considering the probabilistic aspect of ESCC phenomena, and the environmental conditions which lead to occurrence of ESCC in the stainless steel equipment. Hence, the purposes of this study are to obtain the stress-ESCC failure time relationship for SUS304L stainless steel, and also to make a statistical analysis on ESCC crack size distribution.

2. Experimental

2.1 Material

Austenitic stainless steel (SS) plates, SUS304L (304L), SUS316L (316L) and SUS304 (304), were examined in this study, since these SS are widely used as the structural materials for chemical plants and also nuclear power plants. Table 1 shows chemical composition of the test materials. Tensile specimens with a gage section of 2.0 mm thick, 5.0 mm wide, and 30 mm long were machined from the plate materials. After machining, the specimen was polished by emery papers to #600, degreased with acetone, rinsed with de-ionized water, and then attached to a loading apparatus that uses a spring to apply stress. Some specimens from 304L SS were aged at 923 K to simulate the heat history during welding process.

2.2. Test procedure

Stress-ESCC failure tests were conducted on 304L and 316L SS by a constant load method using a spring for load-

Table 1 Chemical composition of specimen.

	C	Si	Mn	P	S	Ni	Cr	Mo
SUS304L	0.020	0.67	1.34	0.032	0.002	9.69	18.13	-
SUS316L	0.019	0.65	1.23	0.034	0.002	12.07	17.51	2.08
SUS304	0.06	0.61	0.95	0.028	0.011	8.12	18.10	-

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** 2-12-1, O-okayama, Meguro-ku, Tokyo, 152-8552 Japan

*** 2-6-1, Nagasaka, Yokosuka-shi, Kanagawa-ken, 240-0196 Japan

ing⁶⁾. Applied stress (σ_{ap}) ranges from 0.25 σ_y to 1.75 σ_y of the SS (where σ_y : 0.2% proof stress). To deposit chlorides simulating sea salt particles on the gage section of the specimen, droplets (10 μ L each) of synthetic sea water were put on the gage section by a micro-pipette and dried. The resultant surface chlorine concentration was higher than 10 g/m² as Cl. The loading apparatus with the specimen was placed in a constant temperature and humidity chamber kept at test temperatures from 333 K to 353 K with RH = 35% after chloride deposition for the test to obtain the stress-failure time relationships of 304L SS and 316L SS. RH = 35% was selected for the test condition since RH = 35% was the most aggressive environment to the SS contaminated with sea salt particles⁵⁾. After ESCC tests, the surface of some specimens was observed by scanning electron microscopy (SEM) to determine the cracking or corrosion morphologies and also the threshold stress of ESCC at the test condition.

In addition, 10 specimens of 304 SS were tested under the environmental condition of 353 K with RH = 35% after applying the stress of σ_y (300MPa) to examine the probabilistic aspect of ESCC. The test time was set up to 260 h so as to avoid decrease in the applied stress by a large displacement of the spring because of the elongation of the specimen at the cracked region. The droplets of synthetic sea water were put on 2 or 3 points in the gage section in this case. After exposure to the environment, the crack length and depth were measured by SEM after revealing the maximum ESCC fracture surface at each chloride spot.

A relatively short term test (interrupting ESCC test) also was done to estimate the time when incipient cracks initiated. The test environment was the same as mentioned above, and the test times were set to 3 h, 5 h, 10 h and 20 h. After the test, the specimen surface was observed carefully by SEM to examine the corrosion morphology at each exposure time.

3. Results and Discussion

3.1 Stress-ESCC failure time relationship

Fig. 1 shows the relationship between applied stress and failure time for 304L SS obtained at temperature of 343 K with relative humidity of 35%. The failure time changed dependent on the applied stress, the larger the applied stress the smaller the failure time. For example, failure times of 410 h and 700 h were obtained for the applied stress of 475 MPa and 200 MPa, respectively. The aged specimens showed a tendency to fail in smaller time than the as received specimens in this particular test temperature. However, such a tendency was not observed in the test results at 353 K⁶⁾ and the effect of sensitization was not expected from the carbon content of 0.02%. Thus it was concluded that there was no difference in ESCC susceptibility for 304L SS with as received or aged conditions.

In general, a stress-failure time relationship was expressed as the following equation⁷⁾ for the applied stress

Fig. 1 Effect of the applied stress on the ESCC failure time of 304L SS under the test condition of RH = 35% at 343 K.

larger than the threshold stress at a given temperature ;

$$\sigma = -A \log(t_f) + B, \quad (1)$$

where σ : applied stress (MPa), t_f : time to failure (h). Equation (1) can be derived after the assumptions of a) the failure time (t_f) being equal to the incubation time (t_i) in a constant load SCC test, and b) the incubation time (t_i) being described by the Arrhenius type equation. By applying equation (1) to the minimum failure time for each applied stress in the test results at 353 K⁶⁾ and 343 K, the following two stress-failure time relationships can be obtained ;

$$\sigma = -1340 \log(t_f) + 3810 \quad (\text{at } 353 \text{ K}), \quad (2)$$

$$\sigma = -1100 \log(t_f) + 3370 \quad (\text{at } 343 \text{ K}). \quad (3)$$

Thus we can obtain temperature dependency of the constants, A and B, as follows ;

$$A = 23.7T - 7020, \quad (4)$$

$$B = 43.7T - 11600. \quad (5)$$

Although the above treatment is an expedient one, the following estimation can be made for the stress-failure time relationship at 333 K ;

$$\sigma = -865 \log(t_f) + 2930. \quad (6)$$

The stress-failure time relationship calculated from equation (6) was plotted in Fig. 2 as a solid line, together with the experimental data of 304L SS. The predicted failure times coincided moderately with the corresponding experi-

Fig. 2 Effect of the applied stress on the ESCC failure time of 304L SS under the test condition of RH = 35% at 333 K. The solid line shows the estimated failure time.

Fig. 3 Effect of the applied stress on the ESCC failure time of 316L SS under the test condition of RH = 35% at 353 K.

mental values for the higher applied stress region, although further analysis should be done to improve the applicability to the lower applied stress region.

Stress-ESCC failure test also was done on 316L SS having a higher resistance to pitting corrosion due to chlorides owing to Mo addition. Fig. 3 shows the applied stress-failure time relationship for 316L SS obtained at 353 K with RH = 35%. ESCC failure was observed only on the applied stress of 1.5 γ . The minimum failure time was 533 h for the applied stress of 560 MPa in contrast to the minimum failure time of 242 h for 304L SS with the applied stress of 496 MPa at the same environmental condition. Thus 316L SS had a higher resistance to ESCC than 304L SS. This test result is in a good accordance with an electrochemical study showing 316L SS had a higher pitting potential than 304L SS in saturated synthetic sea water at a temperature region of 303 K to 353 K⁸⁾.

3.2 Threshold stress for ESCC

It is well known that a threshold stress, under which SCC does not occur or SCC failure time increases remarkably, appears on an applied stress-failure time relationship⁷⁾. Usually, a threshold stress is dependent on the combination of materials and corrosion environments. A very low threshold stress will be expected for ESCC from the field data⁹⁾ showing ESCC of the piping without weld joints or any geometrical discontinuities nearby. There is few experimental data available¹⁰⁾ at present for the threshold stress of ESCC for SS in air. In this study, no visible crack was observed on the specimen surface for the applied stress of 0.25 γ (78 MPa) as shown in Figs. 1 and 2 (dashed arrow). Hence, the specimen surface was observed carefully by SEM for a micro-crack after removing corrosion products. Fig. 4 shows the surface appearance of the specimens after the tests at (a) 343 K for 8127 h, and (b) 333 K for 2089 h with the applied stress of 0.25 γ . No evidence of SCC cracks was found on the corroded region of 304L SS at both the test temperatures. The same results were obtained for 304 SS and aged 304L SS at 353 K⁶⁾, and also for 316L SS tested at 353 K as shown in Fig. 3 (dashed

Fig. 4 Surface appearance of 304L SS after exposure to the test environments of RH = 35% at (a) 343 K for 8127 h, and (b) 333 K for 2089 h.

arrow). Thus it can be concluded that the threshold stress of ESCC is as high as 0.25 γ (78 MPa and 85 MPa for 304L SS and 316L SS, respectively) for these SS at the temperature region of less than 353 K. The threshold stress was almost the same as that reported by Takemoto, et al.¹⁰⁾ for 304 SS. When a sensitization treatment was applied, 304 SS was failed for 403 h at the applied stress of 0.25 γ , although the fracture surface showed entirely trans-granular cracking⁶⁾. Thus further studies will be necessary to determine the threshold stress for ESCC of sensitized parts, as weld joints, of SS.

Pitting corrosion only was observed on the corroded area as shown in Fig. 4. The actual threshold stress might be larger than the value discussed above, since the corrosion pit will be expected to act as a stress concentration site. Stress concentration factors of 2.23 and 1.75¹¹⁾ are calculated at the circumference and the bottom of a pit, respectively, when a semi-spherical shape of the pit was assumed together with the Poisson's ratio of 0.25. Thus the threshold stress would increase at least to 0.56 γ or 0.44 γ if ESCC initiated from a smooth surface without the accelerating contribution of pitting corrosion.

3.3 Statistical analysis on ESCC

SCC essentially has a probabilistic aspect and, hence, a statistical analysis¹²⁾ was made on the ESCC crack length and the crack depth. The crack lengths and the crack depths we obtained for 304 SS were the maximum values at each chloride spot on the gage section. Hence the double exponential distribution was applied to the crack lengths and the crack depths, since Akashi et al. suggested that the distribution of the maximum crack depths of IGSCC could conform to both the normal probability distribution and the double exponential distribution¹³⁾. Fig. 5 shows the double exponential distribution plot for the crack length (a) and the crack depth (b) both divided by the test time (261 h or 162 h). It is obvious from the linearity of the plots that both the crack length and the crack depth conformed to the double exponential distribution, although two data from the crack lengths showed a relatively large deviation from the straight line. Fig. 6 shows the fracture surface of the specimen with the crack deviating from the double exponential plots. It was suggested that the fracture surface was produced through a macro-

Fig. 5 The double exponential distribution plot for (a) the ESCC crack length on the specimen surface and (b) the crack depth.

scopic coalition of two cracks into one larger crack, as shown in the line on the Fig. The same tendency was observed also on the fracture surface of the other one specimen. Thus the deviation of the two data in Fig. 5 (a) would have been caused by the macroscopic crack coalition and the resultant abrupt increase in the crack length on the specimen surface.

As mentioned above, both the ESCC crack length and the crack depth conformed to the double exponential distribution. One prerequisite for SCC phenomena to fit the distribution would be that the SCC process is dominated by either of the crack initiation sub-process or the crack propagation sub-process, and the time necessary to reach a certain crack length or crack depth is determined by one of the sub-processes¹²⁾. To examine which of the sub-process controls the entire ESCC process in this test condition, the interrupting ESCC test was conducted for 3 h through 20 h at 353 K with RH = 35%, and the corroded surfaces were observed by SEM for incipient cracks. Fig. 7(a) and 7(b) shows the surface appearance of the specimens tested for 3 h and 5 h, respectively. It is obvious from the Fig. that ESCC initiated only after 3 h or 5 h of exposure to the environment and, thus, the crack propagation sub-process occupied almost all of the test durations of 261 h or 162 h. Thus the crack propagation sub-process determined the crack size in this study. However, this result could be obtained since both the surface chlorine concentration and the environmental condition were severe

Fig. 6 ESCC failure surface showing the coalition of two cracks into one larger crack.

Fig. 7 Surface appearance of the specimens tested for (a) 3 h and (b) 5 h at 353 K with RH = 35% (applied stress : σ_y).

enough for 304 SS to cause ESCC within a very short exposure time. In actual components, however, the time for the crack initiation sub-process or the incubation time would be almost equal to the time necessary to contaminate the SS component surface by chlorides beyond the critical surface chlorine concentration¹⁴⁾, and determine the failure time of the components by ESCC.

4. Conclusions

(1) A stress-failure time relationship was formulated for SUS304L SS as $[\text{MPa}] = -A \log(t/h) + B$, where $A = 23.7T - 7020$ and $B = 43.7T - 11600$, in the temperature range between 333 K and 353 K. SUS316L SS had a higher resistance to ESCC than SUS304L SS.

(2) Even an incipient micro-crack was not observed on SUS304L SS and SUS316L SS surface for an applied stress level of $0.25 \sigma_y$ after exposure to the test environment of RH = 35% at temperatures < 353 K. Thus the threshold stress of ESCC would be larger than $0.25 \sigma_y$ for these stainless steels. If the stress concentration from a corrosion pit was taken into account, the threshold stress will increase to $0.56 \sigma_y$.

(3) The ESCC crack length and crack depth conformed to the double exponential distribution, since the SCC process was dominated by the crack propagation sub-process in the test condition.

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要 旨

SUS304L, SUS316L および SUS304 ステンレス鋼の塩化物応力腐食割れ (ESCC) 特性を 333 K から 353 K の温度範囲, 相対湿度 35% の条件下で, 海塩粒子を模擬した人工海水を付着させて検討した. 304L ステンレス鋼に対しては, 応力と破断時間の関係を $(\text{MPa}) = -A \log(t/h) + B$ の形で定式化した. ここで $A = 23.7T - 7020$, $B = 43.7T - 11600$ (T : 絶対温度) である. 負荷応力が 0.2% 耐力の 0.25 倍の場合, 試験片表面に微視的な割れさえ認められず, これらのステンレス鋼に対する ESCC のしきい応力は耐力の 0.25 倍より大きいことがわかった. また孔食による応力集中を考慮すれば, この値はさらに大きくなるものと推定される. さらに統計的な解析結果によれば ESCC クラック長さおよびクラック深さは, 二重指数分布に従うことが示唆された.

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