In-Situ* Observation and Acoustic Emission Analysis for SCC of MgCl₂ Droplet in SUS304 Stainless Steel

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Acoustic emission and optical video microscope monitoring was proposed to investigate the stress corrosion cracking of work-hardened SUS304 stainless steel caused by a small magnesium-chloride droplet. The crack propagation length could measure clearly under the droplet by VMS. The SCC started at 45–82 ks with pitting. The crack velocity was 3.2–4.7 $\mu\text{m}/\text{ks}$ and it propagated almost continuously. AE signals were generated at early stage of SCC testing of 55 and 82 ks, after that they were generated discontinuously. With the SEM observations, the detected AE signals were mainly attributed to cracking of the oxidation products and discontinuous crack propagation at the falling-off surface grain. [\[doi:10.2320/matertrans.M2013331\]](https://doi.org/10.2320/matertrans.M2013331)

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1. Introduction

Electrochemical techniques (EN and, CPF) and acoustic emission (AE) which generated by crack nucleation and propagation have been applied as monitoring techniques of stress corrosion cracking (SCC).¹⁾ Takemoto reported in detail the advantages of AE techniques for corrosion analysis.²⁾ When many uncertainties exist in AE analysis, it is necessary to estimate the AE source during corrosion.

We developed a new AE-based corrosion-monitoring technique.^{3,4)} The technique is based on the droplet SCC testing method with a high-sensitivity AE sensor⁵⁾ and a continuous AE waveform monitor.⁶⁾ AE properties of work-hardened type 304⁷⁾ and type 316L⁸⁾ austenite stainless steels were evaluated during SCC propagation. AE properties of the droplet testing were found to be similar to the result of using a water bath and corrosion-cell SCC testing. We then applied AE to evaluate the initiation of SCC such as pitting nucleation without loading in the work-hardened type 304 stainless steel.^{9,10)} Two types of corrosion phenomena were observed, open pitting and covered pitting. There was no AE activity in open pitting. In contrast, AE activity similar to that of SCC testing was observed in covered pitting. Some cracking was observed by cross-section SEM observation both on the surface skin of covered pitting and in the corroded microstructure around the pitting. We assumed that micro cracking around the covered pitting structures must have initiated SCC. We therefore developed a high-magnification *in-situ* optical observation technique using a video microscope (VMS) with near-field AE measurement to estimate AE sources of the corrosion testing in a droplet.¹¹⁾ As a result, we observed AE activity after the corrosion-product sheet was covered with pitting. Some cracking in the oxidization film located on the pitting surface was observed by SEM observation after the testing. The AE source may have been cracking in the oxidization film.

This report describes the new *in-situ* optical observation technique applied for SCC testing to observe crack propagation and to estimate AE sources.

2. Experimental Procedure

2.1 Specimen and corrosion set up

Commercial SUS304 stainless steel (Cr: 18.17 mass%, Ni: 8.06 mass%, C: 0.07 mass%, Si: 0.44 mass%, Mn: 0.78 mass%, P: 0.007 mass%, and S: 0.007 mass%) was used in the present study. Two specimens were prepared for the testing (No. 1, and No. 2). The specimens were 20 mm wide, 100 mm long, and 0.2 mm thick with surfaces mechanically polished. The Vickers's hardness was Hv 420, meaning that the surface of the thin plate had been work-hardened.²⁾ A droplet of 25 mass% MgCl₂ solution was set in the center of the surface of specimens placed inside a thermostatic bath (343 K, 30% humidity) for three days.

2.2 *In-situ* optical observation by VMS

In-situ surface optical observation was conducted during SCC testing using a VMS (VB7000+VH-Z250R; Keyence) with magnification from 250 to 2500. The recorded frame interval was 600 s.

A cover glass was placed on the droplet to directly observe the SCC at high magnification. A 1 mm in the diameter (2 μL droplet) when the gap was 0.4 mm was employed in this experiment.¹¹⁾

2.3 Acoustic emission measurement

A continuous AE waveform monitor (CWM) was used to analyze the AE signals.⁶⁾ The measurement settings were 2 MHz sampling rate with a 12-bit resolution in the 5 V range in two channels. The total gain was 80 dB.

Figures 1(a) and 1(b) indicate specimen and measurement settings. SCC was observed by VMS through a cover glass (a) and a MgCl₂ droplet underneath (b). The gap between the specimen (d) and the cover glass was set to 0.4 mm with glass plate spacers (c). The diameter of the droplet was ~ 1 mm.

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a: cover glass, b: droplet, c: PTFE tape spacer, d: specimen, e: Bending force plate, f: AE sensor, g: AE sensor mounting jig

Fig. 1 Specimen and measurement settings, (a) photo and (b) schematic comprehensive specimen loading and AE sensor mounting.

Two 180 kHz resonant high-sensitivity integrated AE sensors (M204A; Fuji Ceramics)⁵⁾ were mounted on the specimen (f) using mounting jig (g). The bending stress of 1000 MPa that was calculated from the curvature radius was applied by a bending force jig (e). Located AE hits were analyzed with a 40 μV_{0-P} of threshold level.

2.4 Micro structural observation

Corrosion products on the specimen surfaces were removed by ultrasonic bathing after testing. The specimens were then examined by VMS and scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Surface observation

Figures 2 and 3 present the VMS and SEM images after No. 1 (a) and No. 2 (b) were tested.

For specimens No. 1 and No. 2, SCC was initiated by open pitting of 50 to 100 μm in diameter. The cracks propagated from both sides of the pitting to a maximum length of 890 μm . Cracks on the right side were longer than those on the left side. Some cracking of the oxidation products on the pitting was seen in the SEM image.

3.2 VMS observations

Figures 4 and 5 present *in-situ* images of the droplets acquired by VMS for specimen No. 1 and No. 2.

The pitting that initiated SCC was observed within 60 s of being attached to the droplet for both specimens No. 1 and No. 2 (Fig. 4(a)). Cracks were observed under corrosion-product films covering upper part of the pitting. In specimen No. 2, there was small additional pitting near the main pitting in the first stage of testing. Also, a corrosion-product film covered the pitting (Fig. 5(a)). In addition, a corrosion-product film of 30 μm in diameter was observed on the left side of the crack in specimen No. 2 (Fig. 5(b)). The cracks propagated at a small angle in a local of zigzag line. The

Fig. 2 VMS image of SCC after the droplet was removed, (a) No. 1, (b) No. 2.

Fig. 3 SEM image of SCC, (a) No. 1, (b) No. 2.

Table 1 Summarized the crack length, starting time and crack velocity.

		Crack length, μm	Starting time, ks	Crack velocity, $\mu\text{m/ks}$
No. 1	Right	890	44.68	4.71
	Left	240	46.73	3.29
No. 2	Right	565	115.78	3.19
	Left	123	81.85	4.05

cracks propagated almost continuously except the line angle was relatively smaller (Fig. 5(c)).

Table 1 lists the crack lengths, starting time and crack velocities for specimens No. 1 and No. 2. The crack starting times were 45 to 82 ks and the crack velocities were 3.2 to 4.7 $\mu\text{m/ks}$ except for suspended part of the right side cracks.

3.3 AE results

Figures 6 to 8 present cumulative AE event counts, AE peak amplitudes, peak frequencies of events and crack lengths with time for specimens No. 1 (a) and No. 2 (b).

In both specimens of No. 1 and No. 2, AE events increased rapidly to the first stage (54 and 90 ks) of the crack nucleation and/or propagation. The AE events then increased rapidly at 81 and 163 ks in specimen No. 1 and No. 2 respectively. AE amplitudes ranged from 40 to 150 μV . Low-amplitude AEs (around 50 μV) were detected where

Fig. 4 VMS images of pitting and SCC under a droplet of No. 1 at (a) 60 s, (b) 55 ks, and (c) 83 ks.

Fig. 5 VMS images of pitting and SCC under a droplet of No. 2 at (a) 73 ks, (b) 118 ks, and (c) 262 ks.

the zigzag crack lines stopped. The peak frequencies of the low-amplitude AE events were distributed from 250 to 400 kHz in the high-amplitude AE inactive region, from 300 to 400 kHz in the high-amplitude AE activity region.

Figure 9 shows AE peak amplitude distribution for specimen No. 1 and No. 2. In both specimens of No. 1 and No. 2, the AE events were distributed in the peak frequency from 350 to 400 kHz.

3.4 Discussion of AE source

Four theory for SCC of the chloride in the austenitic stainless steel have been proposed in recent years: active path corrosion (APC), concurrent effect of APC, hydrogen embrittlement cracking²⁾ and hydrogen-induced transformation.⁴⁾ In our previous droplet SCC testing, pitting initiated SCC and the cracks were transgranular fractures.⁶⁾ The pitting

site could be identified within 60 s after a droplet was set on the specimen. The corrosion-product film covered the pitting during as it expanded. The nucleation times of SCC were 45 to 82 ks, and crack velocities were 3.2 to 4.7 μm/ks. AE activity was detected during crack nucleation, but the activity was not directly related to crack propagation. The activity was mainly related to discontinuous crack propagation.

The AE waveform of our corrosion testing and SCC testing was similar to SCC with 30 mass% MgCl₂ solution of sensitized Type 304 stainless steel in Yonezu *et al.*¹²⁾ Figure 10 presents SEM image of estimated AE sources, shell oxide (a) and surface grains falling-off. In Ref. 12), the AE source of low-frequency events for the potential fluctuation and AE measurement, detected in the SCC propagation region was shell oxide (cracking-oxidization). Similar shell oxide was observed inside the pitting in our

Fig. 6 Cumulative AE event counts and crack lengths with time, (a) No. 1, (b) No. 2.

Fig. 8 Crack lengths and AE peak frequency with time, (a) No. 1, (b) No. 2.

Fig. 7 Crack lengths and AE peak amplitude with time, (a) No. 1, (b) No. 2.

Fig. 9 AE peak frequency distribution, (a) No. 1, (b) No. 2.

experiment (Fig. 10(a)). The AE source of high-frequency events, detected in early stages of pitting generation with falling surface grain in Ref. 12), was also observed at the crack-stopping position of falling-off surface grains with a low-amplitude event and a frequency range of 300 to 400 kHz in our testing (Fig. 10(b)). The AE peak frequency is theoretically related to the crack nucleation velocity in

half medium of wave propagation. The peak frequency also depends on both the transfer function of plate wave and the frequency response of the AE sensor in the plate medium. However our experimental result indicated similar tendency of Ref. 12).

Based on the discussion, the first AE activity could be related to crack initiation including cracking of oxidation

Fig. 10 SEM image of estimated AE sources, (a) shell oxide (b) falling-off surface grain.

on pitting. In Refs. 9) and 11) of our droplet-corrosion testing, cross-section observation revealed micro cracking around the pitting. The cracking of surface oxidization on pitting and micro cracking around pitting could be AE sources. In addition, AE sources after crack initiation could be related to oxidization cracking and discontinuous crack propagation of the zigzag line with surface grains falling-off as observed in Fig. 10(b).

Further examination, including cross-section observation, will be necessary to determine the mechanism of SCC of the chloride of the austenitic stainless steel and to clarify AE sources.

4. Conclusions

SCC propagation of work-hardened type 304 stainless steel was evaluated by using *in-situ* observation in a droplet

by high magnification VMS and AE measurement in a plate medium.

- (1) SCC propagation in a droplet was successfully observed by using high-magnification VMS (250 to 2500 times) with cover glass over the upper part of the droplet.
- (2) SCC did not propagate a straight line. It propagated with large zigzag angles, and the crack propagation stopped and then continued at relatively smaller angle. The crack velocity was 3.2 to 4.7 $\mu\text{m}/\text{ks}$.
- (3) The AE events increased rapidly until crack nucleation or propagation; discontinuous increase were then observed after 28 ks for specimen No. 1 and after 7 ks for specimen No. 2. There was little AE activity at other times. The AE amplitude in the active time ranged from 40 to 150 μV , and the peak frequencies were 250 to 400 kHz.
- (4) The AE amplitude was around 50 μV , and the peak frequency was 300 to 400 kHz where the crack was arrested.
- (5) The AE signal could be related to the crack nucleation and/or propagation, and the cracking of the oxidization on pitting could be related to AE phenomena.
- (6) The AE signal detected during crack propagation could be related to the cracking of oxidization on new pitting and the crack arrest and propagation in a zigzag line.

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