Abstract

Dual phase stainless steel of austenite and ferrite possesses a susceptibility to both active-path-corrosion type SCC (APC-SCC) and delayed fracture (DF) when it is exposed to a concentrated chloride solution. We utilized acoustic emission (AE) and corrosion potential fluctuation (CPF) to study the fracture mechanism of a dual-phase stainless steel in 42 and 35 % MgCl₂ solution at 90 °C. We detected characteristic CPFs but no AE in the 42 % MgCl₂ solution, while we detected strong AE signals but no CPFs in the 35 % MgCl₂ solution. It was concluded that the environment assisted fracture in the 42 % MgCl₂ solution was caused by the APC-type SCC but that in the 35 % MgCl₂ was by the delayed fracture or hydrogen assisted cracking.

Keywords: Dual phase stainless steel, stress corrosion cracking, delayed fracture, corrosion potential fluctuation, chloride solution

Introduction

Mechanisms of environment-assisted fracture (EAF) have not been well understood in spite of a number of research studies. Here, the EAF includes both the stress-corrosion cracking (SCC) and delayed fracture (DF). The SCC occurs in a limited anodic potential range and can be prevented by the cathodic polarization. Japanese corrosion engineers consider SCC to be separate from the DF. The SCC is often called as the active-path corrosion (APC) type SCC. This means that SCC is caused by the anodic dissolution of metal along the active paths such as slip lines, grain boundaries and martensite laths, and not by the mechanical fracture. As long as the SCC is caused by anodic dissolution of metallic elements, it does not produce strong AE signals [1, 2]. Contrary to this, the DF of high strength ferritic steels is well known to produce strong AE signals [3, 4] and is accelerated by cathodic polarization where hydrogen cations can exist on the surface and in the crack.

Okada [5, 6] first studied the mechanism of APC-SCC by AE and concluded that APC-SCC did not produce strong AE signals, but the DF did produce strong AE signals. We also found that transgranular SCC (TG-SCC) of solution annealed type-304 in a 35 mass % MgCl₂ solution did not emit AE signals, but the intergranular SCC (IG-SCC) of sensitized 304 steel produced AE signals [7, 8]. This mechanism appears to be similar to the intergranular separation [9], observed for the sensitized type-304 stainless steel absorbing the hydrogen.

Duplex stainless steels show excellent resistance to chloride SCC. Kowaka et al. [10] studied in detail the SCC of 26Cr-Ni duplex stainless steel (DP-3 alloy by Sumimoto Metal Co.) in boiling 45 % MgCl₂ solution. They reported that the APC-SCC propagated through the ferrite phase (28Cr-4Ni) and stopped by austenite phase (21Cr-9Ni). Damage mechanism of the EAF is generally estimated from potential
range and fractographic (metallographic) studies, but such inverse estimation of the mechanism often leads to a wrong conclusion. Another powerful tool to study the mechanism of EAF is the corrosion potential fluctuations (CPF). Characteristic potential fluctuations were reported to occur in the APC-SCC [11, 12]. In this paper, we studied the EAF mechanism of DP-3 steel in 42 and 35 % MgCl₂ solution by simultaneous monitoring of AE and CPF.

**Specimen and Experimental Setup**

Plate shaped specimens of 20-mm width and 120-mm length and 2-mm thickness were prepared from a 20-mm thick, 100-mm wide, cold-rolled DP-3 (JIS SUS329J1L) steel plate (0.21C, 0.43Si, 0.85Mn, 0.024P, 0.001S, 25.43Cr, 7.23Ni, 3.11Mo, 0.15N) and submitted to three-point bend EAF test. The cold rolled plate shows a strong elongated texture, as shown in Fig. 1. In the figure, surface corrosion pits and fine cracks produced in 35% MgCl₂ solution is also shown. Specimens were sensitized by heat treatment of 923 K for 20 hours and air cooled. Vickers hardness of ferrite and austenite grains was measured as 280 and 190, respectively. Stress-strain curves of each phase were estimated by dual indentation method and shown in Fig. 2. A stress-strain curve obtained by a tensile test is also shown. It is noted that the yield strength of austenite phase (Δ) is 250 MPa but that of ferrite phase (○) is as high as 800 MPa. Fracture strain is measured as 18% by the tensile test. Sensitization treatment increased the hardness of ferrite phase significantly. This effect appears to be due to the precipitation of sigma phase.

Figure 3 shows test method of environment assisted fracture (EAF). A glass cell of 20-mm diameter was mounted on the tensile surface of a bent specimen, and filled with 42 or 35 mass% MgCl₂ solution. Both the cell and specimen were heated by band heater and plate-shaped ceramic heater, respectively, so that the solution and specimen temperature were at 90°C and 80°C, respectively. Corrosion potential was measured by a digital voltmeter using a platinum electrode immersed into the solution and fed to a personal computer. The measured potential was converted to the potential referred to an Ag/AgCl standard electrode. Vertical resolution of the potential is 0.1 μV, but the time resolution is 0.25 s.

![Fig. 1 Cross-sectional (transverse) microstructures of DP-3 steel, showing surface pitting corrosion and cracks after an EAF test in 35% MgCl₂ solution.](image1)

![Fig. 2 Stress-strain curves of ferrite and austenite phases estimated by dual indentation test and that of DP-3 specimen by tensile test.](image2)

We monitored Lamb wave AE signals by two small resonant-type sensors (PAC, Type-Pico, resonant frequency of 0.45 MHz, sensing diameter of 3 mm) mounted on the tensile surface. Outputs of the sensors were amplified to 80 dB and digitized by an A/D converter and stored in a hard disk.
Results and Discussion

Figure 4 compares the change of corrosion potential and cumulative AE counts with test time in 35 and 42% MgCl₂ solutions. Frequent rapid-drop (RD)-type potential fluctuations were observed in the 42% MgCl₂ solution but no RD fluctuation in the 35% MgCl₂ solution. We detected a number of AE (209 events) in the 35% MgCl₂ solution, starting at ~170 ks, but only 6 AE events in the 42% MgCl₂ solution. Another experiment in the 42% MgCl₂ solution detected only five AE events with frequent RD-type potential fluctuations. Small, branched cracks were observed at around 100 ks in the 42% MgCl₂ solution, when the first AE was detected. AE counts in the 35% MgCl₂ solution increased rapidly at around 170 ks, or 50 ks after visible small corrosion pits appeared at 120 ks. Characterization of AE and CPF in the 42 and 35% solutions will be discussed separately in the next section.

Characterization of AE and CPF in 42% MgCl₂ Solution

In this solution, we detected 79 events of RD-type CPFs prior to the AE detection at 100 ks. Figure 5 shows the magnified potential fluctuation. Fluctuation magnitudes are of a few mV and weak, as shown
in the figure at right. The down-shooting velocity: \(dE/dt\), which determines the anodic current: \(I\), is low. We estimated \(I\) by using Eq. (1).

\[
I = -C_d \times dE/dt
\]  

(1)

Here, \(C_d\) designates the capacitance of the electrochemical double layers and is taken as 20 \(\mu F/cm^2\) [13]. Result is shown in Fig. 6. Current density is of order of 0.02 \(\mu A\) or less and is 200 times smaller than that previously estimated for the APC-SCC of Type-304 stainless steel in a 35% solution [13]. Such a small current of the DP-3 alloy is supposed to be due to the high resistance of this alloy to APC-SCC. It is noteworthy that both the anodic (+) and cathodic (–) currents were exhibited at certain periods, but they were not detected for AE generation period at around 100-130 ks. Figure 7 shows expanded sections of corrosion current vs. time. Except for E.C. 6, little corrosion current flows at the time of AE. Cathodic current suggests that the hydrogen reduction reaction is taking place in the crack and the competition of non-Faradic and Faradic reactions occurs. Hydrogen bubble formation requires prior accumulation of hydrogen reaction.

Fig. 6 Change of current estimated from the rate of RD-type corrosion fluctuation for DP-3 steel in 42% MgCl_2 solution.
Fig. 7 Change of corrosion current corresponding to AE generation for DP-3 steel in 42% MgCl₂ solution. Timing of AE events is given by circles.

Fig. 8 Examples of waveforms and frequency spectra of AE signals detected by channel 1 sensor during EAF test of DP-3 steel in 42% MgCl₂ solution.
Figure 8 shows waveforms and frequency spectra of first three events of total six AE signals detected in the 42% solution. AE signals are typical Lamb waves with first arrival So-mode and late arrival Ao-modes. AE signal of event count 2 (E.C. 2) shows a strong, sharp peak at 0.5 MHz. Events 3-6 also had a similar peak at ~500 kHz. E.C. 4 had a strong peak at 190 kHz in addition. Another event, E.C. 1, had stronger peaks at 650 and 700 kHz, but there was a weak peak at ~500 kHz. This signal may be different from the rest and resembles Type-A signals found in the 35% solution. The Pico sensor used have a broad resonance centering at 450 kHz, but the observed peaks at ~500 kHz are much sharper than the sensor resonance. This is well-known characteristic of acoustic/AE signals produced by hydrogen gas evolution [13]. Morikawa and Ono [14] reported earlier that numerous hydrogen bubbles produced AE as “continuous wave” mode in contrast to cracking AE. AE signals due to gas bubbles have been reported to have a narrow spectrum and this was confirmed in our laboratory [15]. This resonance frequency approximately corresponds to 100 µm hydrogen bubbles [16]. Another support to the hydrogen bubble source was given in Fig. 7. Here, corrosion current curves for most events showed the absence of cathodic current. This implies that fresh cracking did not occur when AE signals were detected. Two events (E.C. 1 and 4) had additional peaks. These can be due to simultaneous evolution of bubbles, larger or smaller. The broader frequency components in E.C. 1 may also originate from other AE sources, such as the friction of crack faces or the fracture of rust, but further confirmation is needed. As shown in Fig. 9, we observe an S-shaped crack and fragmented particles of ferrite grains due to strong texture. This type of SCC tends to produce the friction induced AE.
Crack morphology is shown in Fig. 10. Cracks are observed in ferrite grains and along grain boundaries of ferrite grains. Interesting finding is that the cracks were observed even in the austenite grains. This is contrary to the perfect keying action of the austenite grains in the 35 % MgCl₂ solution as will be discussed later.

These data suggest that the EAF in the 42% solution is caused by the APC-SCC, which does not produce primary AE. When the APC-SCC progresses, solution in narrow grooves or cracks is changed to strong acidic solution due to hydrolysis reaction of chromium chloride with water, and then the hydrogen gas evolution takes place in the crack. Though we did not observed hydrogen gas evolution by visual inspection, this is consistent with the expected small size of hydrogen bubbles.

![Fig. 11 Magnified corrosion potential fluctuation detected for DP-3 steel in 35 % MgCl₂ solution at 90°C.](image)

![Fig. 12 AE counts and change of estimated current from RD-type corrosion fluctuation for DP-3 in 35% MgCl₂ solution.](image)

**Characterization of AE and CPF in 35% MgCl₂ Solution**

We did not observe characteristic RD-type potential fluctuation (see Fig. 4). Figure 11 shows magnified potential changes before and during the AE generation. Current density estimated by Eq. (1) was very low, as shown in Fig. 12. We observed no coincidence of AE timing and CFP.

We detected two types of AE as shown in Fig. 13. These waveforms resemble those detected in the 42% solution, i.e., Type-A with broader frequency content and Type-B with a single frequency peak from hydrogen gas evolution. Here, Type-A signals appear to arise from fracture events, as will be shown below. In the previous section, only E.C. 1 fits Type-A behavior, while the rest were single or
Fig. 13 Two types of AE signals detected for DP-3 steel in 35% MgCl₂ solution.

Fig. 14 Change of cumulative counts of Type-A and -B AE signals during EAF of DP-3 steel in 35% MgCl₂ solution. CPF at 100 ks may be due to pitting.

double peaks. Cumulative AE counts of Type-A and -B are shown in Fig. 14. Event counts (175) of Type-A signals is eight times large that (34) of Type-B. Shown in Fig. 15 are the waveform detected by two sensors. Waveforms of E.C. 60 with opposite polarity of first-arriving So-mode indicate a mixed mode fracture while the E.C. 67 with the same polarity the Mode-I (crack opening) fracture. Mode classification was possible for 39 events with strong amplitudes. Of these, 29 events were from the Mode-I fracture and this is three times large that ten events from the mixed mode fracture. The mixed mode fractures are probably due to zigzag-shaped cracks owing to the elongated grain texture. Short rise time of the first So-component strongly indicates the fast mechanical fracture by the delayed fracture. Fracture dynamics was estimated by waveform simulation of the first So-wave using the experimental transfer function. Detail of this method can be seen elsewhere [17].
Fig. 15 AE waveforms indicating the mixed mode crack (E.C.60) and Mode-I crack (E.C. 67) for DP-3 steel in 35% MgCl₂ solution.

Fig. 16 Overlapping of simulated Lamb waveform on the detected wave.

Figure 16 shows the overlapping of simulated waveform and the detected one. The source parameters, crack volume $\Delta V$ and effective rise time $\Delta Tr^*$, are shown in the figure. Effective rise time is less than 0.1 $\mu$s. This short rise time is indicative of fast fracture due to hydrogen induced cracking. Our previous research on the delayed fracture of dual phase stainless steel R4 (Nippon Yakin Co. Ltd.) under hydrogen charging showed the effective rise times from 0.1 to 0.4 $\mu$s [18].

Figure 17(a, b) show macroscopic and microscopic surface crack geometry. On the surface, branched cracks along the axial direction of the specimen can be seen in addition to the normal (vertical in the photo) cracks. The driving force to the axial cracks is the tensile stress in the width direction of the bent specimen. This stress is calculated as half of the axial tensile stress under the plane strain and stress states. Attacks in the 35 % MgCl₂ solution begin with the localized corrosion of ferrite grains as shown in
This process is needed to produce enough protons for subsequent delayed fracture and corresponds to the incubation period for the delayed fracture. Cross-sectional micrographs, Fig. 17(c, d), show the cracking to be mostly in the ferrite grains or grain/phase boundaries. In this solution, a crack occurs in the ferrite grains and along grain boundaries of ferrite grains, but it is completely stopped by the austenite grains as shown in Fig. 17(c) and (d). Such complicated cracks are likely to produce the mixed mode fracture, combining Modes I and II, and attendant AE signals.

Fig. 17(a, b) Surface crack structures; (c, d) Cross-sectional microstructures of cracked DP-3 steel in 35% MgCl$_2$ solution.

**Discussion**

Results indicate that the EAF of sensitized DP-3 steel in the 42% MgCl$_2$ solution is the APC-SCC, but that in the 35% MgCl$_2$ solution is the delayed fracture. Regarding the APC-SCC in the 42% MgCl$_2$, we observed gradual shift of the corrosion potential to noble direction with frequent RD-type CPFs before 100 ks (Fig. 1(b)), but very few CPF from 100 ks to 130 ks during which AE signals were monitored. This period indicates the progression of APC-SCC into ferrite grains by anodic dissolution. The solution in the initial shallow APC-SCC was converted to acidic solution and reduction of hydrogen ions takes place. Progression of anodic dissolution due to a high concentration of chloride ions in the 42% MgCl$_2$ solution is apparently faster than the delayed fracture due to slow hydrogen diffusion rate.

Corrosion potential of $-305$ mV at around 100 ks in Fig. 1(a) in the 35% MgCl$_2$ solution corresponds to the anodic dissolution of ferrite grains. Acidity of the solution in corrosion pits becomes high and protons are adsorbed on the pits wall. These reactions do not cause RD-type CPF. Hydrogen ions are absorbed on the bottom and sidewalls of the pits and then diffuse into the ferrite grains faster than into the austenite grains, and finally causes delayed fracture of the ferrite grains. Frequent emissions of Type-A AE is produced by delayed fracture of ferrite grains.
Conclusions

Mechanisms of environmental assisted fracture (EAF) of sensitized dual-phase stainless steel, DP-3, in 42 and 35% MgCl$_2$ solutions were studied by simultaneous monitoring of acoustic emission (AE) and corrosion potential fluctuation (CPF). Results are summarized below.

1) For the tensile loaded DP-3 steel in 42 % MgCl$_2$ solution at 90°C, we detected only limited AE events (6 events), but frequent RD-type CPFs (79 events). The CPFs were, however, not detected during the initiation and progression of crack. “Crack” propagated in both the ferrite and austenite grains. The EAF of DP-3 steel in 42% MgCl$_2$ solution was caused by the active-path-corrosion type SCC (APC-SCC). Observed AE signals were due to hydrogen gas bubbles.

2) For the tensile loaded DP-3 steel in 35% MgCl$_2$ solution at 90 °C, we detected frequent AE signals (209 events), but no characteristic CPF. Cracks propagated in the ferrite grains and stopped completely by the austenite grains. Waveform simulation suggested fast fractures with effective rise time of approximately 0.1 µs. The EAF of DP 3 in this solution was caused by the hydrogen-induced delayed fracture.

References


