Acoustic Emission of Hydrogen Bubbles on the Counter Electrode during Pitting Corrosion of 304 Stainless Steel

Kaige Wu1,a,1, Woo-Sang Jung2 and Jai-Won Byeon1,a

1Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul, 139-743, Korea
2High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul, 136-791, Korea

An acoustical investigation into the hydrogen bubbles on the counter electrode during pitting corrosion of 304 stainless steel has been carried out with the potentiodynamic method. After reaching the pitting potential, there was a short time delay before an Acoustic Emission (AE) signal was detected. Given this, the obtained cumulative AE counts were divided into three distinct stages showing their own unique behavior in terms of rise time and duration. The bubble evolution characteristic in each different stage was supposed to be responsible for the feature of AE signal. In the AE Stage III, the cumulative counts of the AE signals provided empirical correlations with both the total number and the total volume of corrosion pits, thus demonstrating the potential of utilizing the AE signal of hydrogen bubble on the counter electrode as a non-intrusive monitoring tool of pitting corrosion. [doi:10.2320/matertrans.M2014373]

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1. Introduction

As an important structural material, stainless steel has been widely used in various fields such as buildings, transportation infrastructure, energy production, nuclear power plants, etc. Corrosion, especially pitting corrosion, is one of the main causes of catastrophes to structural components. To consider any accidental event, it is of great significance to investigate and monitor the corrosion issue of stainless steel. With the characteristic of real-time and full-body scanning in structural integrity monitoring, Acoustic emission (AE) technique is usually favored in corrosion research. Up to now, a great number of AE findings have been reported in various corrosion types such as uniform,1,2) pitting,3-13) stress cracking corrosion,14,15) and crevice corrosion.16)

Regarding the AE reports in pitting corrosion, the most proposed mechanism for AE signal during pitting process is the evolution of hydrogen bubbles generated by corrosion products hydrolysis and acidification within the occluded pits.3-8) Especially, the cumulative AE counts were reported to vary linearly with the amount of hydrogen collected from an iron wire placed in hydrochloric acid.3) Following another report,9) the rupture of an oxide or salt cap covering the pits was suggested to be the possible AE source. Moreover, it was claimed by another report10) that AE source during pitting corrosion could be classified into three groups: bubble activities, primary passive film and re-passive film breakage, and pit growth or pit propagation. Furthermore, based on an in-situ observation and AE analysis,11,12) AE signals for pitting corrosion of MgCl2 droplet were attributed to longitudinal and transverse cracking around the covered pit, cracking of the oxidation products and the early stage of corrosion potential fluctuation. Apparently, the pitting corrosion has been investigating so uninterrupted, but the AE interpretation for the source mechanism is still in great disputation.

In the most previous reports, the test was implemented using three-electrode cell system. Especially, it should be mentioned that the evolution of hydrogen bubbles on the counter electrode surface was always considered as a source of acoustic noise. Given this, the effect of hydrogen bubble evolution on the counter electrode surface was accordingly isolated so as to study the corrosion process itself by setting the counter electrode in a near-by annex cell and connecting it via a salt bridge.4,6,8,9) Luggin capillary7) or an electrolyte bridge.10) As has been reported, the corrosion of a metal, such as steel, in an acid environment containing chloride ions proceeds according to the following overall reaction:17)

\[ 2M + 2nH^+ \rightarrow 2M^{n+} + nH_2 \uparrow \]

Apparently, Hydrogen product generated by reduction reaction is closely associated with the process of corrosion. Consequently, the acoustic emission of hydrogen evolution generated in the reduction reaction can be correlated with the pitting corrosion process.

Based above all, this work will focus on the AE signal behavior of hydrogen bubble evolution on the counter electrode surface. Especially, the correlation between AE signal of hydrogen bubble generated on the counter electrode surface and pitting process will be attached special importance.

2. Experimental Procedure

2.1 Materials

A commercial 304 stainless steel sheet (C: 0.07 mass%, Si: 0.55 mass%, Mn: 2.00 mass%, Cr: 18.19 mass%, Ni: 8.07 mass%, P: 0.02 mass% and S: 0.03 mass%) was used for this study. Polished specimens (75 mm × 15 mm × 2 mm) were subjected to a passivation treatment of 30 min in 20% HNO3 at 60°C, after which they were rinsed using de-ionized water then acetone, and finally dried in a stream of cool air. An exposed surface equal to 10 mm × 10 mm was carefully prepared and controlled by mounting the samples with a fast-curing epoxy resin (Araldite Rapid, Huntsman Advanced Materials GmbH, Switzerland).
2.2 Electrochemical setup for control of pitting corrosion

The pitting corrosion process was controlled by the application of anodic polarization using the potentiodynamic method. For this, a typical three-electrode electrochemical cell was used, which consisted of: A platinum wire counter electrode (CH115, CH Instruments Inc., USA), a silver-silver chloride (Ag/AgCl, 3M) reference electrode (RE-5B, Bioanalytical Systems Inc., USA), and the test specimen as the working electrode. All corrosion tests were conducted using a 3 mass% sodium chloride solution prepared from de-ionized water and extra pure grade NaCl (Duksan Pure Chemicals, Korea), which was acidified to an initial pH of 2 by extra-pure-grade HCl (Duksan Pure Chemicals, Korea). After immersion in this solution for 20 min, the specimens were anodically polarized at room temperature from the open circuit potential (OCP) with a scan rate of 0.4 mV/s.

2.3 Acoustic emission measurement

To study the AE behavior of hydrogen bubbling during pitting corrosion, an experimental setup was designed that incorporated a R15 type sensor (150 kHz Resonant Frequency, Physical Acoustic Co., USA), as shown in Fig. 1. The sensor was mounted on the specimen by using an ultrasonic couplant, and the other end of the sensor was connected to an AE system (PCI-2, Physical Acoustic Co., USA) via a preamplifier. In the previous reports on the corrosion evaluation, various threshold values were suggested within a range from 21.6 dB to 40 dB, or from 40 µV to 5 mV. In our experiment, the background noises were tried to be minimized by controlling surrounding circumstance in the measurement room intentionally and very carefully. The measurement was performed at 2 am–4 am without using any other electrical facilities in the separated measurement space with almost no environmental vibration. Background noise level was checked before every AE measurement for 1 h, which was a litter longer than the corrosion test duration. Then the threshold value was determined as 22 dB, and the pre-amplifier was set at 40 dB. The amplitude is measured in voltage but converted in dB by the PCI-2 system using the relationship: dB = 20 log(V_max/1 µV) – (Preamplifier Gain in dB). The threshold value of 22 dB was converted to be a voltage of 1.259 mV.

3. Results

Figure 2 shows the surface morphologies of the stainless steel specimens before and after anodic polarization. This indicates that severe pitting corrosion occurs on the specimen surface as a result of electrochemical testing.

Figure 3 shows the anodic potentiodynamic polarization curve and the AE signal activity. The current density observed to increase abruptly after a specific potential, indicating the passive film on the metal was ruptured and pits began to form on its surface. Besides, AE signal was not detected immediately after the pit potential was exceeded. A detectable AE signal started to be obtained after the applied potential and current density reached a particular value, which is higher than the pitting potential.

It is worth noting that the AE behavior with corrosion time can be divided into three stages. In Stage I, there was a time delay that no AE signal was detected. The Stage II began with the first detection of an AE signal. And the cumulative number of AE counts exhibited a relatively slow rate.
Stage III is marked by a step increase in the AE count, compared with that of Stage II.

Figure 4 shows the duration and rise time of the AE signals with corrosion time, which again shows three distinct stages of AE signal evolution. In Stage I, the AE signal was zero due to the observed time delay. In Stage II, the AE signals presented a low rise time (<1 ms) and short duration (<12 ms). Whereas in Stage III, they shown a higher rise time (<65 ms) and longer duration (<100 ms). Although the duration of 10 events in Stage III was collected to be the same value of 99.9 ms due to the systematic limitation in this AE setup, true duration of those AE signals may be longer than 100 ms. The unique parameters corresponding to these different stages of AE signals are given in Table 1.

Figure 5 shows the evolution of bubble generated on the electrode surface during stage I, at which no AE signal was detected. It contains a process of bubble formation and bubble expansion.

Figure 6(a) shows the evolution of bubble in AE Stage II. The bubble developed as “a series of single bubbles” and the size of the breaking bubbles observed was around 0.8 mm. Figure 6(b) shows a typical waveform in Stage II and its corresponding fast Fourier transform (FFT) results. The AE signal is characterized by a frequency of between 90 and 200 kHz and with a peak frequency of around 118 kHz.

Figure 7(a) shows the morphology of bubbles during AE Stage III. The bubbles became much stronger and denser like

![Image](image-url)

**Figure 3** (a) Cumulative AE signal of 304-grade stainless steel subjected to anodic polarization in a 3 mass% NaCl solution at a pH = 2, and (b) local zoom of stage II in Fig. 3(a).

**Figure 4** (a) Duration, and (b) rise time of AE signal of 304 stainless steel during anodic polarization in a 3 mass% NaCl solution at a pH = 2.

**Table 1** Parameter for the different stages of AE signal.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Rise time (ms)</th>
<th>Duration (ms)</th>
<th>Amplitude (dB)</th>
<th>Counts rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td>II</td>
<td>&lt;1</td>
<td>&lt;12</td>
<td>22–48</td>
<td>40</td>
</tr>
<tr>
<td>III</td>
<td>Mainly &lt;65</td>
<td>Mainly &lt;100</td>
<td>22–41</td>
<td>3766</td>
</tr>
</tbody>
</table>

*Count rate: the average value calculated by the cumulative AE counts over the corresponding period.

![Image](image-url)

**Figure 5** The evolution of bubble generated on the electrode surface during stage I with no AE signal: (a) bubble formation; (b) bubble expansion.
bubble flow even “bubble cloud”. Figure 7(b) shows a typical waveform and its corresponding FFT result of the AE signal in Stage III. Compared with those of Stage II, the frequency of typical waveform clusters is similarly within the range of 90 and 200 kHz and with a peak frequency of around 100 to 150 kHz.

Figure 8 shows a schematic diagram of bubble evolution during different AE stages based on the analysis above, in attempting to elucidate the different bubble evolution more clearly.

Figure 9 shows the evolution of the size and quantity of corrosion pits generated by a series of reproducible tests with various corrosion time and their resulting AE cumulative counts. The number of corrosion pits increased with testing duration.

Figures 10 and 11 shows empirical correlation between the cumulative AE counts in Stage III and the corresponding total number as well as total volume of corrosion pits, respectively. The relations indicate that the increase in both the volume and quantity of corrosion pits directly corresponds to increase in the amount of corrosion, thus leading to increase in the AE signals.

4. Discussions

4.1 Evolution of hydrogen bubbles and AE signal

In Stage I, the formation and expansion of gas bubbles were observed on the surface of counter electrode. It is only when these bubbles reach sufficient size to break-up that AE signals are recorded. The time required for the bubble expansion is responsible for the time delay observed. The time delay can therefore be closely correlated to the threshold gas pressure for H₂ bubble break-up, which is in turn associated with a minimum detectable amount of corrosion.

In Stage II, The bubbles were observed to break up as a series of single bubbles. During this stage, the bubble size is recorded around 0.8 mm and the peak frequency of the typical waveform is around 118 kHz.

The acoustic energy of single bubble oscillation and break-up was first studied by Minneart,¹⁸ then later investigated by Strasberg¹⁹ and Leighton²⁰,²¹ in the physics area. This revealed that the natural frequency of bubble oscillation can be determined by the following equation:
Where \( f \) is the resonance frequency of the bubble in hertz, \( r \) is the equilibrium bubble radius in meters, \( \gamma \) is the specific heat of a gas \([\text{J/(kg·K)}]\), \( P \) is the hydrostatic pressure and \( \rho \) is the liquid density \([\text{kg/m}^3]\). If a spherical bubble is assumed, this equation shows a simple inverse relationship between the frequency of AE signal and the bubble diameter. The result was calculated from the density of the surrounding fluid: \( \rho = 1000 \text{ kg/m}^3 \), \( \gamma = 1.4 \text{ J/(kg·K)} \), along with the assumption that the bubbles are filled with an ideal gas, \( P = 3.110 \times 10^7 \text{ kg/m}^2 \) and that the liquid is nearly incompressible.\(^{20}\) This computed result is around 115 kHz, which is very close to the spectral analysis shown in Fig. 6(b) in this experimental investigation.

In Stage III, the increasing rate of corrosion changes the hydrogen bubbling from single-bubble breakage to a dense succession of bubbling flow like “bubble cloud”. This increases the bubble flow rate (Fig. 7(a)) and promotes coalescence of the bubbles, thus leading to shape oscillation in the initial bubbles and breakage at a smaller bubble diameter.\(^{22}\) Comparing with the signals from the “single bubbles” in stage II, the continuous-type signal from the bubbles cloud in stage III looks much noisier. Nevertheless, this AE signals are strongly believed to be effective continuous-type signal from the bubble cloud. In this stage, the cumulative counts and counts rates are extremely high. This result is in good agreement with the AE behaviors of the hydrogen collected from an iron wire placed in hydrochloric acid,\(^{3}\) reporting 6 orders of cumulative counts and a similar count rate.
It should be understood that there is a clear difference in the evolution of bubbles at different stages of corrosion, which in turn gives rise to very different AE signals.

### 4.2 Relation between AE signal and pitting corrosion

To investigate the relationship between the corrosion pits and the AE signals detected, a series of reproducible tests (Fig. 9) were carried out with an incremental increase in the corrosion time. From this, it confirmed the small size and quantity of corrosion pits in Stage II, which corresponds to a low extent of bubble evolution by individual bubbles breaking. Furthermore, this can be directly related to the low level of the AE signals recorded. In Stage III, the corrosion pits increased with the increase with the current density, thus inducing bubble evolution of a high density flow. Moreover, this correlates with the sharp increase observed in the AE signals recorded.

In order to quantitatively express the extent of corrosion, the total number and the total volume of corrosion pits were employed. The volume of corrosion pit was calculated based on a configuration assumption of a hemispherical pit. In AE Stage III, the cumulative counts of the AE signals are found to provide empirical correlations with the corresponding total number and total corroded volume of corrosion pits as follows, respectively.

\[ N = -2.16 + 6.57 \times 10^{-6}X \]  
\[ V = -150 + 5.88 \times 10^{-5}X \]

Where \( N \) represents the pit number and \( X \) is the cumulative counts of the AE signals in Stage III.

Where \( V \) represents the total corroded volume of corrosion pits and \( X \) is the cumulative counts of the AE signals.

The AE signals of Stage III seem to be quantitatively correlated with the development extent of pits on the basis of the hydrogen bubble evolution mechanism. It could conceivably provide an effective non-intrusive method for the on-line monitoring and estimation of the process of pitting corrosion.

### 5. Conclusion

The acoustical signal of hydrogen bubbles generated during pitting corrosion of stainless steel was investigated, from which the following conclusions can be drawn:

1. AE signal is detected only after a short time delay since pits generated. Considering the observed time delay, the difference in the cumulative count of AE signals, rise time and duration was used to classify the pitting process into three distinct stages.
2. In stage I, the time delay could be related to a minimum amount of corrosion which is necessary for hydrogen bubbles to be emissive. In stage II, a series of single bubbles evolution is responsible for AE signal with low rise time and short duration. Whereas, in stage III, the dense flow of bubbles can explain the AE signal with high rise time and long duration.
3. Two empirical correlations are established between the cumulative AE counts in Stage III and the corresponding corrosion pits parameters including total number and total corroded volume, respectively. Accordingly, it is confirmed that the extent of pitting corrosion can be non-intrusively studied based on the AE signal of hydrogen bubbles on the counter electrode.

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### REFERENCES