Corrosion analysis of post-heat treatment and post-weld SS316 with electrokinetic reactivation and cyclic polarization method

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Abstract. Austenitic stainless steel 316 has very high mechanical properties and corrosion resistance. This type of steel is widely used both in the nuclear and non-nuclear industries [1]. In the nuclear industry, SS316 is used as cladding material for uranium fuel due to its good corrosion and mechanical properties, and also low neutron absorption cross-section. In the Center for Nuclear Fuel Technology (PTBBN BATAN), it is used as material for the container of nuclear waste that is to be stored on Temporary Storage Installation of Spent Fuel (KHPSB3 BATAN). SS316 is used as material for can to contain high-activity solid waste from the testing activity in Radiometallurgy Installation (IRM BATAN). The lid of the container is sealed with the GTAW welding process in order to tightly contain the solid waste. The main problem with the heat treatment and welding process of austenitic stainless steel is the occurrence of sensitization in a temperature range of 500-800°C. Therefore fully electrochemical analysis of SS316 stainless steel in various mediums has been conducted. SS 316 specimen was heat-treated to simulate the heat generated by the welding process. Sensitization analysis was conducted with qualitative and quantitative methods by EIS and EPR, and pitting corrosion resistance was by cyclic polarization method. The solution used for EIS and cyclic polarization test was 0–3.5% concentration of NaCl, and for EPR test was a mixture of H2SO4 and KSCN. Material characterization before and after corrosion testing was microstructure examination. The result of the corrosion test showed that heat treatment on the temperature range of 500-800°C caused sensitization. The corrosion test curve result showed that a heat treatment temperature of 650°C for 1 hour had the highest activation current. The lowest Rp value for SS316 specimen post heat treatment in 675 °C was 69.410 ohm. The welded SS316 specimen had a higher corrosion current than that of the unwelded specimen. The microstructure of the welded specimen showed that there was intergranular corrosion particularly in the HAZ region. The effect of NaCl concentration on the cyclic polarization test showed that the higher the NaCl concentration, the more easily the pitting corrosion. The indication of pitting corrosion occurrence was evaluated by considering the E_pit and E_rp values. The lower E_pit value meant that pitting corrosion was more easily to occur.

1. Introduction
Austenitic stainless steel SS316 has very high mechanical properties and corrosion resistance. This type of steel is widely used both in the nuclear and non-nuclear industries [1]. In the nuclear industry, the SS316 is broadly used in applications such as material for primary and secondary pipes on pressurized...
water reactor (PWR). On the primary circuit, SS316 is used as a structural material for steam dryer, vessel, piping system, reactor core and reactor pump. While in the secondary circuit, it is used as material for preheater pipe and condenser pipe due to its high mechanical properties and good corrosion resistance [2,3]. SS316 is designed widely as a component material for the high-temperature application, such as a component for nuclear power plants, superheater, and thermal power plants. Meanwhile, in the temperature range of 450-900°C, local corrosion often occurs, such as pitting corrosion, intergranular corrosion, and stress corrosion cracking. Austenitic stainless steels are prone to intergranular corrosion (IGC) since sensitization can easily occur after welding and heat treatments [4]. On a high temperature, the formation of chromium carbide along grain boundaries occurs and makes the adjacent grains become chromium-depleted zone, which leads to intergranular corrosion. The chromium content below 12% causes the susceptibility to intergranular corrosion. The corrosion resistance of stainless steel is the formation of a protective passive layer on the surface [5,6].

The main problems in austenitic stainless steels are local corrosion potential, either intergranular corrosion or pitting corrosion, the corrosion resistance of austenitic stainless steels detriment from classical sensitization when encountering a temperature ranging from 550 to 800°C, which results in precipitation of chromium carbide along grain boundary with simultaneous depletion of Cr from near grain boundaries [7]. The formation of chromium carbides causes the formation of the chromium-depleted zone which leads to sensitization and susceptibility to intergranular corrosion [8]. Aisyah (2010) also explained that in welding of stainless steel, sensitization often occurs, i.e., the formation of chromium carbide precipitate (Cr₂₃C₆), which causes the decreasing of material strength due to intergranular corrosion. Sensitization occurs in austenitic stainless steel that undergoes the thermal cycle caused by the welding process or other heat treatment i.e., heating on sensitization temperature (500-800°C) followed by slow cooling [9]. One of the cases in the nuclear industry that is caused by sensitization occurred in Germany. The damage found in the welding joint in Germany Boiling Water Reactor pipe that was made of stable stainless steel especially caused by thermal sensitization of Heat Affected Zones (HAZ) [10]. In Japan, in early 1980, there were several cases of Stress Corrosion Cracking (SCC) on stainless steel type 304, which reportedly occurs in HAZ of recirculation pipe. On of the root cause of SCC reportedly was increasing susceptibility to Intergranular Stress Corrosion Cracking (IGSCC) that is caused by thermal sensitization during the welding process [10]. In the passive layer on the surface of austenitic stainless steel, including SS316, pitting corrosion potentially occur due to chloride ion attack.

IRM is PTBBN BATAN’s facility, which produces high-activity waste from post-irradiation nuclear fuel test activity. High-activity nuclear solid waste is handled by containment inside a special shielded container. The special shielded container is a cylindrical tube-shaped can and made of stainless steel SS316. They can consist of an inner container and outer container, which both are made of the same material, i.e., SS316. In order to contain as well as to prevent leakage during storage in Temporary Storage Installation of Spent Fuel (KHIPS3 BATAN) pool, the lid is sealed by welding with Gas Tungsten Arc Welding (GTAW) process. The main function of a spent-fuel interim storage pool in KHIPS3 BATAN is to store spent fuel and other irradiated material, including irradiated material and remaining pieces of spent fuel from post-irradiation test activity in IRM’s hot cells. The pool contains demineralized water with certain quality according to Operational Limits and Conditions (BKO). The conditions of quality of water inside the pool is limitation for Cl ion content i.e. 0.2 mol/cm³; acidity level i.e. pH of 6 – 7.7; and conductivity < 15 S/cm[11].

The aim of this research was to understand and to fully evaluate the corrosion phenomena on SS316 after heat treatment and welding. Heat treatment was conducted at a temperature of 400, 675 and 800°C for 1 hour then followed by slow cooling. The variations in heat treatment temperature were selected based on the sensitization temperature range i.e. 500-800°C. Therefore, annealing was conducted on temperature below sensitization temperature i.e. 450°C; the temperature of 675°C was selected because that is the temperature where sensitization has mostly occurred; and temperature of 800°C was selected as maximum temperature of sensitization to occur. The welding method was GTAW with a certain current. Corrosion phenomena examination was focused more on the local corrosion i.e. pitting and
intergranular corrosion. Corrosion test was conducted by electrochemical method i.e. Electrochemical Impedance Spectroscopy (EIS), Electrochemical Reactivation (EPR), and cyclic polarization. The test solution used for cyclic polarization and EIS test was NaCl solution with variations in concentration, and for EPR test was a mixture of H₂SO₄ and KSCN solution.

2. Methodology
The material used for the experiment was a commercial SS316 plate with a thickness of 3 mm. The test specimen was pretreated with heat treatment and welding. A piece of 1 x 1 cm of the specimen was cut and heat-treated on the temperature of 450, 675, and 800 °C for 1 hour and others welded by GTAW welding with filler from austenitic stainless steel as shown in figure 1.

![Figure 1. Schematic process of GTAW.](image)

Specimen for corrosion test was prepared with metallography preparation until as-polished condition, then rinsed by alcohol. Corrosion test was conducted with Electrochemical Impedance Spectroscopy (EIS), Electrochemical Potensiokinetic Reactivation (EPR), and Cyclic Polarization method. Characterization of un-welded and welded specimens involved microstructure examination. The electrochemical test was conducted by using a corrosion cell, which consists of three-electrode i.e. specimen SS316 as a working electrode, Saturated Calomel Electrode (SCE) as reference electrode and graphite rod as a counter electrode. SCE was selected as a reference electrode because its electrochemical potential is not affected by chloride content and current that flows through it. The graphite rod was selected as a reference electrode due to its conductive property that allows the current to flow in the circuit. Moreover, the graphite rod is inert and inexpensive compared to platinum wire. Specimens that were already prepared for corrosion test were immersed in corrosion medium (electrolyte solution) of H₂SO₄ 0,5 M + KSCN 0,01 M solution on the temperature of 30°C ± 1°C and arranged as shown in figure 2.

![Figure 2. Electrochemical corrosion cell.](image)

Before testing, the specimen is immersed in an electrolyte solution for 10-15 minutes for conditioning. After immersion, the corrosion test with potentiostat is carried out based on ASTM G108
with the EPR method and then continued with EIS and cyclic polarization test. The EIS test was carried out in 3.5% NaCl media and cyclic polarization test in 100 ppm and 3.5% NaCl media. The choice of NaCl concentration is adjusted to the level of chloride ion in seawater, which is around 3.5%. The concentration is also used to see the condition or extreme response of the test specimen during cyclic polarization testing. SS316 specimen before and after welding treatment were metallography tested using an optical microscope. Unwelded and welded SS316 stainless steel test specimens, with and without heat treatment, were observed for their microstructure with a Leica compound optical microscope. To bring out the microstructure, after being polished with alumina, SS316 specimens were etched with aquaria solution i.e. a mixture of concentrated HCl and concentrated HNO₃ with a concentration ratio of 3 : 1. Furthermore, the samples were observed with an optical microscope and the photos were taken with a digital camera.

3. Results and discussion

3.1. Microstructure
The microstructure of the as-received SS316 specimen is shown in Figure 3. In Figure 3, the grain structure of SS316 with austenite matrix (γFe) can be seen. The grain structure was equiaxial with relatively homogeneous size and there were twinning in several parts of the grain. The grain structure was clean and showed no inclusions.

![Figure 3. The microstructure of as-received SS 316.](image)

The microstructure of the SS316 specimen after GTAW welding is shown in Figure 4 (a-c). The microstructure in Figure 4a shows the HAZ region between the weld and the base metal. In the HAZ area, grain coarsening occurred due to recrystallization and grain growth because of heating. In Figures 4b and 4c, it can be seen black inclusions, which were carbide deposits (Cr₂₃C₆) that surrounded the grain boundary. Upon heating, the chromium and carbon atoms diffused to the grain boundary to form carbide compounds left a chromium-depleted zone adjacent to the grain boundary and made the area more susceptible to corrosion.
Figure 4. The microstructure of GTAW-welded SS 316, a) weld metal, b) left HAZ, c) right HAZ.
Figure 5 shows the microstructure of the welded SS316 specimen after the EPR test in 0.5M H$_2$SO$_4$ + 0.01M KSCN solution medium. In this figure, it can be seen that the presence of carbide deposits and thickened grain boundaries due to post-weld sensitization.

![Image of microstructure](image.png)

**Figure 5.** The microstructure of the GTAW-welded SS316 specimen after the EPR test in the H$_2$SO$_4$+KSCN solution.

### 3.2. Electrochemical corrosion

Electrochemical corrosion testing was carried out with EIS, EPR, and cyclic polarization methods. EPR test results for SS316 specimens with and without GTAW welding can be seen in Figure 6 and Figure 7. In Figure 7, activation of welded SS316 specimen occurred which was characterized by an increase in corrosion current during scanning from high to low potential. While in the unwelded SS316 specimen, there was no increase in current strength. The change in the current strength indicated that the welded SS316 specimen underwent sensitization, so intergranular corrosion easily occurred especially in a very corrosive environment. Sensitivity analysis of SS316 specimens with variations in heating temperature was also carried out by the corrosion test using the EPR method and resulted in the EPR curve, as shown in Figure 8. Upon heating on the temperature of 675 and 800°C, the changes in corrosion currents relatively significant compared to without heating. This shows the susceptibility of SS316 specimen to intergranular corrosion attacks when subjected to heat treatment, especially at 675°C. A high level of chromium can produce a stable passive Cr$_2$O$_3$ layer with a thickness of around 1-3 nm [1]). During heating, carbon atoms diffuse, and with chromium atoms form Cr$_{23}$C$_6$ compounds along the grain boundary, make the area around the grain boundary chromium-depleted which results in decreased corrosion resistance due to rupture of the passive Cr$_2$O$_3$ layer.
Figures 6 and 7 show the EPR curves of unwelded and welded SS316 specimens, respectively. Test was carried out in 3.5% NaCl media. It can be seen in Figure 6 that the unwelded SS316 specimen had a larger semicircular curve than that of the welded specimen. The larger diameter of the curve represents the higher polarization resistance and better corrosion resistance. The welded
specimen had smaller polarization resistance so that the corrosion resistance decreased. The polarization resistance Rp value of unwelded and welded specimens was 846,600 and 41,980 ohms respectively.

![Figure 9](image_url) Nyquist curves of unwelded and GTAW-welded SS316 specimens in NaCl 3.5% solution.

Qualitative analysis based on the Nyquist curve of SS316 specimen with variations in heating temperature in a 3.5% NaCl salt solution showed various corrosion behavior. The decrease in corrosion resistance was not proportional to the increase in heating temperature. In Figure 10, it can be seen that the diameter of the Nyquist is smaller with the increase of heating temperature from no heating to a temperature of 675°C, but the diameter was widened again at a heating temperature of 800°C. It showed that the corrosion resistance decreased to a heating temperature of 675°C but increased again at 800°C. It was correspondence to the results of Nyquist graph data plotting with the CPE equivalent circuit model that produce the parameters of charge transfer resistance (Rp) and solution resistance (Ru), as shown in Table 1. The lowest value of Rp is for the specimen with 675°C heating, which is 69,410 ohms. Another research showed that sensitized SS304 has higher polarization resistance than that of an as-received SS304 specimen[4].

![Figure 10](image_url) Nyquist Curve of SS 316 with variations in heating temperature in NaCl 3.5% solution.
Table 1. Electrochemical parameter of SS 316 with variations in heating temperature in NaCl 3.5% solution.

| Heating Temp | Rp (ohms) | Ru (ohms) |
|--------------|-----------|-----------|
| No heating   | 846600    | 2.076     |
| 450°C        | 100500    | 3.53      |
| 675°C        | 69410     | 1.438     |
| 800°C        | 426300    | 0.7833    |

Cyclic polarization curves of as-received and welded SS 316 specimens are shown in Figure 11. Test conditions in NaCl solution with variations of 0%, 100 ppm and 3.5% concentration. The cyclic polarization experiment is a combination of anodic and cathodic polarization, which forms a cyclic process. The cyclic polarization method is carried out to investigate the tendency of pitting on the material in any environment. The tendency for pitting corrosion to occur is measured by considering the pitting potential (Epit) and the repressive potential (Erp)[6,12]. Figure 11.a to 11.c is a cyclic polarization curve of as-received SS316 specimen with variations in NaCl concentration. The figure shows that the Cl- concentration affected the pitting corrosion resistance. The higher the Cl- concentration, the higher the tendency of pitting corrosion to occur. This is indicated by the low Epit and Erprot values. Table 2 shows that the Epit and Erp values became lower as increasing in Cl- concentration. The Epit and Erp values of SS316 specimen in 3.5% NaCl media were 437.8 mV and -160.3 mV respectively.
Figure 11. Cyclic polarization graph of as-received SS 316 with variations in NaCl concentration. a) NaCl 0%, b) NaCl 100 ppm and c) NaCl 3.5%.

The cyclic polarization behavior of the welded specimen also shows the same. NaCl concentration can affect the tendency of pitting corrosion. Epit values of specimen in NaCl 0, 100 ppm and 3.5% solutions were 558.3 mV, 391.0 mV and 80.39 mV, respectively. The lowest Epit value shows that the passive layer formed was easily broke so that pitting corrosion occurs.
Figure 12. Cyclic polarization graph of GTAW-welded SS316 specimens with variations in NaCl concentration. a) NaCl 0%, b) NaCl 100 ppm and c) NaCl 3.5%.

Table 2. Epit dan eprot value in variations of NaCl concentration.

| Specimen          | Corrosion Medium | $E_{\text{pits}}$ mV | $E_{\text{ep}}$ mV |
|-------------------|------------------|-----------------------|---------------------|
| As-received SS 316| NaCl 0%          | 1243                  | 171.9               |
|                   | NaCl 100 ppm     | 1161                  | 90.80               |
|                   | NaCl 3.5%        | 437.8                 | -160.3              |
| Welded SS 316     | NaCl 0%          | 558.3                 | -20.58              |
|                   | NaCl 100 ppm     | 391.0                 | -145                |
|                   | NaCl 3.5%        | 80.39                 | -144                |

4. Conclusion
The electrochemical corrosion test of welded and heat-treated SS316 material was carried out with the EPR, EIS and CP methods. The results showed that the welded specimen was sensitized and susceptible to intergranular corrosion, more likely compared to the unwelded specimen. The microstructure of the welded specimen showed intergranular corrosion in the HAZ region due to sensitization. The heat-treated specimen at the temperature of 675 and 800°C had a bigger tendency for sensitization, which was indicated by a higher activation current on the EPR curve. The corrosion test with the EIS method showed a relatively similar trend. Welded specimen produced smaller polarization resistance or Rct than that of without welding. The smaller the Rct value, the more likely corrosion to occur. The heat-treated specimen on the temperature of 675 °C had the smallest polarization resistance, which made the corrosion easier to occur. The cyclic test was carried out in NaCl solution medium with concentrations of 0, 100 ppm and 3.5%. The higher the concentration of NaCl, the more likely pitting corrosion to occur (the lowest E pit value) both on the unwelded and welded specimen. E pitting value of welded SS316 specimen in demineralized water, 100 ppm NaCl, and 3.5% NaCl medium were 558.3; 391.0 and 80.39 mV, respectively.

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