The Degradation of Austenitic Stainless Steel at High Temperature in Simulated Carbon Monoxide Containing Atmosphere of Biomass-to-Liquid Plants

Paweea Treewiriyakitja1, Penpisuth Thongyong2, Suwijak Pokwitidkul1, Jennarong Tungrongpairoj1*

1High Temperature Corrosion Research Centre, Department of Materials and Production Technology Engineering, Faculty of Engineering, King Mongkut’s University of Technology North Bangkok, Bangkok 10800, Thailand
2Department of Industrial Engineering and Management, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand

Jennarong.t@eng.kmutnb.ac.th

Abstract. Biomass fuel is effective renewable energy and being used for replacing fossil fuel energy. It can be produced from synthesis gas containing a high percentage of carbon monoxide (CO) and hydrogen (H2) in biomass-to-liquid plants. Austenitic stainless steel AISI 316L (Cr17% Ni 10% Mo 2%) is used for equipment parts in chemical and petrochemical industries due to good corrosion resistance at various operating conditions. The corrosion resistance of stainless steel may be degraded by the reduction reaction of the passive film and carbide formation from carbon diffusion, which leads to the intergranular corrosion on the steel surface. This research aims to study the degradation of stainless steel AISI 316L in a simulated carbon monoxide containing atmosphere at 15-45%CO and a sensitizing temperature of 800 °C. Before the test, the samples were preoxidized in the air at 800 °C for 6 hours. An electrochemical reactivation (EPR) technique was used to analyze for detecting sensitization. The mass change of AISI 316L slightly increased after the reduction test. Besides, the high carbon diffusion was shown on the steel surfaces as chromium carbides at the high percentage of carbon monoxide.

1. Introduction
Biomass fuel is effective renewable energy and being used for replacing fossil fuel energy and utilizing agricultural and rubber wastes. Hydrocarbon compounds from the wastes are transformed to biomass pyrolysis products such as water, acetone, ethanol, formic acid, and char at a temperature of 500-600°C. Synthesis gases containing carbon monoxide (CO), carbon dioxide (CO2), hydrogen (H2), and hydrocarbon-containing gases (CnHm) such as methane (CH4) are produced when heated at the temperature between 500 - 1400°C in gasification processes. The syngas with a high percentage of carbon monoxide (CO) and hydrogen (H2) (Table 1) is further cleaned up and adjusted the proportion of carbon monoxide and hydrogen for producing liquid oil in the next process [1–4]. AISI 316L austenitic stainless steels (Cr17% Ni 10% Mo 2%) uses for various applications in corrosion environment due to the protective-oxide film formation. However, the carbide formation of Cr23C6 and
Cr$_7$C$_3$ were found at grain boundaries after gas carburization at high temperature [5–7]. The carbide formation and the deterioration of passive film when using in a reduction atmosphere can decrease the corrosion resistance, which leads to intergranular corrosion on steel surfaces (Equation 1-4) [8–10].

$$\text{Cr}_x\text{O}_y (s) + 2y\text{C}(s) = \text{Cr}_x\text{C}_y (s) + y\text{CO}(g)$$  \hspace{1cm} (1)

$$\frac{3}{2}\text{Cr} + \text{C} = \frac{1}{2}\text{Cr}_3\text{C}_2$$  \hspace{1cm} (2)

$$\frac{7}{3}\text{Cr} + \text{C} = \frac{1}{3}\text{Cr}_7\text{C}_3$$  \hspace{1cm} (3)

$$\frac{23}{6}\text{Cr} + \text{C} = \frac{1}{6}\text{Cr}_{23}\text{C}_6$$  \hspace{1cm} (4)

| Table 1. Composition of synthesis gas |
|-------------------------------------|
| **Substance** | **Composition (%)** |
| H$_2$ | 20-40 |
| CO | 35-40 |
| CO$_2$ | 25-35 |
| CH$_4$ | 0-15 |
| N$_2$ | 2-5 |

This research aims to study the degradation of austenitic stainless steel in simulated carbon monoxide containing atmosphere of biomass-to-liquid plants between 15-45%CO at 800°C. The effect of different percentages of carbon monoxide on the degradation and carbide formation can be investigated. The degree of sensitization (%DOS) with EPR double loop technique can be analyzed chromium depleted zone caused by chromium carbide formation [11, 12]. The result can be used to predict the appropriate application of AISI 316L in the biomass-to-liquid plants.

2. Experimental method

The AISI 316L specimens were cut with dimension 20 mm x 20 mm x1 mm and ground to 1000 grit SiC paper, then cleaned by acetone. The samples were pre-oxidized at 800°C for 6 hours and measured weight change. After the preoxidization, the samples were heated to 800°C for 1 hour as shown in Fig.1. CO-N$_2$ gas mixtures were fed into the furnace atmosphere with different percentages of 15%CO, 30%CO, and 45%CO, relating to the flow rate of 3, 4.5, and 6 L/min, respectively. The cross-sectional microstructure of the reduced AISI 316L samples were investigated by optical microscope after etching with glyceroria. Electrochemical Potentiodynamic Reactivation (EPR) technique was used to analyzed carbide on steel surfaces. The electrochemical technique is related to the ASTM 108 standard using reagent water (1 L of 0.5 M H$_2$SO$_4$ +0.01 M KSCN and distilled water or deionized water) as electrolytes. The testing samples were anodically polarized from open circuit potential to a passivation potential of +300mV versus SCE (saturated calomel electrode) and reference electrode (Platinum), using sweep rate of 1.67 mV/s. The applied potential was then reversed and calculate the potentiokinetic reactivation ratio values of activation current peak (Ia) and reactivation current peak (Ir) or % degree of sensitization to evaluate chromium depleted zones on steel surfaces.
3. Results and Discussion

The average weight of AISI 316L samples slightly increased around 10.36 µg/mm² after the preoxidation test in the air atmosphere at 800 °C for 6 hours. After the reduction test at 800 °C, the mass gain of preoxidized samples were increased insignificantly about 0.01144, 0.00802, and 0.02283 µg/mm² in the simulated carbon monoxide containing atmospheres at 15, 30, and 45%CO, respectively, as shown in Figure 2. Comparing the mass gain at different carbon monoxide percentages, it showed the highest amount at the reduction of the 45%CO-55%N₂ atmosphere, which was more than the previous two conditions around two times. Furthermore, the microstructures of the preoxidized and reduced specimens in the cross-sectional areas were examined by optical microscope, as illustrated in Figure 3 and Figure 4. The sensitized microstructure with chromium carbides at grain boundaries was clearly presented in every specimen after the preoxidation and reduction test but did not exist in the as-received specimen before the tests. The carbide network formation increased when increasing the percentage of carbon monoxide in mixture gas, especially on the surface area of steel specimens contacting the simulated atmosphere. The carbon from carbon monoxide gas can diffuse into the steel substrate following the reverse Boudouard reaction as the decomposition of carbon monoxide at a temperature lower than around 900 °C (Equation 1) [13]. Besides, the diffused carbon can react with the chromium and iron to be chromium and iron carbides following the equation 2 and 3.

$$2CO = CO_2 + C \quad (1)$$
$$xCr + yC = Cr_xC_y \quad (2)$$
$$Fe + 3C = Fe_3C \quad (3)$$

From a thermodynamics point of view, the stability of chromium carbide is higher than that of iron carbide, which means the chromium carbide can easily occur. The chromium carbide can possibly be formed into Cr₂₃C₆, Cr₇C₃, and Cr₇C₃ following the Gibbs free energies (ΔG°) of around -750, -625, and -500 kJ/mol of C at 800 °C, respectively [14, 15]. For this reason, it can be presumed the Cr₂₃C₆ was initially presented and transformed to be Cr₇C₃ and Cr₇C₂. In addition, the carbide formations are in good agreement of the previous works of T. Turpin et al. and H.M. Tawancy et al., which observed the Cr₂₃C₆ and Cr₇C₃ after gas carburizing of martensitic stainless steels and AISI 310 at the high temperature around 900 °C [5, 6].
Figure 2. Mass change of preoxidized AISI 316L after reduction test with different percentage of CO in gas mixtures.

Figure 3. The cross-section of AISI 316L steel (a) before (b) after exposure at 800 °C for 6 hours in air atmosphere.
Figure 4. The cross-section of preoxidized AISI 316L steel after the reduction test in the simulated carbon monoxide containing atmospheres at (a) 15%, (b) 30%, and (c) 45% CO.

The AISI 316L specimens were further analyzed by Double-loop electrochemical potentiokinetic reactivation (DL-EPR) analysis after sensitizing in the simulated carbon monoxide containing atmosphere to observe the intergranular corrosion (IGC) susceptibility by etching with glyceregia. The activation and reactivation current density profiles of those specimens at different test conditions were shown in Figure 5. The high-skewed reactivation current (Ir) profile which is indicated the reformation of the passive film layer, was detected in all sensitized specimens and raised after feeding more fraction of CO gas. Besides, the ratio of reactivation and anodic current densities (Ir/Ia) was more than one percent, which can indicate the sensitivity of IGC. The degree of sensitization of the sensitized specimens was also plotted in Figure 6, which is reasonably related to the ratio (Ir/Ia). It can be concluded the degree of sensitization will increase around 2 times when adding 15 percent carbon monoxide which may promote the high sensitivity of intergranular corrosion in AISI 316L and cause to failure at high temperature. After the DL-EPR test, the specimens were characterized to present the microstructure when passive film breakdown, as shown in Figure 7.
Figure 5. The activation and reactivation current density profile of the preoxidized AISI 316L specimens (a) after exposure in 15% CO (b), 30% CO (c), and 45% CO (d) atmospheres.

Figure 6. The degree of sensitization of AISI 316L at different testing conditions.
Figure 7. The cross-section of preoxidized AISI 316L steel (a) exposed in the 45%CO-55%N₂ atmosphere (b) after the DL-EPR test.

4. Conclusion
   • The mass gain of preoxidized AISI 316L seemed to be not changed and unaffected after the reduction at 800 °C in various simulated carbon monoxide atmospheres.
   • The carbide network can be formed after heating to the sensitization temperature and increased after feeding more percentages of carbon monoxide gas in the simulated atmosphere.
   • The Cr₂₃C₆, Cr₇C₃, and Cr₂C₃ can possibly be formed at the grain boundaries due to the high stability formation with the more negative change of Gibbs free energy.
   • The carburizing reaction plays an essential role in the carbon monoxide atmospheres following the high carbon diffusion and carbide formation on steel surfaces.
   • The degree of sensitivity relating to the severity of intergranular corrosion in AISI 316L is double when the carbon monoxide increases in the atmosphere by around 15%.

Acknowledgment
This research is funded by King Mongkut’s University of Technology North Bangkok with contract no. KMUTNB-64-NEW-12.

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