JURNAL PENDIDIKAN TEKNOLOGI KEJURUAN

Vol. 4, No. 4 November 2021

P-ISSN: 2621-3273
E-ISSN: 2621-1548

Corrosion behavior of super austenitic stainless steel, Duplex 2205 and 316L in sulfamic acid environment

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https://doi.org/10.24036/jptk.v4i4.24323

Abstract—Currently, sulfamic acid as a primary chemical industrial material is ubiquitous. One of its uses is a sweetener. Due to its corrosive nature, it is necessary to use a suitable container to avoid contamination of the solution. Corrosion behavior of super austenitic stainless steel, duplex 2205, and 316L uncovered to sulfamic acid in diverse attention at ambient temperature had been investigated. Concentration Weight loss method, Potentiodynamic Polarization, and Electrochemical Impedance Spectroscopy (EIS) examined the corrosion rate. The result showed that the corrosion rate of material increased with the increasing concentration of sulfamic acid. Super austenitic stainless steel has higher corrosion resistance than duplex 2205 and 316L.

Keywords: *corrosion rate, super austenitic stainless steel, duplex 2205, 316L, sulfamic acid*

I. INTRODUCTION

The chemical process industry is one of the industries that play an essential role in developing the science and technology industry. Chemical industry products are needed and used in various aspects of life. In addition, many chemicals never reach the public directly but are traded within the chemical industry for further processing or use in the production of other chemicals needed by the public. Therefore, the chemical industry is often referred to as the best consumer.

One of the chemical compounds is sulfamic acid, also known as amino sulfuric acid. Although sulfamic acid is not well-known as other prevalent acids such as hydrochloric acid, sulfuric acid, or nitric acid, the products or their derivatives are widely used in the modern chemical industry, including as sweeteners, cleaners, rust and limescale removers, catalysts for esterification processes, herbicides (Clapp, 1943) manufacture of dyes, bleaches (Yoshikubo et al., 2001) to modern medical research for therapeutic agents such as antibiotics, cancer drugs (steroid sulfatase and carbonic-anhydrase inhibitors), weight loss and HIV protease inhibitors (Winum et al., 2005)

Similar to other chemicals, one of the problems in the production process is that sulfamic acid is very corrosive, so it requires a material container or heat exchanger system that can withstand the chemical reactions, especially at high concentrations and temperatures. The failure of the container material against the corrosion process causes the metal container to fail or leak; the metal elements of the reacting container will dissolve and cause contamination. This will be dangerous primarily if it is used as a food product container.

Several studies have been carried out, and several types of metal materials have been tested in a sulfamic acid environment. Hesham et al. (2012) studied low chromium-molybdenum steels in a sulfamic acid environment. They used ASTM A213 grade steel T12 (1.0Cr-0.5Mo) and T22 (2.25Cr-1Mo) in 0.6M sulfamic acid environment with different temperatures (25, 40 and 60^{o}C). In addition, they also tested the use of tryptophan inhibitors to reduce high corrosion rates. Although the inhibitor showed high inhibition efficiency in this study, the corrosion rate was still high, especially at a solution temperature of 60^{o}C. Rehim et al. (2011) also tested Cystine inhibition on T22 alloy in 0.5M sulfamic acid solution. In addition to temperature variations, Rehim et al. also provide variations in the stirring speed treatment. The investigation shows that the inhibition efficiency increased with increasing inhibitor concentration but decreased with increasing the solution temperature and stirring velocity. In their research, Hermas and Morad (2008) compared the corrosion rate of austenitic 304 stainless steel in sulfamic acid and sulfuric acid. Their research provides variations in concentration (0.1-0.5M) and temperature (20-60^{o}C). The corrosion rate is higher in H_2SO_4 than NH_2SO_3H solution. EIS data showed that the display of Nyquist plots, and hence the corrosion mechanism, depends not only on the acid concentration but also on the solution temperature.

Kish et al. (2009) separately researched corrosion control in stainless steels 316L, 304, and duplex 2205 in sulfamic acid. They tested the weight loss of the alloy in a 10% solution by weight and a temperature of 65^{o}C and compared it with the diethyl thiourea inhibitor. Their results showed that the 316L and 2205 materials exhibited significantly better corrosion resistance than 304 with corrosion rates of up to 10 mpy (0.25 mm/year). Of the three stainless steel studied, type 2205 duplex stainless steel exhibits the relative highest corrosion resistance to deaerated, inhibited 10 wt% NH_2HSO_3 at 65^{o}C. Fouda et al. (2014) further investigated the effect of oxazole derivatives as corrosion inhibitors of 316L stainless steel in a solution of sulfamic acid. They used 0.6M sulfamic acid with varying oxazole derivatives and temperature concentrations. The results showed the inhibition performance of the inhibitors with varying concentrations and temperatures. The maximum efficiency was 91% at 2 x 10^{-4} M concentrations of inhibitors for an immersion period of 3 hours. Potentiodynamic polarization study revealed that these compounds act as mixed-type inhibitors. The results of the electrochemical impedance study showed a decrease in double-layer capacitance and an increase in charge transfer resistance. The results of various electrochemical techniques show good agreements with each other.

As the corrosion data for super austenitic stainless steel, duplex 2205, and 316L in wide range sulfamic acid concentration is lacking and limited, a systemic study has been carried out to provide basic information quantitatively. It is hoped that the result of this investigation will contribute to the existing knowledge in the selection of type material for further industrial and environmental use.

II. METHODS

The material used in this study was cut using the wire cut method with 5 x 5 x 3.5 mm for super austenitic stainless steel and 10 x 10 x 10 mm for 316L and Duplex 2205. Chemical composition examination of the material is carried out by optical emission spectroscopy. The corrosion resistance testing of stainless steel metal alloys will be carried out in a sulfamic acid environment with different concentrations. In its preparation, the solution will be diluted to concentrations of 20%, 40%, 60 %, and 80% by weight of sulfamic acid. Weight loss (mass technique), Potentiodynamic, and electrochemical impedance spectroscopy (EIS) were employed to investigate corrosion rate and mechanism.

The polarization and EIS measurements were conducted in the frequency range of 0.01-100 kHz. $Ag/AgSO_4$ was used as a reference electrode, and glassy carbon was used as a counter electrode. The working electrode was in the square form embedded in high-quality epoxy resin, leaving an open surface area of 25-mm^2 for SASS and 100-mm^2 for D2205 and 316L. In the weight loss method, metal specimens were immersed in experimental media for 1 to 5 days. Before weight measurement, samples were pickling with immersion in NaOH 8,2% wt dan KMnO4 2,8% wt and rinsing with DI water. Samples were dried and weighed, and the reading was taken to the nearest 0.0001 gram.

III. RESULTS AND DISCUSSION

Based on actual optical emission spectroscopy, the following samples have the following chemical composition (as qa weight percentage).

Table 1. Chemical composition of samples

Element	**Chemical Composition (%)**		
	316L	**Duplex**	**SASS**
C	0.065	0.055	0.0095
Si	0.351	0.360	0.196
Mn	1,638	1.635	0.605
P	0.0007	<0.0005	0.011
S	0.0049	<0.0003	<0.0005
Cr	16.73	22.75	27.26
Ni	9.771	5.433	34.50
Mo	2.212	3	7.172
Cu	0.440	0.150	0.172
N	0.069	0.235	0.091
Fe	66.97	65.51	29.70

Increasing the alloying element (chromium, nickel and molybdenum) is expected to increase the corrosion resistance of the material in an acidic environment. Therefore, the importance of corrosion potential study is to explore the stability of the alloy in the corrosive environment. Such stability depends on the thermodynamic properties and kinetics of the chemical or electrochemical reactions occurring at the substrate surface in contact with corrosive agents (Kish et al., 2009).

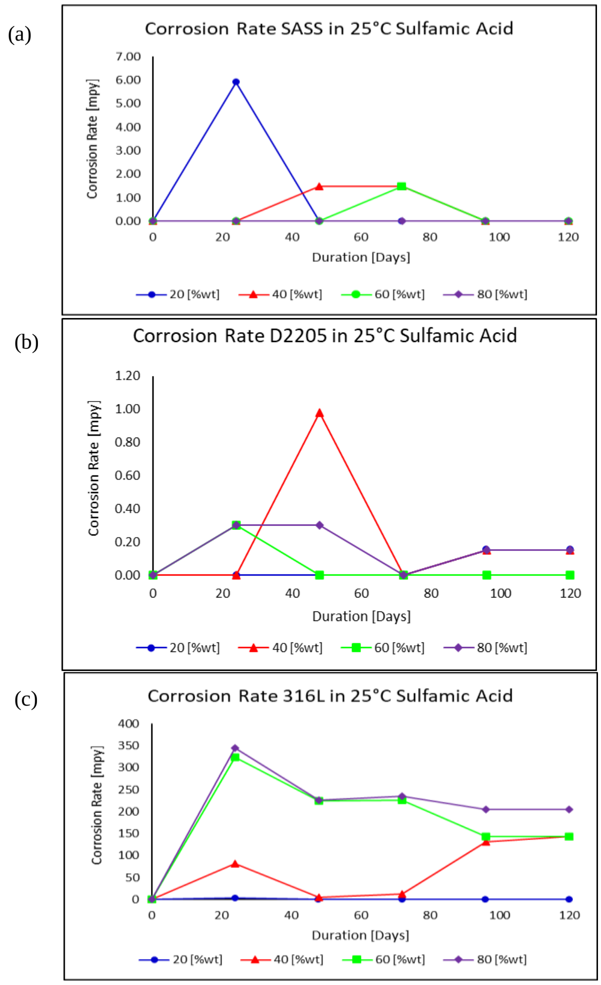

Figure 1. Corrosion rate SASS (a), D2205 (b) and 316L (c) in various concentration sulfamic acid

Experiment results from the weight loss method for corrosion rate of super austenitic and duplex 2205 show additional weight at the beginning of immersion. It is caused by forming of metal-oxide/hydroxide layer on the surface. The passive film provides high corrosion resistance, thin, protective, corrosion product surface film that acts as a barrier to the anodic dissolution reaction. Depending on the potential or oxidizing power of the solution, an alloy may exist in the passive state above E_p or the active state below it (Jones, 1992). In Fe-Cr ferritic and Fe-Cr-Ni austenitic, the passive film's Cr(III)-enriched composition is crucial in corrosion resistance. In aqueous environments, it results from the competitive oxidation of iron and chromium with the faster dissolution of Fe(II)/Fe(III) compared to Cr(III) species, especially in acid solutions (Wang et al., 2019 and Keller, 2004). Since the stability of the passive layer, it can be protective or break and cause further corrosion in the metal surface. In SASS, a high concentration of chromium alloy gives maximum protection and reduces the corrosion rate of metal to nearly zero. Meanwhile, the corrosion rate of 316L already started at a high rate, in 60% and 80% almost reached 350 mpy. Lower concentration reduces corrosion rate of this metal.

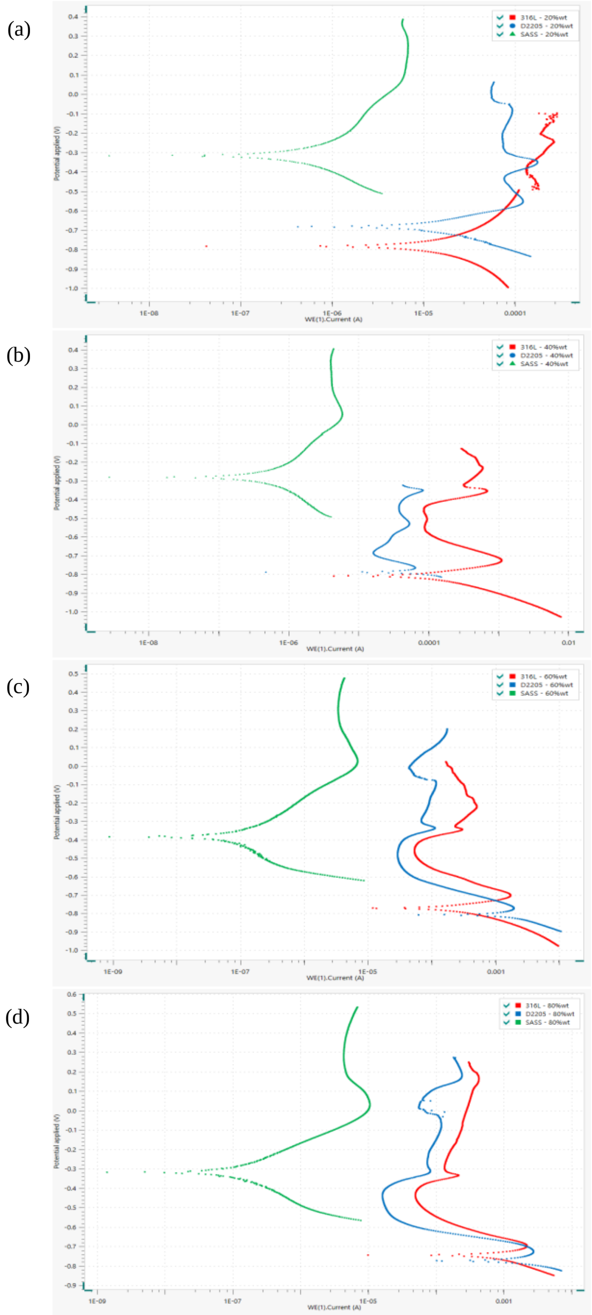

Figure 2. Tafel Plot Potentiodynamic Polarization of material SASS, D2205 and 316L in (a) 20%wt, (b) 40%wt, (c) 60%wt and (d) 80%wt sulfamic acid

Based on polarization analysis, the corrosion rate of SASS (green) is far lower than D2205 and 316L. This is because, in the material SASS active-passive polarization graphic, we can see that the passive layer is more stable than others. Meanwhile, in D2205 and 316L, we can see that material has experienced an active-passive-trans-passive several times. In other words, it can be explained that the passive layer formed on the metal surface is vulnerable and unstable, easy to break up, and causing further corrosion.

In the polarization diagram between duplex 2205 and 316L, the corrosion resistance performance of duplex 2205 material decreases with increasing concentration. For example, in solutions with concentrations of 60% and 80%wt, it was seen that the corrosion rate of the duplex 2205 material was more significant than 316L.

The formation of a passive layer on the metal surface occurs more effectively at high concentrations such as 60% and 80%wt. The passive layer is quite significant in reducing the corrosion current. However, the passive layer resistance does not last long, with increasing polarization potential causing the layer to break and increasing the corrosion current again. Corrosion rate calculation using polarization described in Fig.3 with result SASS is smaller than Duplex 2205 and 316L.

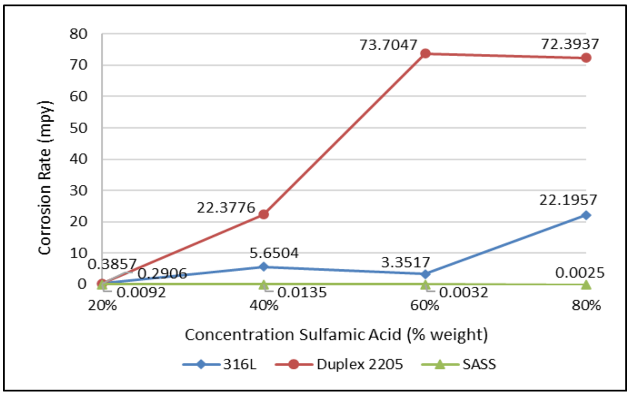

Figure 3. Corrosion rate using Polarization Method.

In Nyquist Plot of Electrochemical Impedance Spectroscopy measurement, the semi-circular arch radius is associated with the polarization resistance (Rp) (Zhao et al., 2019). $Z_{imaginer}$ of SASS is much bigger than Zim duplex 2205 and 316L. Impedance imaginer ratio between SASS, Duplex 2205, and 316L in 20%wt sulfamic acid almost equal to 3,200 : 14 : 1 respectively. This indicates that the corrosion resistance and passive layer stability is higher than D2205 and 316L. With increasing concentration to 80%wt, Zi for SASS is significantly reduced to a ratio almost equal with 700 : 2 : 1, which means the corrosion resistance of SASS is significantly reduced, while corrosion resistance of 316L is increased.

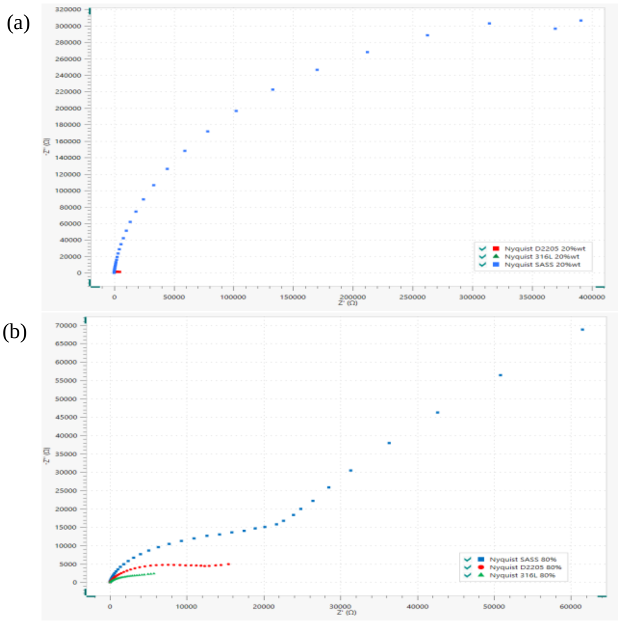

Figure 4. Nyquist Plot of material SASS, D2205 and 316L in (a) 20%wt, (b) 80%wt sulfamic acid.

Corrosion resistance also influenced by PREN (Pitting Resistance Equivalen Number) as described in following formula (Chai & Kangas, 2016):

$$PREN = \%Cr + 3.3\%Mo + 16\%N \quad \text{.......................} \quad (1)$$

Based on above formula, PREN of these 316L, Duplex 2205 and Super Austenite Stainless Steel are 25.1, 36.4 and 50 respectively. This value have correlation with surface resistance based on EIS measurement and early immersion phase on weight loss measurement in ambient temperature. Additional element nickel in these alloy also significantly improve corrosion resistance, while total alloying element (Cr, Ni, Mo & N) are 28.7, 31.2 and 68.9 respectively make super austenitic stainless steel have superior corrosion resistance.

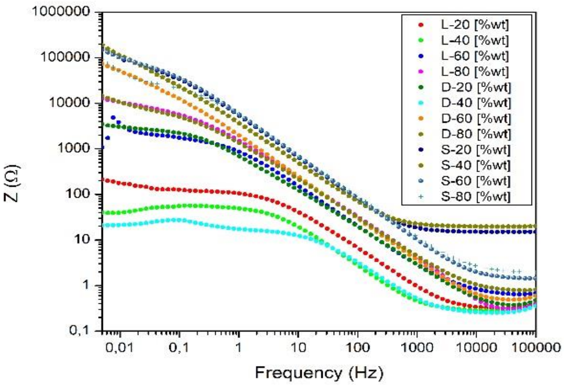

Figure 5. Bode Plot of 316L, Duplex 2205 dan SASS in sulfamic acid 25ºC.

The impedance of the material decreases with increasing frequency. The low-frequency impedance spectrum of 316L and Duplex 2205 appears between 0.01-10 Hz. It shows that the lowest impedance of the 316L and Duplex 2205 is in a 40% solution by weight of sulfamic acid. This indicates that both materials are susceptible at initial exposure to 40% by weight sulfuric acid environment. Almost all material impedance is reduced at high frequencies except for SASS material at 20% and 40%wt sulfamic acid. This linear impedance is means the impedance is purely resistive due to the formation of a passive layer on the metal surface (Syahril, 2012).

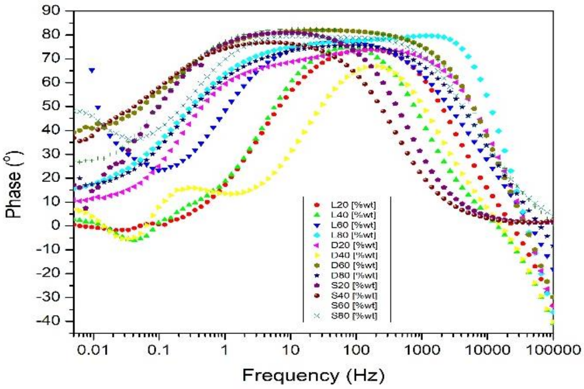

Figure 6. Bode Plot 316L, Duplex 2205 dan SASS in sulfamic acid 25ºC.

In sulfamic acid 25ºC, specimens material has a similar character. They tend to increase phase from capacitive zone to resistive zone, then when reaches a maximum around 80º and then drops back to the capacitive zone. This trend indicated that the passive layer appears in the metalic surface with different characteristics before the passive layer is finally broken and corrosion occurs—for example, material duplex 2205 in 40%wt sulfamic acid experiences several time change phase directions. 316L almost has a similar tendency with Duplex 2205 in 40% wt sulfamic acid. SASS specimen shows more extended stability in the resistive zone before it drops and finally forms a stable passive layer as described by forming a convergence line from frequency 10 kHz and above 0° (Syahril, 2012). This phenomenon is different from the other two materials, which continue to show a negative trend into the capacitive zone, which indicates that both materials continue to undergo significant corrosion processes.

IV. CONCLUSION

Super Austenitic Stainless Steel has shown outstanding corrosion resistance against sulfamic acid in various concentrations compared to Duplex 2205 and 316L. The corrosion resistance of SASS cannot be separated from the large number of alloying elements added to the steel, especially chromium, so the alloy element's passive layer is formed and protects the material from further corrosion. Meanwhile, weight loss analysis gave different results with polarization. In weight loss analysis, the corrosion rate of Duplex 2205 is closed to zero, smaller than 316L. Whereas the polarization corrosion rate of Duplex 2205 is higher than 316L. Especially in the shifting phenomena of Duplex 2205 in the rising of sulfamic concentration.

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