

The Use of Cyclic Polarization Method for Corrosion Resistance Evaluation of Austenitic Stainless Steel 304L and 316L in Aqueous Sodium Chloride Solution

Andi Rustandi

University of Indonesia/Metallurgy and Material Department, Depok, Indonesia
Email: rustandia@gmail.com

Nuradityatama, M. Faisal Rendi, and Suganta Setiawan

University of Indonesia/Metallurgy and Material Department, Depok, Indonesia
Email: {nuradityatama, mf.rendi22, suganta.handaru}@gmail.com

Abstract—Corrosion behavior of austenitic stainless steels 304L and 316L types in various concentrations of aqueous sodium chloride solutions were investigated related to its pitting corrosion resistance. Experimental testing was carried out by using cyclic polarization method at room temperature (27°C) to evaluate the corrosion mechanism by considering breakdown potential (E_b) and protection potential (E_p). Aqueous sodium chloride solutions were prepared with various concentration i.e. 1%, 2%, 3.5%, 4% and 5% w/v. The testing results were represented by cyclic potentiodynamic polarization curves for both alloys which showed potentials that indicated the onset of potentials E_b and E_p respectively. The results were influenced by sodium chloride concentrations and the chemical composition of alloys. Rank of the values of E_b and E_p of 304L and 316L at various sodium chloride concentrations from the highest to the lowest were 1%, 2%, 5%, 4%, 3.5% w/v NaCl consecutively. It was observed that the lowest corrosion resistance of both alloys was at 3.5% w/v NaCl which was similar to typical seawater solution with maximum dissolved oxygen solubility. It was shown that 316L has more positive potentials for both E_b and E_p as well as its difference values compared to SS 304L at all concentrations of aqueous sodium chloride solution.

Index Terms—Austenitic Stainless Steel, Corrosion Behavior, Pitting Corrosion Resistance, NaCl Aqueous Solution, Cyclic Polarization

I. INTRODUCTION

Stainless steels are widely used in various industries and environments. Stainless steels are used due to its better corrosion resistance at various environments than carbon steel. Stainless steels can be classified as: austenitic, ferritic, martensitic and duplex stainless steels. Suitable material depends on the material selection technique and the needs of application speciality such as

corrosion resistance. This study will focus on austenitic stainless steels related to its corrosion behavior.

In austenitic grades of stainless steel, carbon usually kept to low levels ($C < 0.08\%$), chromium content ranges from 16 to 28%, and nickel content ranges from 3.5 to 32 %. The key properties of austenitic stainless steel are excellent corrosion resistance, ductility, and toughness. Basically, chromium is the most important alloying element in order to increase corrosion resistance of steel. Chromium protect steel from corrosion through formation of an adherent, insoluble film of reaction products that shields the metal substrate from uniform and localised attack. The protective film called passive layer that formed on alloy's surface. In some types of austenitic stainless steel, 2 – 4% molybdenum was added to improve the stability of passive layer by reducing the intensity of the oxidizing effect.

Among the types of austenitic stainless steels, 304L and 316L are the most commonly used in various industries. "L" is a classification of low carbon stainless steels. SS 304L is the most widely used stainless steels and described as standard 18Cr 8Ni steel. The corrosion resistance of SS 304L is classified as fair to good in various environments. Type 304L is mostly used in food and beverages industry, automotive, chemical containers, construction, and heat exchangers. SS 316L is the second most used austenitic stainless steels in various industries. The corrosion resistance of SS 316L is also classified as fair to good in various environments[1]. SS 316L is used mostly in severe corrosion environment such as chloride solution and is better known corrosion resistant due to its molybdenum content. SS 316L is widely used especially in marine applications. However, SS 316L is relatively expensive material so that in some cases SS 316L is substituted by SS 304L for lower cost. Austenitic stainless steels have a wide spectrum of resistance to corrosion by chemical environment due to the formation of protective passive film on its surface[2]. However,

such passive film is susceptible to breakdown in the presence of chloride ions resulting in pitting attack as localized form of corrosion[3].

Corrosion has been a major problem in various industry, especially oil and gas industry. Corrosion failure has caused a major damage commonly found in oil and gas production facilities. Corrosion itself is a degradation process of metals due to its reaction with the environment. Corrosion occurs in the form of oxidation/reduction reactions where metal at anode site, transfers its electron to cathode site. This process will increase the oxidation number of metal accordingly turns metal to ion. This ion then reacts with substance in the environment and forms a corrosion product which will adhere in the surface of metal.

The most common reactions in corrosion are hydrogen ion reaction, reduction of dissolved oxygen, metal ion reduction, and metal deposition. The reduction of dissolved oxygen reaction is very common because of the fact that aqueous solutions in contact with air will contain significant amounts of dissolved oxygen[4]. The corrosion rate of a metal in aqueous environments tend to be determined by the rate at which dissolved oxygen can be delivered to the metal surface[5].

For stainless steels, numerous interrelated metallurgical, geometrical, and environmental affect both corrosion initiation and propagation[6]. Although the passivity of the exposed surfaces of stainless steels are maintained by dissolved oxygen, the release of metal ions particularly chromium produces an acidic condition as a result of a series of hydrolysis reactions which can initiate corrosion process[7]. Because of acidic condition in environment, chloride ions migrate and concentrate from the bulk environment and the initiation of corrosion will occur if the concentration becomes sufficient to cause breakdown of the passive film. And after the breakdown of passive film, dissolved oxygen will further propagate corrosion process so the corrosion process will be faster and more aggressive[8].

Corrosion is a natural phenomena that occurs in almost every metal. Therefore, corrosion is a process which can not be stopped. Material selection is one of the well-known methods that can be used to mitigate corrosion[9]. Material selection is a method that control the corrosion rate by choosing the suitable material based on its application or working environment.

Pitting corrosion is a localized form of corrosion that produces small holes and propagate deep inside the material[10]. Pitting corrosion is considered to be more severe impact than uniform corrosion due to its unanticipated occurrence and unpredictable propagation rate[11]. Once pits are initiated, it may continue to grow by a self-sustaining or autocatalytic process that produce conditions that are both stimulating and necessary for the continuing activity of the pit. The corrosion rate of pitting corrosion is extremely faster than general corrosion[12]. Its aggressiveness is due to the very small size and high penetration ability of chloride ion through passive layer[13].

Marine corrosion is deterioration of structures and vessels immersed in seawater, the corrosion of machinery and piping systems that use seawater for cooling and other industrial purposes and also corrosion in marine atmospheres[14]. Although salt water is generally known as a corrosive environment, it is not widely understood how much the aggressiveness of its corrosive behavior[15]. It is because there are many factors affecting the aggressiveness of marine environment such as the season, tidal and wave, velocity, chloride ion content, dissolved oxygen concentration, and living organism.

Because of those factors, seawater is not easily simulated in the laboratory for corrosion testing purposes. Stored seawater is notorious for exhibiting behavior as a corrosive medium that is different from the condition before it was taken[16]. Researcher often put one or two factors to approach the real condition of seawater such as chloride concentration and dissolved oxygen concentration[17].

The aims of this study are to compare and determine the corrosion resistance of SS 304L and SS 316L in various aqueous sodium chloride solutions. Aqueous solutions were prepared in 1%,2%,3.5%,4%,and 5%, expected to be similar to marine environment. Corrosion resistance of both alloys are represented by the evaluation of the cyclic potentiodynamic polarization curves.

II. EXPERIMENTAL DETAILS

A. Materials Specification

Materials used in this study were commercial grade SS 316L and SS 304L. SS 316L and SS 304L both were machined and well prepared prior to polarization testing. The chemical compositions of both alloys were evaluated using a optical emission spectrometer machine according to ASTM E415 and E1086. The results are shown in Table I.

TABLE I. CHEMICAL COMPOSITION OF SS 304L AND SS 316L

Metal	C	Si	Mn	P	S
SS 304L	0.039	0.418	1.14	0.0313	<0.005
SS 316L	0.039	0.438	1.65	0.023	<0.005

Metal	Cr	Mo	Ni	Cu	Fe
SS 304L	18.89	0.001	8.16	0.027	70.98
SS 316L	16.5	2.38	9.89	0.076	68.7

B. NaCl Solutions

Aqueous sodium chloride solutions containing 1%, 2%, 3.5%, 4% and 5% of sodium chloride were prepared by dissolving 10 gr, 20 gr, 35 gr, 40 gr and 50 gr NaCl in 1 liter of water and stirred with magnetic stirrer to produce homogeneous solution. Solutions were made at room temperature 27^o C.

C. Samples Preparation

Both stainless steels were cut into 4cm x 4cm x 0,5cm plates from their original plates form. Samples then were ground by grinding machine with 40, 60, 100, 180, 400, 500, 600, and 800 grades abrasive papers followed by polishing, cleaning and drying.

D. Dissolved Oxygen Solubility Measurement

Dissolved oxygen concentration was measured by using dissolved oxygen meter. Each concentration of aqueous sodium chloride solution were tested by putting the probe of dissolved oxygen meter into 100 ml solution of aqueous sodium chloride solution.

E. Polarization Cell

Electrochemical measurement by using cyclic polarization method was conducted in a cell chamber with three electrodes which composed of carbon counter electrode, stainless steel as working electrode and saturated Ag/AgCl electrode as reference electrode. The connection of the three electrodes is shown by Fig. 1.

F. Cyclic Polarization Experiment

Cyclic polarization experiment was carried out by AUTOLAB potentiostat and NOVA AUTOLAB 1.10 software. The measured potentials were referred to Ag/AgCl electrode. The illustrative connection between potentiostat and polarization cell is shown by Fig. 1.

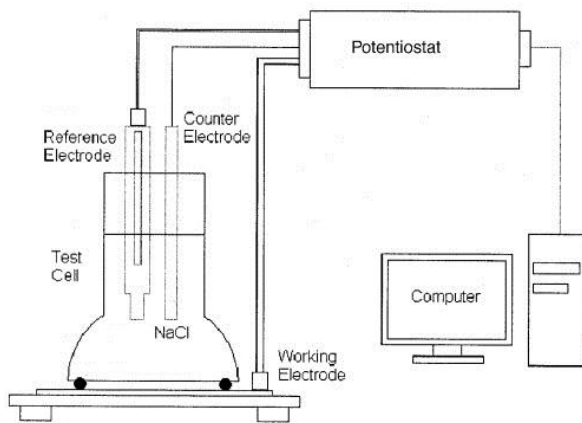


Figure 1. The scheme of cyclic polarization experiment.

III. RESULTS AND DISCUSSION

A. Dissolved Oxygen Solubility Measurement

Dissolved oxygen solubility measurement was carried out in order to measure the solubility of the dissolved oxygen in aqueous sodium chloride solution at various concentration by using parts per million (ppm) unit. The purpose of this experiment is to find out the relation between dissolved oxygen solubility and its effect to corrosion resistance to material especially stainless steel in this study.

Based on the literature, at first the addition of sodium chloride salts in water will increase the dissolved oxygen solubility. But after its reached the maximum point the dissolved oxygen solubility will drop due to excessive

addition of sodium chloride concentration in environment or the solution[18]. Therefore, higher solubility of dissolved oxygen in a solution will increase the corrosion rate of the material. But after it reached the maximum point, corrosion rate will drop following the depletion of dissolved oxygen in the solution[19].

Table II and Fig. 2 below are the results of dissolved oxygen solubility measurement by using the dissolved oxygen meter.

TABLE II. OXYGEN CONCENTRATION VALUES AT VARIOUS AQUEOUS SODIUM CHLORIDE CONCENTRATION

NaCl Concentration (%)	Oxygen Concentration (ppm)
1.0	2.6
2.0	3.9
3.5	4.5
4.0	4.4
5.0	4.0

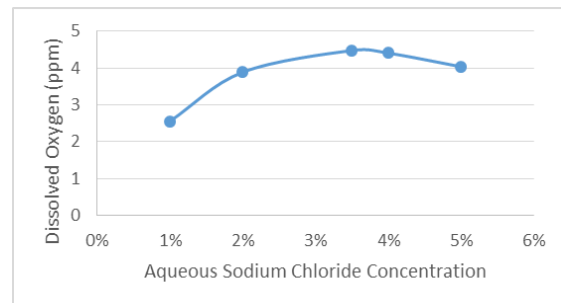


Figure 2. Dissolved oxygen concentration at various aqueous sodium chloride concentration.

Based on the dissolved oxygen solubility measurement results, it is shown that dissolved oxygen solubilities increase with increasing aqueous sodium chloride concentration until reaching its maximum point at 3.5% aqueous sodium chloride concentration and decrease with further increasing aqueous sodium chloride concentration. The rank of dissolved oxygen concentrations in aqueous sodium chloride from lowest to highest are 1%, 2%, 5%, 4%, 3.5%.

B. Cyclic Polarization Experiment

Cyclic polarization experiment is a combination of anodic and cathodic polarization that form a cyclic process. Cyclic polarization methods were conducted in order to investigate the tendency of pitting occurrence for a specimen in any environment. The tendency of pitting were evaluated by considering its breakdown potential (E_b) and protection potential (E_p). And also, size of the loop curve indicated the propagation process of pitting occurrence.

The results of the experiments were cyclic polarization curves for both alloy at various aqueous sodium chloride concentrations. Interpretation E_b and E_p from this method was done by using qualitative analysis.

Eb or breakdown potential is the potential that indicates the onset of pitting and Ep or protection potential is the potential that halted pitting propagation. The higher values of breakdown potential and protection potential, the specimen will exhibit better corrosion resistance[20].

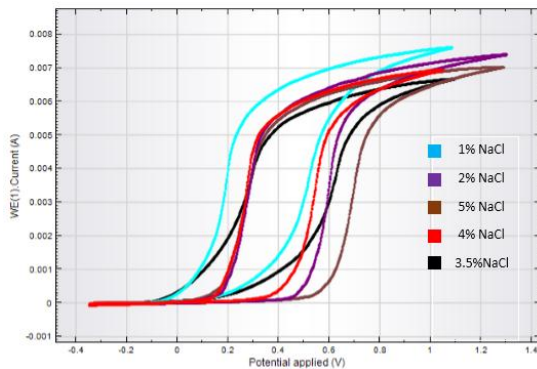


Figure 3. Cyclic polarization curves of SS 316L in various sodium chloride concentration.

TABLE III. EB AND EP VALUES FOR SS 316L

NaCl Concentration (%)	Eb (V)	Ep (V)
1.00	0.47	-0.09
2.00	0.55	0.02
3.50	0.31	-0.10
4.00	0.37	0.05
5.00	0.46	0.11

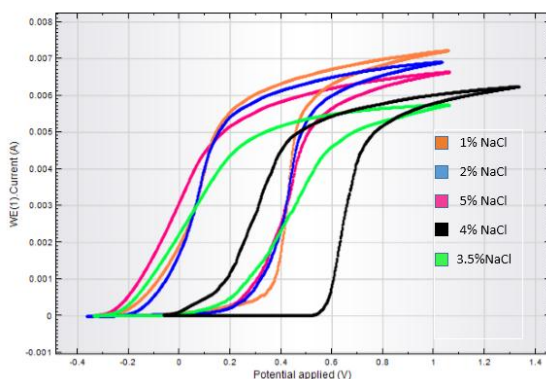


Figure 4. Cyclic polarization curves of SS 304L in various sodium chloride concentration.

TABLE IV. EB AND EP VALUES FOR SS 304L

NaCl Concentration (%)	Eb (V)	Ep (V)
1.00	0.39	-0.15
2.00	0.37	-0.21
3.50	0.27	-0.28
4.00	0.61	-0.10
5.00	0.31	-0.27

Fig. 3 and Fig. 4 shows the cyclic polarization curves for both alloys at various aqueous sodium chloride concentration. The values of Eb and Ep for both alloys are shown by Table III for SS 316L and Table IV for SS 304L. The variety of curves revealed corrosion behavior of both alloys depending on sodium chloride concentration[21]. With qualitative analysis based on the figures, it can be interpreted that the higher the values of breakdown potential and protection potential in cyclic polarization curve, the higher its corrosion resistance. The corrosion resistance from the highest to the lowest were 1%, 2%, 5%, 4%, 3.5% w/v NaCl consecutively. According to those results, the rank of corrosion resistance follows the rank of dissolved oxygen solubility from experiment above. It is shown that dissolved oxygen solubility is also a considerable factor affecting corrosion resistance of an alloy.

Both figures shows that corrosion resistance of both alloys will drop at 3.5% NaCl concentration which is similar of typical seawater with maximum dissolved oxygen solubility[22].

It was proven by the value of Eb and Ep of both alloys at 3.5% are 0.31V and 0.1V for SS 316L and 0.27V and -0.28V respectively which was the lowest value from both alloys.

C. Comparison of Cyclic Polarization Curves between SS 316L and SS 304L

Fig. 5 – 9 and Table V - IX below are the data comparison between alloy SS 316L and SS 304L at various aqueous sodium chloride concentration.

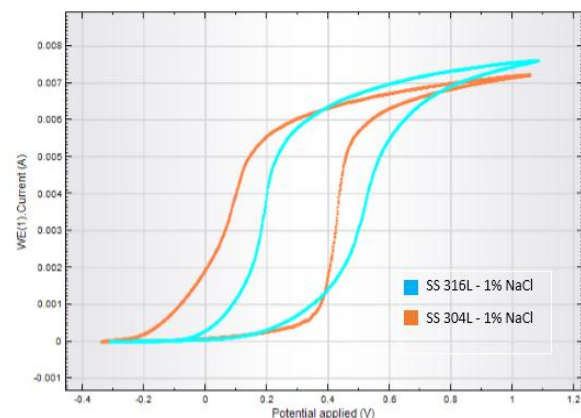


Figure 5. Cyclic polarization curves of SS 316L and SS 304L in 1% w/v sodium chloride concentration.

TABLE V. EB AND EP VALUES IN 1% w/v SODIUM CHLORIDE CONCENTRATION

Material	Eb (V)	Ep (V)
SS 316L	0.47	-0.09
SS 304 L	0.39	-0.15

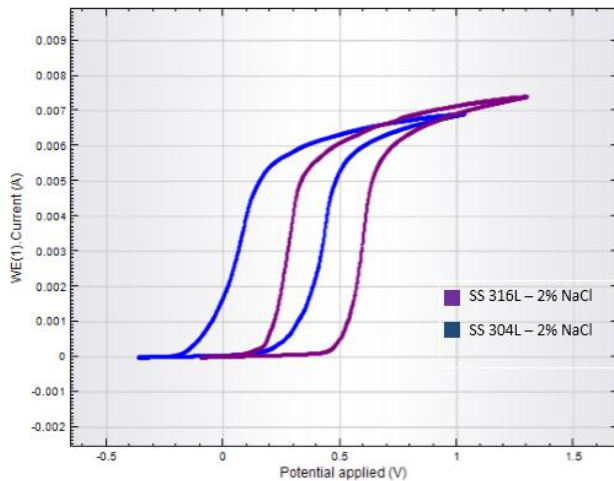


Figure 6. Cyclic polarization curves of SS 316L and SS 304L in 2% w/v sodium chloride concentration.

TABLE VI. Eb AND Ep VALUES IN 2% w/v SODIUM CHLORIDE CONCENTRATION

Material	Eb(V)	Ep(V)
SS 316L	0.55	0.02
SS 304L	0.37	-0.21

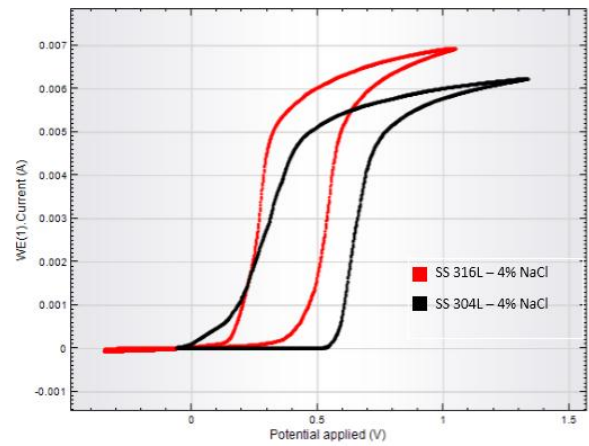


Figure 8. Cyclic polarization curves of SS 316L and SS 304L in 4% w/v sodium chloride concentration.

TABLE VIII. Eb AND Ep VALUES IN 4% w/v SODIUM CHLORIDE CONCENTRATION

Material	Eb (V)	Ep (V)
SS 316L	0,37	0,05
SS 304L	0,61	-0,1

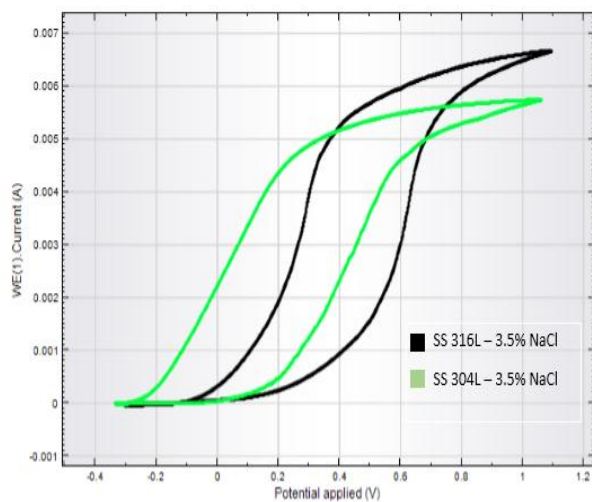


Figure 7. Cyclic polarization curves of SS 316L and SS 304L in 3.5% w/v sodium chloride concentration.

TABLE VII. Eb AND Ep VALUES IN 3.5% w/v SODIUM CHLORIDE CONCENTRATION

Material	Eb(V)	Ep(V)
SS 316L	0.31	-0.10
SS 304L	0.27	-0.28

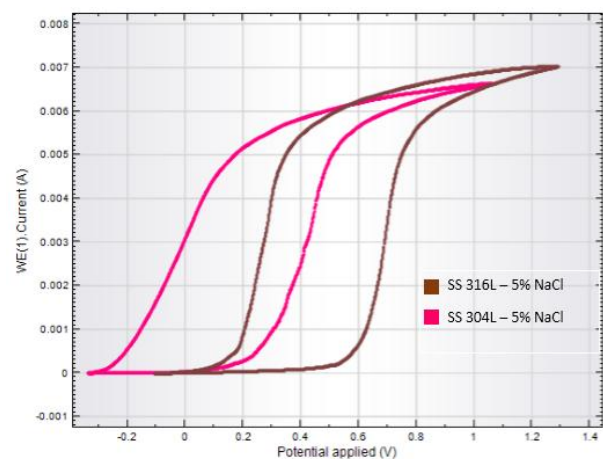


Figure 9. Cyclic polarization curves of SS 316L and SS 304L in 5% w/v sodium chloride concentration.

TABLE IX. Eb AND Ep VALUES IN 5% w/v SODIUM CHLORIDE CONCENTRATION

Material	Eb(V)	Ep(V)
SS 316L	0.46	0.11
SS 304L	0.31	-0.27

Fig. 4-8 and Table V-IX shows the comparison of corrosion behavior of both alloys at various aqueous sodium chloride concentration. Based on Fig. 4 – 8, SS 316L tend to has higher corrosion resistance at various aqueous sodium chloride concentration. By looking at the cyclic polarization curve's width on Fig. 3-7, it is known that pitting corrosion propagates more aggressively in SS 304L because it has larger width than SS 316L[23].

As shown in Table IV-VII, SS 316L also has better corrosion resistance by looking at its breakdown (Eb) and protection (Ep) potential which is higher than SS 314L at various aqueous sodium chloride concentration.

The difference in corrosion behavior of both alloys was because the addition of 2% molybdenum in SS 316L which influenced stainless steel to form better and more stable passive layer and more resistant to pitting corrosion[24,25].

IV. CONCLUSIONS

Experimental studies of corrosion for austenitic stainless steel type 304L and 316L are conducted by cyclic polarization technique. The rank of corrosion behavior according to cyclic polarization curve results for SS 316L and 304L at various chloride concentration from the highest to the lowest are 1%, 2%, 5%, 4%, 3.5% w/v NaCl consecutively. The results shows that both alloys have the lowest corrosion resistance at 3.5 w/v NaCl. It is due to dissolved oxygen solubility reaches its maximum point at 3.5% w/v NaCl which is similar to seawater condition. It is recommended that SS 316L is preferred for material design than SS 304L in high corrosive chloride ions environment because it has better corrosion resistance due to the higher molybdenum content in its composition.

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Andi Rustandi received PhD degree in Metallurgy and Material Engineering from Universitas Indonesia, Indonesia, in 2012. Now he works at Universitas Indonesia as Associate Professor. His current research interests include materials selection, protective coating, corrosion inhibitor and cathodic protection.



Nuradityatama was an undergraduate student in Metallurgy and Materials Engineering from Universitas Indonesia. Now he works at Mechanical Metallurgy Laboratory as an assistant. His current research interest includes corrosion resistant alloys.



Suganta Handaru Setiawan received Master Degree in Metallurgy and Material Engineering from Universitas Indonesia, in 2016. Currently, he work as R&D Manager at Voestalpine Bohler Welding Group South East Asia, PT. His current research interests include in alloy design and welding technology.



Muhammad Faisal Rendi received Bachelor of Engineering degree in Metallurgy and Materials Engineering from Universitas Indonesia, Depok, Indonesia in 2016. His research interests include corrosion resistant alloys and heat treatment. Currently he is a member of Indonesian Association of Corrosion (INDOCOR).