



EFFECT OF VARIATION OF KALIUM HYDROXIDE SOLUTION CONCENTRATION AND TEMPERATURE TO THE CORROSION RESISTANCE OF AISI 304, AISI 316, AND COPPER ALLOYS IN WATER ELECTROLYSIS APPARATUS

Ida Hamidah, Agus Solehudin and Agus Setiawan

Department of Mechanical Engineering Education, Indonesia University of Education, Jl. Dr. Setiabudi No. Bandung, Indonesia

E-Mail: idahamidah@upi.edu

ABSTRACT

The corrosion resistance properties of various metals which were used as electrodes in water electrolysis apparatus had been analyzed. This analysis is important to improve the performance of the water electrolysis apparatus. Stainless steel was used as an electrode in water electrolysis apparatus and it was immersed in KOH solution. KOH solution with various concentrations and temperatures were used to test the corrosion resistance of AISI 304, AISI 316, and Copper Alloys. To analyze the corrosion resistance, calculation of corrosion rate was conducted by using mass loss method. Through the calculation, it was found that the corrosion rate was increased linearly by increasing the concentration and temperature of the solution. This means that the metal has poor corrosion resistance at high concentrations and high temperatures. Among the three metals that were tested, it was also found that AISI 316 showed the most resistant to alkaline environment.

Keywords: corrosion resistance, mass loss method, water electrolysis.

INTRODUCTION

Currently, research on renewable energy with more incentive has been done to overcome the problems of fossil energy reserves. There are many energy alternatives that can be used by humans to meet their needs. One such alternative energy is hydrogen, which can be produced through the electrolysis of water. Research on hydrogen technology was found in the 17th century when the internal combustion engine which was operated by hydrogen was successfully created. Since that time, hydrogen technologies have continued to be developed. To increase the productivity of hydrogen from water electrolysis process, some researchers have used a piece of membrane on water electrolysis apparatus for separating hydrogen and oxygen produced [1, 2, 3].

In line with the development of hydrogen technology, water electrolysis apparatus which has five electrodes and each electrode is separated by an insulator gasket has been successfully built. The electrolysis apparatus has been patented in Indonesia with patent number of IDS000001310. This apparatus was able to produce hydrogen gas which was directly used in the combustion process of a motor vehicle. The use of fuel on a motor vehicle can be saved as much as 10% and exhaust gas can be reduced as much as 23% [4].

To improve the performance of this water electrolysis apparatus, further research has been done to analyze the effect of the variation of concentrations and temperatures to the corrosion resistance of electrodes on the apparatus.

LITERATURE REVIEW

Stainless Steel Corrosion

The main reason for the use of the stainless steels is their resistance to corrosion. The main alloying element of stainless steel are Chromium (Cr) and Nickel (Ni). Cr is a reactive element, but it and its alloys passivate and exhibit excellent resistance to many environments. Higher Cr contents may be necessary for improving the corrosion resistance of stainless steels in more aggressive media. Compared to Cr, Ni is more important: it is added to control the Alloys microstructure and to improve the corrosion resistance in acidic or caustic media. The addition of other elements such as Molybdenum, Tungsten, Copper, Silicon, Titanium, Niobium, Nitrogen, etc. enables a wide range of properties to be obtained.

AISI 304 and AISI 316 as austenitic stainless steel are the largest and most important group in the stainless steel range. These steels, which exhibit a high level of weldability, are available in a wide range of compositions which are used for general stainless steel fabrications, elevated temperature applications and resistance to pitting corrosion respectively. This material has a good corrosion resistance due to the formation of passive film of chromium oxide. The film is stable, invisible, thin, durable, extremely adherent and self-repairing. Passivation reduces the anodic reaction involved in the corrosion process, but quite severe pitting corrosion can occur in acidic environments [5]. The failure of some stainless steels resulting from pitting, corrosion is sometimes considered a technological problem [6]. Consequently, much effort has been expended in attempting to understand and overcome pitting, corrosion,



thus many stainless steel/environment combinations have been studied [7]. In many studies of the structure of the passive film on chromium stainless steels, it has been demonstrated that the properties of the steel is due to the selective dissolution of Cr Alloys and accumulation of Cr_2O_3 on the surface of a passive layer, i.e., practically the formation of chromium passive layer [8]. Alloying metals are very important factors to stabilize an Alloy against general and localized corrosion. Among these; Cr plays a very important role for iron and nickel base metals. It accumulates in the passive layer because of its extremely small dissolution currents even in strongly acidic electrolytes [9].

Copper Corrosion

Copper (Cu) is a relatively noble metal and is more stable in atmosphere than e.g. iron and zinc, but it can form ion in water. Cu can thus react with oxygen in water. Together with oxygen, Cu ions are all parts of the major corrosion products. Corrosion resistance of Cu relies upon a small amount of corrosion at the surface to form a protective (semi-passive) layer that stifles a further corrosion [10].

Cu alloys which are used in water or sea water service have low general corrosion rates but also a high resistance to many localised forms of corrosion which can lead to rapid failure. In solution of pH 3, the Cu surface was covered with porous corrosion products of cuprous oxide (Cu_2O). In solutions of pH 4 to pH 5, formation of cubic Cu_2O on the Cu surface provided a diffusion barrier to copper dissolution. In solutions of pH 6 to pH 9, the oxide films (Cu_2O) became more protective. In solution of pH 10, a thin, compact Cu_2O film formed, and at pH 12 and pH 13, a protective monoclinic cupric oxide (CuO) layer is formed [11]. The ion hydrogen concentration (as pH) also influences the corrosion rate. The corrosion rate is minimized at pH values approaching 8.5 and greater. For pH values below 7.0, the copper ion is stable in solution. Formation of the ion occurs from the oxide state when pH is just below 7.0. Replacement of the oxygen component of the oxide occurs readily under these conditions. For pH values above 7.0, the preferred form of the metal is the oxide. Replacement of the oxygen component of the oxide does not occur and slows the corrosion mechanism [12].

The chemical properties of AISI 316, AISI 304, and Cu Alloys are presented in Table-1.

Table-1. The chemical composition of AISI 304, AISI 316, and Cu alloys.

| Composition (% Wt) | AISI 304 | AISI 316 | Cu alloys |
|--------------------|-------------|-------------|-----------|
| Carbon | 0.08 max. | 0.08 max. | - |
| Manganese | 2.00 max. | 2.00 max. | - |
| Phosphorus | 0.045 max. | 0.045 max. | - |
| Sulfur | 0.030 max. | 0.030 max. | - |
| Silicon | 0.75 max. | 0.75 max. | - |
| Chromium | 18.00-20.00 | 16.00-18.00 | - |
| Nickel | 8.00-12.00 | 10.00-14.00 | 18 |
| Nitrogen | 0.10 max. | 0.10 max. | - |
| Iron | Balance | Balance | - |
| Molybdenum | - | 2.00-3.00 | - |
| Copper | - | - | 65 |
| Zinc | - | - | 17 |

Corrosion Resistance

The process of corrosion is a slow chemical reaction. During the corrosion process, there is a loss of mass of the metal. The loss in mg/dm^2 per day or mils per year (mpy) measures the extent of corrosion. Furthermore, to determine the nature of the corrosion resistance of AISI 316, AISI 304, and Cu alloys, the corrosion rate of each metal using equation was calculated (1). Low corrosion rate showed high corrosion resistance.

$$CR = \frac{534W}{DAT} \quad (1)$$

where CR is corrosion rate (mpy), W is mass loss (mg), D is density (g/cm^3), A is area (in^2), and T is exposure time (h).



METHODS

AISI 304, AISI 316, and copper studied in this experiment have a thin plate shape with dimensions of 20 x 10 x 1.5 mm. Plate shape is preferable to the cylindrical shape because it has better performance as an electrode in an electrolysis apparatus [13]. Prior to the experiment, all specimens were mechanically polished with silicon carbide paper of 320, 600, and 1000 grades, respectively to produce a smooth surface. After that, the specimens were de-greased with acetone, rinsed in distilled water, and then dried in air.

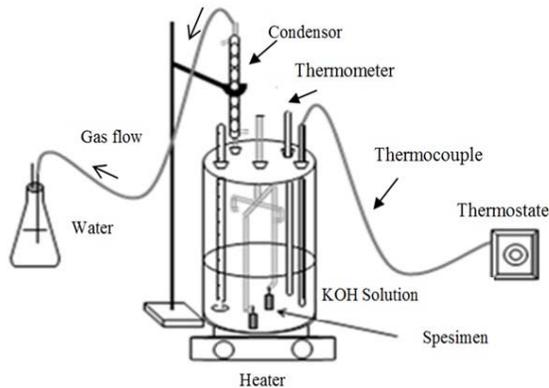


Figure-1. Corrosion cell autoclave.

The corrosion test was carried out in a glass autoclave containing the KOH solution, as shown in Figure-1. Thermometer and thermocouple were mounted on the inside of the autoclave and connected to a thermostat to control the temperature of the test solution. The test solution used was KOH with varying concentrations of 15,000, 22,500, and 30,000 ppm. The specimens were immersed in the test solutions in the autoclave with time variations of 336, 672, and 1008 hours at temperature of 25 °C and 50 °C. The complete parameters is shown in Table-2.

Table-2. The corrosion rate test parameters.

| Condition | Value |
|------------------------|---------------------|
| Solution concentration | 15,000 – 30,000 ppm |
| Solution temperature | 25 – 50°C |
| Exposure time | 336 – 1008 h |
| Air pressure | ± 960 mbar |
| Relative humidity | ±72 |

Before the specimens were immersed in the test solution, the specimens were weighed with digital scales with an accuracy of 0,0001g. After the corrosion test, the specimens were removed from the autoclave, and then were cleaned with distilled water and were dried in air.

The corrosion products on the surface of the specimens were cleaned carefully using a pickling solution. Finally, the specimens were weighed again to get the final mass. Mass loss method was used to determine the corrosion rate according to ASTM G31 standard procedures [14] following the equation (1).

RESULTS AND DISCUSSIONS

The corrosion test was monitored on temperature of 25 °C and 336 hours intervals for a period of 1008 hours. The variation of corrosion rate to the exposure time for specimens immersed in 15,000, 22,500, and 30,000 ppm KOH solution are presented in Figure-2 to Figure-4.

At 15,000 ppm solution concentration and 1008 hours exposure time, it is seen that AISI 316 has the lowest corrosion rate, which is about 0.012065 mpy (see Figure-2). However, measurements at 336 hours exposure time, the corrosion rate of AISI 316 is still higher than the AISI 304. Meanwhile, the corrosion rate of Cu Alloys shows higher values than the AISI 304 and AISI 316 for all exposure time.

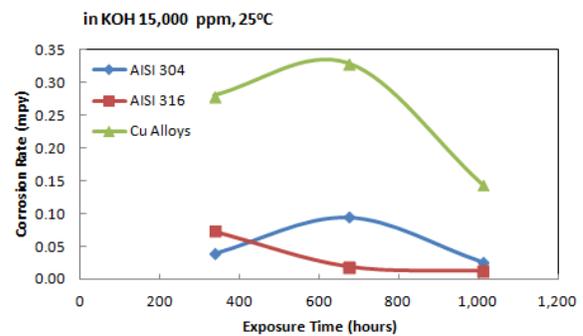


Figure-2. The corrosion rate of AISI 316, AISI 304, and Cu Alloys in 15,000 ppm KOH solution.

Measurement of the corrosion rate in 22,500 ppm KOH concentration indicates that the AISI 316 has the lowest corrosion rate (see Figure-3). AISI 316 corrosion rate decreases linearly to the exposure time of 0.052810, 0.051850, and 0.018215 mpy, respectively. On the other hand, AISI 304 corrosion rate increases linearly to the exposure time of 0.071017, 0.289118, and 0.29148 mpy, respectively. Meanwhile, the corrosion rate of Cu Alloys shows a nonlinear relationship to the exposure time and it has a higher corrosion rate compared to the AISI 304 and AISI 316.

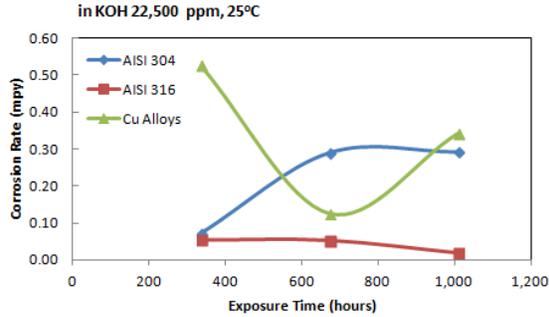


Figure-3. The corrosion rate of AISI 316, AISI 304, and Cu Alloys in 22,500 ppm KOH solution.

When the concentration of the electrolyte solution is added, namely at 30,000 ppm as shown in Figure-4, the measurement results indicate a different state. For this concentration, AISI 304 shows the lowest corrosion rate compared to the AISI 316 and Cu Alloys. AISI 304 corrosion rate indicates the number of 0.020307 and 0.042043 mpy at the exposure time of 672 and 1008 hours, respectively.

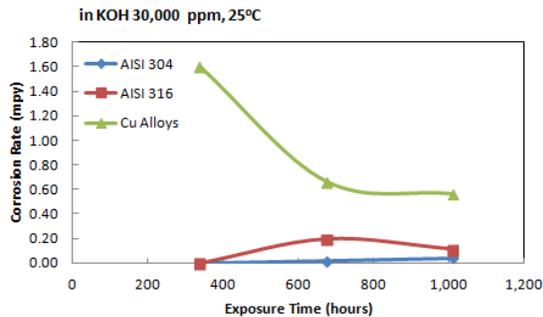


Figure-4. The corrosion rate of AISI 316, AISI 304, and Cu Alloys in 30,000 ppm KOH solution.

Other reviews to measure the corrosion rate are from the exposure time. From Figure-5, it is shown that the AISI 316 corrosion rate increased linearly by increasing the KOH solution concentration. However, for AISI 304 and Cu Alloys, additional KOH solution concentration is not accompanied by the increasing of corrosion rate.

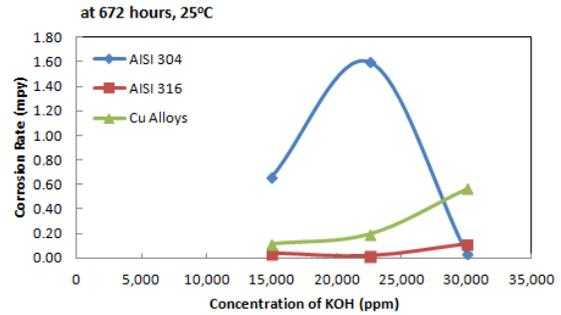


Figure-5. The corrosion rate of AISI 316, AISI 304, and Cu Alloys at 672 hours exposure time.

Meanwhile, as seen in Figure-6, it appears that the AISI 316 and AISI 304 corrosion rate increased linearly by increasing the KOH solution concentration. Only Cu Alloys which did not show a linear relationship between the increasing in solution concentration to the corrosion rate.

The study of water electrolysis apparatus showed that the increase in electrolyte solution concentration can increase HHO gas flow rate. However, enhancement of the HHO gas flow rate which was due to higher ionization and electrical current will decrease the efficiency of water electrolysis apparatus [13]. To that end, the selection of the appropriate electrolyte solution concentration, in addition to improve the electrode corrosion resistance also can improve the efficiency of electrolysis apparatus.

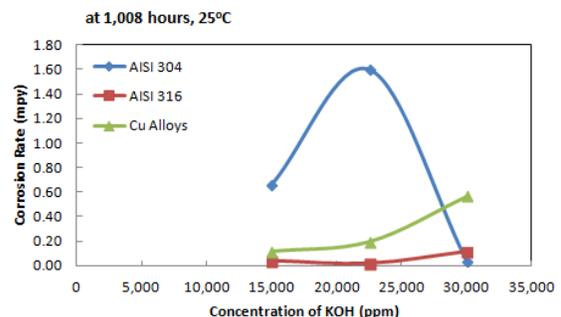


Figure-6. The corrosion rate of AISI 316, AISI 304, and Cu Alloys at 1008 hours exposure time.

From Figure-4 to Figure-6, it can be seen that although AISI 304 shows a lower corrosion rate in 30,000 ppm KOH solution i.e. 0.042043 mpy, but the AISI 304 corrosion rate is still higher than the AISI 316 corrosion rate in 22,500 ppm KOH solution of 0.018215 mpy. Thus, it can be noted that the AISI 316 is a promising material for use as an electrode in water electrolysis apparatus. The corrosion characteristics of AISI 316 in line with the results of our previous study on the water electrolysis



apparatus. The highest efficiency of the water electrolysis apparatus in reducing exhaust gas and saving fuel gas occurred at concentrations of 22,500 ppm KOH solution or the electric current of 10 A [4].

To optimize the corrosion resistance, the tests then were done at 50°C KOH solution temperature and 22,500 ppm KOH solution concentration. The results are shown in Figure-7. The corrosion rate of AISI 316 is still lowest compared to the corrosion rate of AISI 304 and Cu Alloys, that is 0.10151 mpy. However, the corrosion rate of AISI 316 at 50°C is higher than the corrosion rate of AISI 316 at room temperature which only has value of 0.018215 mpy. Thus, it can be proposed that the use of KOH solution for water electrolysis process should be performed at room temperature. This suggestion is actually somewhat contradicts with other studies which stated that at high temperatures water electrolysis process will be more efficient [15, 16]. For that reason, further study is required to completely understand the compatibility between metal corrosion resistances with an efficiency of water electrolysis apparatus.

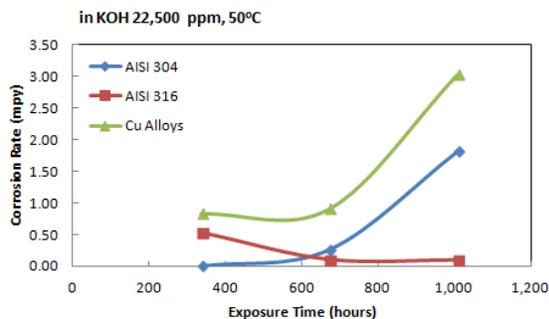


Figure-7. The corrosion rate of AISI 316, AISI 304, and Cu Alloys at 50 °C and 22,500 ppm KOH solution.

The observations of corrosion resistance for all of the examined specimens showed that the highest corrosion resistance in all of the parameters was observed for AISI 316. The corrosion resistance of AISI 316 in various test solution concentrations is due to the influence of the chemical composition of AISI 316 containing about at least 16% Cr and 10% Ni (see Table-1). The function of the Cr is to form a thin passive layer of Cr_2O_3 on the specimen surface which ultimately can improve the corrosion resistance. The Cr_2O_3 layer can act as a barrier layer to protect the specimen surface from the solution. In addition, the presence of Ni can improve the corrosion resistance of AISI 316. In a pure state, nickel is mushy, but if it is combined with iron, chrome, and other metals, nickel can form a hard stainless steel as the AISI 316.

To further enhance the corrosion resistance, many researchers used a variety of materials as inhibitors. These inhibitors work effectively to reduce the rate of corrosion. One example, for instance, it was found that L-methionine,

L-methionine sulfoxide, and L-methionine sulfone act as safe corrosion inhibitors for copper [17].

CONCLUSIONS

From the results obtained it was found that the corrosion rate of AISI 304, AISI 316, and Cu alloys depends on concentration and temperature of KOH solution. The enhancement of KOH solution concentration and temperature will increase the corrosion rate. Based on observations on all of the specimens, it was found that the AISI 316 has the most excellent corrosion resistance compared to the AISI 304 and copper alloys, where the lowest corrosion rate is 0.018215 mpy at room temperature and 22,500 ppm. Investigation on the long term performance of the water electrolysis apparatus which uses AISI 316 as an electrode is the subject of future studies.

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