Study on Pitting Corrosion of AlMg₂ in Solution Containing Chloride

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Abstract. The AlMg₂ is an aluminium alloy that used as cladding material for the RSG GA. Siwabessy (RSG-GAS) research reactor in Serpong, Indonesia. The reactor uses demineralized water as primary coolant with 6.5 to 7.5 of pH. The chloride ion concentration in water in primary is lower than 0.0094 ppm. Poor of primary water condition can cause the cladding corrosion. The purpose of this study is to determine the effect of temperature and chloride ion concentration toward AlMg₂ pitting corrosion. The method used in this research is to observe the pitting corrosion of AlMg₂ material using Potentiostat. The laboratory experiments were conducted in various temperatures (28, 35, 40, 45 and 50 °C) and various concentration of sodium chloride of 0.005, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040, 0.045 and 0.050 ppm. The results show the corrosion rates were very small, and the highest corrosion rate occurred is 983 x 10⁻³ mpy in 0.050 ppm of NaCl at 50°C

Keywords: AlMg₂, corrosion, cladding material, chloride ion, temperature, Potentiostat

1. Introduction
The corrosion surveillance for primary and secondary cooling system of RSG_GAS have been published else where [1,2,3,4,5,6,7,8]. The material used for those are, AlMg₂, SS 304, carbon steel and AlMg₃. The AlMg₂ is used as material cladding for RSG-GAS reactor. AlMg₂ as cladding material has a function for containing fuel and fission products. Aluminium and its alloys have a good resistance toward corrosion at low temperature. Aluminium owes its excellent corrosion resistance and its usage as one of the primary metals of commerce to the barrier oxide film that is bonded strongly to its surface [9,10]. These will form a thin oxide film at its surface which separate the metal from its environment and protects from further oxidation. This self-protecting characteristic gives aluminium its high resistance to corrosion [11,12,13]. Even though aluminium is resistant to most of the corrosive media, it is attacked by several chemicals. The presence of chloride ion in aqueous media in contact with aluminium metal or aluminium alloys, causes pitting attack [14]. The presence of chloride ion was found accelerating the corrosion of aluminium. This oxide film can inhibit further corrosion process, but some of them vulnerable to localized corrosion in solution containing chloride. For aluminium, pitting corrosion is most commonly produced by halide ions, of which chloride (Cl⁻) is the most frequently encountered in service. The passive film become destroy in environment containing the aggressive ion such as chloride ion. Temperature also has an effect to corrosion of materials. Temperature increasing is usually followed by increasing corrosion rate [15,16,17,18].

However, if corrosion occur, it forms at random in pits. Pitting is most likely to occur in the presence of chloride ions, combined with such depolarizers as oxygen or oxidizing salts. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion [19,20,21]. AlMg₂ degradation can cause an effect to reactor safety. The cladding failure will release radioactive to environment. In research reactors, corrosion processes are strongly affected by operational measured variables such as environment medium, pH, temperature, conductivity and...
chloride ion. The protection mechanism to be outlined focuses mainly on maintaining high quality of coolant water.

The purpose of this study is to study of AlMg2 pitting corrosion in chloride containing solution. The method that used in this research is using Potentiostat. Tests were conducted in 28, 30, 35, 40 and 45 °C. The AlMg2 material corrode in solution containing NaCl solution. The chloride ion content of the water should be maintained as low as achievable and at less than 0.0094 ppm for optimum corrosion protection. Chloride ions break down the passive film on aluminium and promote metal dissolution. The chloride ions in these chemicals in small amount will destroy the passive film on aluminium and cause aggressive pitting corrosion. The corrosion process of aluminum increases with increasing temperature. Corrosion resistance is used as criterion in determining the lifetime of components and structures.

2. Theory

Corrosion involves the reaction of a metallic material with its environment. Metal is attempting to revert to the natural form that has a more stable condition. Corrosion is a natural process that can cause the degradation on material, component and other structures. The corrosion process can not be stopped. Corrosion can be controlled through many was; such as, using the material resist to corrosion or controlling the environment. The environment of material has an influence to the integrity of material toward corrosion.

Pits often appear to be rather small at the surface, but may have larger cross-section areas deeper inside the metal. Since the attack is small at the surface and may be covered by corrosion products, a pitting attack often remains undiscovered until it causes perforation. Pitting corrosion is localized accelerated dissolution of metal that occurs as a result of a breakdown of the otherwise protective passive film on metal surface. Pitting is most likely to occur in the presence of chloride ions, combined with such depolarizers as oxygen or oxidizing salts. Aggressive ions such as chloride tend to prevent the formation of protective oxide films on the metal surface and thus increase corrosion [19,20,21].

Almost all metals have the ability to form a protective layer on its surface. This passive layer is usually formed of metal oxides or other compounds that will separate the metal from the media which is usually in the form of a solution. But if it's passive metal contact with media containing aggressive ions such as chlorine ions (Cl-) ions, flour (F-) and sulphate (SO4-) then the corrosion can occur. The corrosion occurs in the form of small holes on the surface of metals. This corrosion is known as pitting corrosion. Pits that occur can be a single small holes or small pits are clumped. A group of these tiny holes later can change become a single and large. Metal loss due to pitting corrosion relatively less than the loss of mass due to general corrosion. But the risk of damage from pitting corrosion is much greater than the risk of general corrosion. A small pit which happens it can penetrate to the deep of the material and sometimes can cause a leakage [19,20,21,22]. Pitting Corrosion process can be divided in three steps;

2.1 Incubation period

This incubation time is the time from the addition of aggressive ion until the moment of starting the destruction of the passive layer.

2.2. Pit Initiation period

This stage begins when the first hole appears after the onset of incubation time. The Cl \- will react with the metal ions on a layer of film then dissolved in the media.

2.3 Pit Propagation period

Pits that occur will continue to take place. At the beginning, destroying the passive layer that protects the metal surface and pits continue to occur faster on metal base. Many type of material are used in nuclear reactor depend on function and environment. AlMg2 as material cladding has to keep its integrity in order to operate the reactor safely. RSG – GAS coolant system consist to primary and secondary coolant. Demineralized water is produced by demineralized production system that has requirement as noted in Table 1. The specification of the primary coolant is shown in Table 1.
Table 1. RSG-GAS demineralized water specification [9]

|               |          |
|---------------|----------|
| pH            | 6.5 – 7.5|
| Conductivity (max) | 2 μS/cm  |
| Chloride ion (max)    | 0.0094 ppm|
| Copper ion (max)       | 0.0056 ppm|

The conductivity, chloride ion and Copper ion in reactor coolant are very small. Chloride ion as an aggressive ion in small concentration can cause the pitting corrosion. Pitting is a localized form of corrosive attack. Pitting corrosion is typified by the formation of holes or pits on the metal surface.

3. Methodology

The experiment was conducted in several steps i.e.:

3.1 Specimen preparation.
AlMg₂ was used as specimen in this experiment. The specimen dimension, is 10 mm in length, 10 mm in width and 5 mm in thickness. The specimen surface was polished with polished paper from grade 400, 600, 800 and 1000 and then polished with Metadi II diamond paste.

3.2 Electrochemical Measurements

The polarisation curves were recorded by changing the electrode potential automatically with a potentiostate, type e-corder 410 manufactured by eDAQ. Anodic polarization was obtained by a potential scanning from –500 mV at an open circuit potential (OCP) to 600 mV OCP at a rate of 0.2 mV/sec. A Silver/Silver chloride (Ag/AgCl) and Pt wire were used as reference electrode and a counter electrode, respectively. For each condition, temperature was changed to simulate the corrosion testing. Corrosion testing was conducted in various temperatures and various NaCl concentrations. The demineralized water with pH 6.7 and conductivity 0.4 μS/cm was used in the experiment. Corrosion testing was conducted in various temperatures (28, 35, 40 and 45 °C) in 0.005, 0.010, 0.015, 0.020, 0.025, 0.030 and 0.035 ppm of sodium chloride concentrations.

3.3. Data Analysis

Corrosion current that find from the corrosion experiment was analyzed by using Tafel analysis to get corrosion rate.

4. Result and Discussion

4.1 The Effect of the NaCl Concentration

Table 2. AlMg₂ corrosion rate at several temperatures (°C) and NaCl concentration (ppm)

| Temperature (°C) | Corrosion rate (mpy) in NaCl Concentration |
|-----------------|------------------------------------------|
|                 | 40 ppm | 50 ppm |
| 28              | 8.74 x10⁻³ | 2.17 x10⁻³ |
| 35              | 8.90 x10⁻³ | 3.34 x10⁻³ |
| 40              | 1.11 x10⁻³ | 4.03 x10⁻³ |
| 45              | 1.78 x10⁻³ | 5.41 x10⁻³ |
| 50              | 6.34 x10⁻³ | 8.17 x10⁻³ |
The effect of the aggressive ion concentration, on pitting corrosion was studied by Potentiostate measurement in NaCl solution. The results are shown in Figure 1 and Table 2. The corrosion rate was function of the chloride ion concentration, the higher the NaCl concentration generated the higher corrosion rate. The corrosion rate of AlMg2 in NaCl 0.040 ppm at 28 °C is 0.000874 ppm and corrosion rate change to 0.00382 ppm in NaCl 0.050 ppm at the same temperature 28 (°C). At the figure 1, we can see that in 0.040 ppm NaCl corrosion rate increased sharply at temperature 45 °C but in 0.045 ppm NaCl corrosion rate increased sharply at temperature 40 °C. It means that the higher aggressive ion concentration increased the corrosion rate and faster the pitting corrosion occurs. Chloride ion concentration determined the time of pitting corrosion initiation. Higher chloride ion concentration resulted the higher possibility for chloride absorption at surface material, it will make the shorten time for pitting corrosion growth.

4.2. The temperature effect on AlMg2 pitting corrosion

Almost all the chemistry reaction rate will increase with temperature increase. Higher temperatures increase the corrosion rate by accelerating the diffusion of oxygen. In open vessel, where the oxygen free to escape, the corrosion rate increases with temperature up to 80 °C. Then, as the temperature is increased further, the corrosion rate decrease. This is due to a drop in the oxygen solubility of water above 80 °C. In closed system, oxygen cannot escape, and the corrosion rate increase with temperature until all of the oxygen is consumed.
Table 3. AlMg₂ corrosion rate in NaCl concentration (ppm) at several temperatures (°C)

| NaCl (ppm) | Temperature (°C) / Corrosion rate (mpy) |
|------------|-----------------------------------------|
|            | 8 (°C)  | 5 (°C) | 0 (°C) |
| 0.005      | 2.08 x 10⁻⁶ | 3.09 x 10⁻⁴ | 1.83 x 10⁻³ |
| 0.010      | 2.61 x 10⁻⁶ | 3.14 x 10⁻⁴ | 1.89 x 10⁻³ |
| 0.015      | 2.70 x 10⁻⁶ | 3.15 x 10⁻⁴ | 2.54 x 10⁻³ |
| 0.020      | 4.59 x 10⁻⁶ | 5.34 x 10⁻⁴ | 3.36 x 10⁻³ |
| 0.025      | 6.63 x 10⁻⁶ | 7.30 x 10⁻⁴ | 3.82 x 10⁻³ |
| 0.030      | 1.14 x 10⁻⁴ | 8.47 x 10⁻⁴ | 4.11 x 10⁻³ |
| 0.035      | 2.06 x 10⁻⁴ | 8.51 x 10⁻⁴ | 4.31 x 10⁻³ |
| 0.040      | 8.74 x 10⁻⁴ | 1.23 x 10⁻³ | 6.34 x 10⁻³ |
| 0.045      | 2.17 x 10⁻¹ | 1.78 x 10⁻³ | 8.17 x 10⁻³ |
| 0.050      | 3.82 x 10⁻¹ | 5.41 x 10⁻³ | 9.83 x 10⁻³ |

Figure 2. AlMg₂ pitting corrosion rate at various NaCl concentration and temperatures

When a specimen was exposed at 50 °C, in 0.005 ppm aggressive ion, the corrosion rate is 0.00183 mpy and increased to 0.00189 ppm in 0.010 ppm NaCl, and corrosion rate tend to increase significantly. At 0.035 ppm concentration NaCl, the measured value of corrosion rates were increased so sharply. The corrosion rate was function of the chloride ion concentration, the higher the
concentration the higher corrosion rate and faster for pitting corrosion to occur. The highest AlMg₂ pitting corrosion occurs at temperature 50°C in 0.050 ppm NaCl, namely 9.83 x 10⁻³ mpy.

According to Competitive Ion Adsorption theory by Uhlig [23], when chloride is added to solution will occur competition between chloride and oxygen to be absorbed at material surface. If the oxygen to absorb at material surface, it will form passivity, if the chloride to be absorbed passivity will not be formed. According to Complex Ion Formation theory by T. Hoar [24], chloride ion at material surface will form complexes containing chloride ion which are more soluble than complexes formed in absence of chloride ion [16]. According to the following reaction [1]

\[
\text{Al} + n\text{Cl}^- \rightarrow \text{AlCl}_n^{(n-1)-} + 3e^-
\]

The formed complexes will be diluted into solution and make the material surface open to solution causes thinning of passive layer and pitting corrosion. Pitting corrosion is an anodic electrochemical process which it depend on surface excess of chloride ions, which, in turn, is determined by the bulk the chloride ion concentration through transport, adsorption chemical reaction. Leckie [25] states that the presence of neutral and acid salts in water tends to increase the corrosion rate of iron, steel and low alloy steel by influencing anodic polarization, the conductivity of the solution, the diffusion and solubility of oxygen, and the solubility of the corrosion products.

5. Conclusion
In this study the pitting corrosion of AlMg₂ was investigated in NaCl solutions at various temperature. The results obtained indicate significant role of the chloride concentration on the pitting corrosion of AlMg₂. The following conclusion can be drawn: during the anodic potentiodynamic polarization, specimens show pitting corrosion behaviour in solutions containing chloride ions. The result of experiment shows that the highest AlMg₂ pitting corrosion rate occur in NaCl 0.050 ppm solution at temperature 50°C, namely 9.83 x 10⁻³ mpy. Increasing the NaCl concentration tend to increased the pitting corrosion. Increasing the media temperature also increased the pitting corrosion even though it is not so significant. Ion chloride concentration has been controlled in tightly to ensure the reactor safety.

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