Improving Efficiency of Aluminium Sacrificial Anode Using Cold Work Process

Y. P. Asmara¹, J. P. Siregar¹, C. Tezara², Chang Tai Ann
¹Faculty of Mechanical Engineering, Universiti Malaysia Pahang
26600 Pekan, Pahang, Malaysia
²Department of Mechanical Engineering, Faculty of Science, Technology, Engineering and Mathematics, INTI International University
71800 Nilai, Negeri Sembilan, Malaysia

Email: ¹YPanca@ump.edu.my

Abstract. Aluminium is one of the preferred materials to be used as sacrificial anode for carbon steel protection. The efficiency of these can be low due to the formation of oxide layer which passivate the anodes. Currently, to improve its efficiency, there are efforts using a new technique called surface modifications. The objective of this research is to study corrosion mechanism of aluminium sacrificial anode which has been processed by cold work. The cold works are applied by reducing the thickness of aluminium sacrificial anodes at 20% and 40% of thickness reduction. The cathodic protection experiments were performed by immersion of aluminium connected to carbon steel cylinder in 3% NaCl solutions. Visual inspections using SEM had been conducted during the experiments and corrosion rate data were taken in every week for 8 weeks of immersion time. Corrosion rate data were measured using weight loss and linear polarization technique (LPR). From the results, it is observed that cold worked aluminium sacrificial anode have a better corrosion performance. It shows higher corrosion rate and lower corrosion potential. The anodes also provided a long functional for sacrificial anode before it stop working. From SEM investigation, it is shown that cold works have changed the microstructure of anodes which is suspected in increasing corrosion rate and cause de-passivate of the surface anodes.

Keywords: Aluminium anode, cold works, corrosion resistance.

1. Introduction
Aluminium has considerably selected for a sacrificial anode in oil and gas industries due to its large electrochemical equivalent, good thermal and electrical conductivity, low density and weight, availability, high current capacity, and reasonable cost [1]. Moreover, aluminium are also adaptable to variety of corrosive environment such as seawater, blackish waters and marine muds. However, due to its tendency to form oxide layer on its surface, the protection efficiency can be low [2]. The formation of film formation on the anode surface will increase polarization resistance and reduce corrosion reaction of the anode [3, 4]. Currently, aluminium anodes used in cathodic protection are ternary or higher alloy systems. The following elements is designed to lower the anode potential by 0.1 to 0.3 Volts and improve the performance characteristics when added in concentrations of up to 10 wt. %. [5, 6] These alloying elements are termed modifiers; for instance zinc, magnesium, cadmium or barium [7]. The other alloying element such as indium, mercury, tin will further decrease the anode potential by 0.3 to 0.9 Volts, and further improve the performance characteristics when added in concentration of less than 0.5%. These alloying elements are termed de-passivators [8]. Apart from the mechanism by which the modifiers and depassivators improve the anode performance, it is also important to understand their distribution throughout the anode and the relevance it has on the anode performance. To improve its efficiency some efforts have been done by researchers. One of the methods to increase anode efficiency is by applying cold works [9]. Cold work increases the galvanic site in the
microstructure of material. This changes cause possibility of acceleration of corrosion rate to eliminate the oxide film formation [9].

2. Methodology

2.1 Sample Fabrication
The samples were cold worked by using hydraulic press machine into different percentages of height reduction: 0%, 20% and 40%. The illustration of height reduction is shown in Figure 1. Each height reduction samples are prepared by 12 pieces of aluminium. Data were collected from three samples per week in each percentage of height reduction.

2.2 Performance Measurements
Cathodic protection was stimulated in sacrificial anode experiment. Experiment was conducted by immersed the 36 pairs of aluminium sacrificial anode and steel bar in the solution for four weeks. Aluminium sacrificial anodes were taken out every week to cleaned and weighed for weight loss measurement. Corrosion potential was recorded twice per week to measure electrochemical performance and corrosion rate. Visual inspection weight loss measurement.

2.3 Corrosion Rate
To measurement corrosion rate, potentiostat was used to obtain the electrical potential data and polarization resistance to calculate corrosion rate. Electrical potential is one of the measurements to measure how active of the aluminium samples in the corrosion as known as corrosion potential. The software WonATech is applied to collect the corrosion potential and polarization graph.

3. Results and discussion

3.1 Visual Inspections
As can be seen in Figure 2, in first week, bubbles were appeared around the three of 0%, 20%, and 40% cold worked aluminium anode. Figure 2 shows that the 40% cold worked aluminium anode has been observed that produced most bubbles around anode among three type of cold worked anode, follows by 20% cold worked anode whereas the 0% cold worked anode produce the least bubbles. In second week, the bubbles produced had increased within three types of cold working samples. In the week three, brownish color started to appear around the cathode/mild steel bar due to the steel bar had been corroded and dissolved into the solution. There are three samples from 0% cold work and one sample from 20% cold work had found corroded. While 40% cold work sample had found no sample corrode. For the bubbles, 40% cold worked produced the largest bubbles among the three.
In third week, the solution from 0% and 20% cold work had turned into brownish color due to the increases of steel bar samples that dissolved into solution. Whereas for the 40% cold working samples, the solution have turned into slightly brownish however the overall steel bar samples are found protected and no dissolving. In fourth week, the solution from 0% and 20% cold work had turn completely into brownish solution. All steel bar samples that connected with 0% cold work had corroded and dissolved into solution in the fourth week. Besides that, the steel bars from 20% cold working dissolved into solution as well but some were still being protected by anodes. Bubbles had become lesser from 0% and 20% cold working samples. For the 40% cold work samples, the conditions remain the same as previous.

| Week | Cold work (%) |
|------|---------------|
| 0    | 20            | 40            |

![Figure 2: Visual investigation of anodes samples during protections.](image)

The bubbles produced are the emission of hydrogen gas when aluminum reacted with water/solution. The reaction that occurs as follow [2]:

$$\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \frac{3}{2}\text{H}_2$$  \hspace{1cm} (1)

The emission of hydrogen indicated the reaction occurred on aluminium instead of steel bar. Thus, cathodic protection was performed and every anode is functioning sacrificial anode [8]. The amount of hydrogen emission indicated the rate of reaction. The more the hydrogen released, the higher the rate of reaction. Therefore, 40% cold worked aluminium had the highest rate of reaction according to its largest amount of hydrogen released. This also indicated that cold working affects the corrosion performance by increased the corrosion rate.

By comparing the period that the brownish colour started to occur (steel bar start to corrode), 0% cold working samples is the earliest, follow by 20% cold working samples while the 40% cold working samples still remain undissolved. Thus, the higher percentages of deformation toward aluminium anode had increased its functional period as sacrificial anode. The higher the deformation level, the longer the sacrificial anode will last.

### 3.2 Surface Condition

Figure 3 shows the surface condition of aluminium anode of 0%, 20%, and 40% cold work had been cleaned for comparison. By observing visually, the result stated that 40% cold worked aluminium has the finest surface condition after four week of corrosion testing. While 20% cold worked aluminium is considered as average condition but 0% cold worked aluminium is the worst condition among the
three. Therefore, the higher the deformation level, its might improve the surface condition from corrosion. Thus, improve protection performances [10].

**Figure 3:** Comparison of surface condition of different percentage cold working aluminium anodes.

### 3.3 Weight Loss

The weight loss of aluminium anode had been shown in Table 1. In first week, 0% cold worked aluminium had the highest weight loss followed by 20% cold worked and 40% cold worked aluminium has the lowest weight loss. In second week, the weight loss of 20% cold worked aluminium increased over the 0% cold worked aluminium whereas 0% cold work aluminium increases steadily and 40% increasing sharply. In third and fourth week, weight loss of 40% cold worked aluminium continue increasing and beyond the others, followed by 20% and 0% cold worked aluminium.

**Table 1:** Weight loss of different percentage cold work aluminium anodes.

| Cold Work | Sample | Week 1 | Week 2 | Week 3 | Week 4 |
|-----------|--------|--------|--------|--------|--------|
| 0%        | 1      | 0.045  | 0.086  | 0.085  | 0.081  |
|           | 2      | 0.033  | 0.051  | 0.041  | 0.152  |
|           | 3      | 0.048  | 0.081  | 0.118  | 0.069  |
| Average:  |        | 0.042  | 0.073  | 0.081  | 0.101  |
| 20%       | 1      | 0.030  | 0.082  | 0.123  | 0.118  |
|           | 2      | 0.040  | 0.104  | 0.069  | 0.131  |
|           | 3      | 0.039  | 0.070  | 0.077  | 0.123  |
| Average:  |        | 0.036  | 0.085  | 0.090  | 0.124  |
| 40%       | 1      | 0.011  | 0.057  | 0.107  | 0.129  |
|           | 2      | 0.017  | 0.080  | 0.102  | 0.117  |
|           | 3      | 0.016  | 0.073  | 0.098  | 0.151  |
| Average:  |        | 0.015  | 0.070  | 0.102  | 0.132  |

### 3.4 Corrosion Rate

The result of linear polarisation resistance (LPR) for different deformation of aluminium anodes had been recorded in Figure 4. From the graph, the overall corrosion rates decreased during the test. The 0% cold work had the lowest corrosion throughout experiment. The corrosion rate of 20% cold work was highest at the beginning but it decreased sharply after third week. The average corrosion rate of 40% cold worked considered to be the highest compare to the others. This result is corresponding to the result of hydrogen emission in previous which higher percentages of cold working increase the rate of corrosion [11]. Therefore, the corrosion rate can be stated directly proportional to the deformation level of aluminium anodes.
Figure 4: Corrosion rate of different percentage cold worked aluminium anodes.

Table 2: Potential corrosion ($E_{\text{corr}}$) at different percentage cold work at third week.

| Cold Work (%) | $E_{\text{corr}}$ (mV) | Al      | Fe      | Fe-Al   |
|---------------|------------------------|---------|---------|---------|
| 0%            | 0%                     | -430    | -510    | -600    |
| 20%           | 20%                    | -800    | -600    | -650    |
| 40%           | 40%                    | -750    | -470    | -690    |

From Table 2 it is noted that there was no longer providing cathodic protection for 0% of cold work. At that samples, the corrosion potential of aluminium is higher than the steel bar. The lower corrosion potential of steel bar will tend to corrode instead of aluminium. Thus, it also explained the situation of brownish solution occur where the steel bars were dissolved as happened in Figure 3. In Table 2, the corrosion potential for 20% and 40% cold worked aluminium anodes are lower than the steel bar cathode. Thus, the cold worked aluminium had providing cathodic protection for a longer period before it corrosion potential higher than cathode. The largest different corrosion potential had occurred at 40% cold work which strongly can be reacted with the highest protection efficiency.

4. Conclusion
From the result of visual inspection, corrosion rate measurements and corrosion potential recorded, it has been proven that higher cold work will improve corrosion protection efficiency. The aluminium anodes with the cold working up to 40% have worked longer period before steel bar dissolved. The activities of aluminum anodes in protecting carbon steel can be shown by number of hydrogen bubbles produced. The higher percentages of cold working on aluminium might increase its corrosion rate by releasing more hydrogen gas.

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6. References
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