

AMM016

Effect of Stress on Electrochemical Property of High Pressure Die Cast Aluminum Alloy in Corrosive Environment

Osamu Kuwazuru^{1,*}, Kazuhiro Ode², Wenli Liu², and Kiwamu Watanabe³

¹ Department of Nuclear Power & Energy Safety Engineering, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan

² Graduate Student, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan

³ Former Graduate Student, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan

* Corresponding Author: kuwa@u-fukui.ac.jp, Phone +81-776-27-2798, Fax +81-776-27-9728

Abstract

The effect of stress on the electrochemical property of high pressure die cast aluminum alloy in sodium chloride solution at room temperature. Since the electrochemical property is affected by the metallographic structure of specimen surface, we investigated two types of specimens, that is, the casting skin and the polished surface. The electrochemical property was evaluated by the polarization curve. When the stress is applied, the passive film is damaged by the local stress concentration around grain boundaries even in the elastic region. Due to the damage of passive film, the polarization curve varies. The polarization curve was measured under the constant tensile stress applied. The stress was increased stepwise and the variation of polarization curve was examined. We found that the spontaneous potential was lower on the polished surface than on the casting skin. In other words, the corrosion resistance of the polished surface was lower than that of the casting skin. For the numerical simulation of corrosion electrostatic field, the empirical formula of polarization curve considering the effect of stress was proposed based on the experimental results.

Keywords: Corrosion, Electrochemistry, Polarization, Die Cast Aluminum Alloy, Passive Film.

1. Introduction

High pressure die cast aluminum alloy has been widely used in the automobile industries. Its advantage is the light weight and low manufacturing cost with near-net shaping. Moreover, the aluminum alloys inherently have a high resistance to corrosion owing to the passive film. However, once the passive film was damaged by a mechanical stress in a corrosive environment, the galvanic corrosion occurs between the damaged surface and intact passive film as an anode and a cathode, respectively. This kind of local corrosion cell is formed in microscopic scale as small as the metallographic structure level, therefore its detailed electrochemical property is hard to measure *in situ*. Since the microscopic damage is caused by the heterogeneity of the metallographic structure, the macroscopic electrochemical property also depends on the metallographic structure of the surface. There is a few studies [1-3] on the metal corrosion associated with the mechanical stress and damage, and the quantitative and detailed information is not available yet. So, first, to understand the macroscopic corrosion property with the effect of micromechanical damages, it is necessary to evaluate and summarize the macroscopic electrochemical behavior with the effect of stress. This kind of knowledge can help to quantitatively estimate the effect of stress on the corrosion in the corrosion fatigue or stress corrosion cracking.

In this study, the electrochemical property of high pressure die cast aluminum alloy is experimentally measured under a mechanical stress. To consider the effect of casting skin, two types of specimens, that is,

as-cast surface and mirror-polished surface are used. First, the electrochemical property is evaluated by the polarization curve measured under a constant stress. The stress is changed to several levels under the proof stress. Next, the continuous variation of electric potential during the tensile test until the break is measured to confirm the effect of stress on the spontaneous potential of the surfaces.

2. Experimental Method

The material used was JIS ADC12 high pressure die cast aluminum alloy. A plate of 3 mm in thickness was casted and the tensile specimen was cut from this cast plate by the wire electric discharge machining. The shape of specimen is shown in Fig. 1. One surface was polished until the thickness of 2 mm and finished as a mirror surface, and the other surface was kept as the casting skin. Leaving the white part in Fig. 1 as the corrosion window of working electrode, we coated the grey part with a nail polish. The side and back surface was also all coated. Before the coating, a lead wire and a strain gauge were attached on the backside surface. The corrosion window was set to the casting skin and the mirror-polished surface. The former and latter are called the as-cast surface specimen and the polished surface specimen, respectively. The effect of casting skin was evaluated by comparing these two types of specimen.

Sodium chloride solution of 0.1% was employed as the corrosive environment. The corrosion chamber made of acrylic plate was fixed to the lower rig of tensile test apparatus as shown in Fig. 2, the solution was slowly circulated from a sufficiently large

AMM016

reservoir tank by a pump to keep the solution condition constant. The electrochemical behavior was measured by the three-electrode method, i.e., the counter electrode and reference electrode were inserted into the chamber and the tip of Luggin capillary was located near the center of the specimen fixed by the test rigs. The platinum counter electrode and Ag|AgCl reference electrode were used. The potential difference and electric current were measured by the potentiogalvanostat VersaSTAT3.

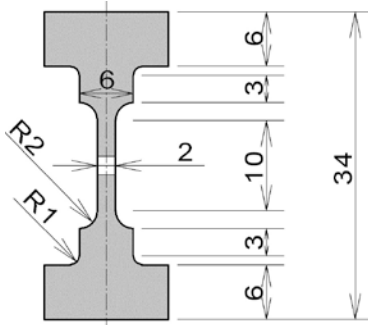


Fig. 1 Tensile specimen.

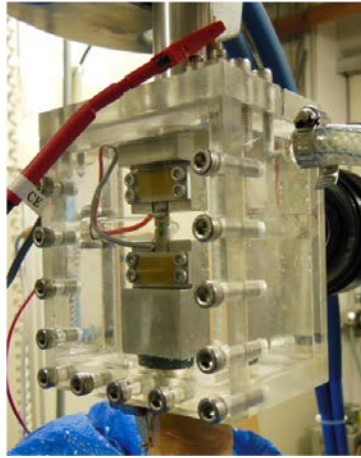


Fig. 2 Mechanical and electrochemical test apparatus.

Two types of test were conducted. The first test was the measurement of polarization curve under the constant tensile stress. The stress was set to 0, 50, 100 and 150 MPa, while the proof stress of ADC12 was 190 MPa as a result of tensile test. One stress condition was measured by one specimen, so totally eight specimens were used for the measurement of polarization curves. The sweep rate was 1 mV/s, and the range of measurement was from -1.0 to 0.0 V vs. Ag|AgCl. The measurement was started at 10 minutes after applying the tensile stress. After the tests, the polarization curves for casting skin and polished surface were respectively approximated by the least-square fitting with an empirical formula considering the effect of stress.

The second test was the measurement of natural potential during the tensile test until the specimen broke. The cross-head speed was 0.1 mm/min. The data sampling rates were 50 Hz for the stress and strain and 10 Hz for the potential and current. The continuous effect of stress on the natural potential was evaluated for the casting skin and polished surface.

3. Experimental Results

3.1 Polarization Curve under Constant Stress

Figure 3 and 4 show the polarization curves obtained from the first test of the as-cast surface specimens and the polished surface specimens, respectively. The abscissa indicates the current density in absolute and log scale, and the ordinate indicates the potential difference between the specimen and the reference electrode in normal scale. Note that the lower part of the polarization curve corresponds to a negative current density. The leftward sharp spike

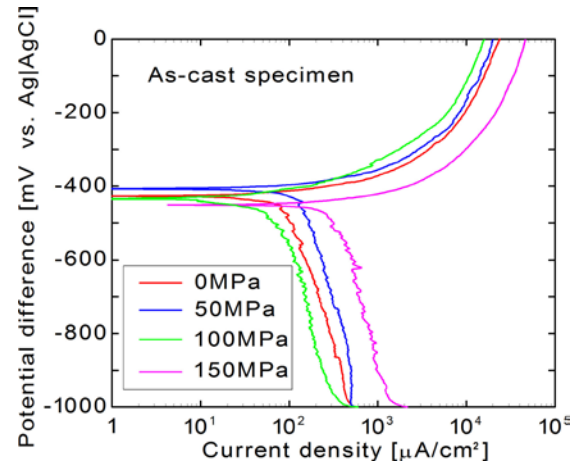


Fig. 3 Polarization curve of as-cast surface.

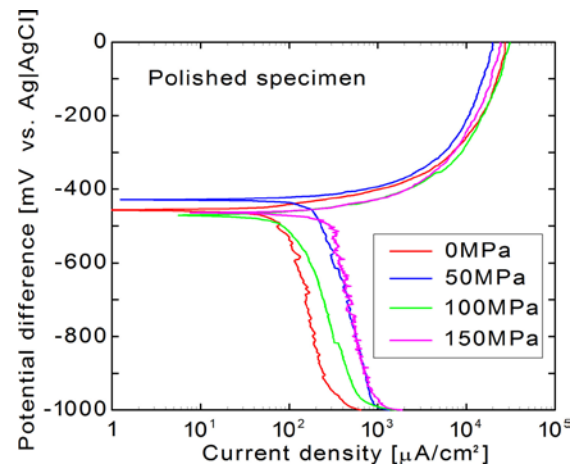


Fig. 4 Polarization curve of polished surface. means the null current density corresponding to the spontaneous potential. The spontaneous potential was changed by the applied stress. The shape of

AMM016

polarization curve and magnitude of current density are almost same between the as-cast surface and polished surface. The effect of stress also seems to be same between them.

The relationship between spontaneous potential and the applied stress is shown in Fig. 5. The straight lines indicate a linear least-square fitting. Clearly we can find that the spontaneous potential of as-cast surface is higher than that of polished surface. This means that the as-cast surface has a slightly strong resistance to corrosion under the effect of stress. That is because, the exposed silicon phases on the polished surface generated the microscopic local cells between aluminum and silicon [2], and undermined the corrosion resistance of polished surface. The tendency of spontaneous potential variation with respect to the stress is similar between the as-cast and polished surfaces, and the potential tend to decrease as the stress increases. The ionization tendency of aluminum atoms in the oxide film increases due to the elastic strain leading to the enlargement of atomic lattice spacing, therefore the corrosion resistance should be weakened. The mechanical damage of the oxide film caused by the local stress concentration around the grain boundaries also degrade the corrosion resistance of both the as-cast and polished surfaces.

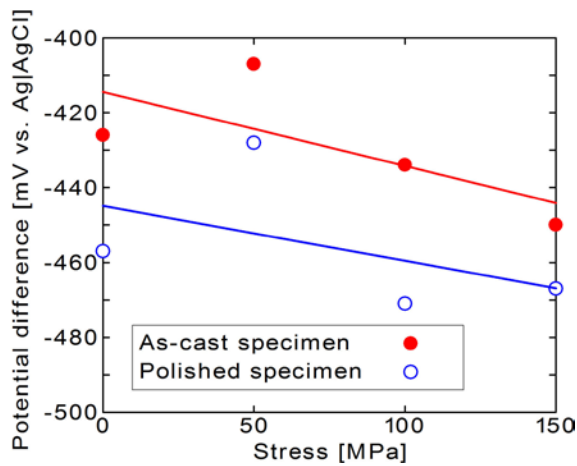


Fig. 5 Relationship between spontaneous potential and applied nominal stress.

3.2 Tensile Test

From the tensile tests, the tensile strength and breaking strain were 310 MPa and 2.5 % for the as-cast surface specimen and 262 MPa and 1.2 % for the polished surface specimen, respectively. The fracture position was out of the corrosion window and the origin of fracture was relatively large pores for the as-cast surface specimen and a chill layer for the polished surface specimen.

The variation of potential difference during the tensile test are shown in Fig. 6. The abscissa is the applied nominal stress. The potential of the as-cast

surface was higher than that of the polished surface similarly to the spontaneous potential obtained in previous section, and the difference was about 60 mV. For the as-cast surface, the potential began to decrease around 70 MPa and became constant after 150 MPa until the break. Likewise, for the polished surface specimen, the potential began to decrease around 50 MPa and became constant after 100 MPa. This decrease of potential was caused by the microscopic break of oxide film around the grain boundaries. The oxide film of polished surface was easier to break than that of as-cast surface due to the exposed silicon phases, therefore the decrease of potential of the polished surface was slightly earlier than that of the as-cast surface.

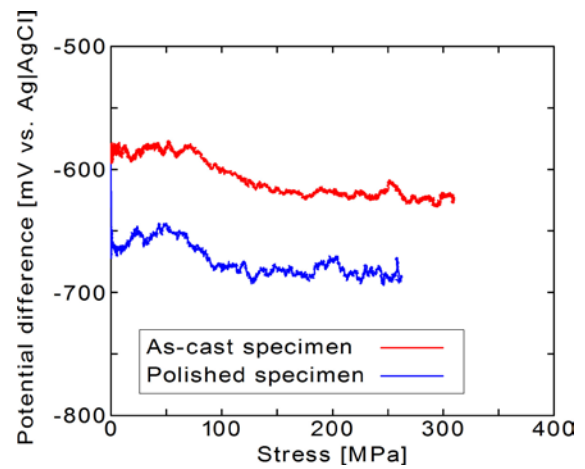


Fig. 6 Variation of potential with respect to stress.

4. Discussions

To quantitatively evaluate the corrosion speed as a result of electric field, we are planning to use the numerical simulation [4-6] such as the boundary element method. The polarization curve is required as a boundary condition of metal surface in the numerical analysis for the corrosion electrostatic field in the solution. To consider the effect of stress, the polarization curve should be formulated as a function of stress. We tried to obtain an empirical formula for polarization curve which was defined as

$$E = E_0 + R(I - I_0) + \frac{D}{1 + \exp[-(I - I_0)/B]} \quad (1)$$

where E and I were the potential difference in mV vs. Ag|AgCl and the current density in $\mu\text{A}/\text{cm}^2$, and E_0 , I_0 , R , D , B were the constants for regression. In the right-hand side of Eq. (1), the second term is the linear term corresponding to the Ohm's law, and the third term is the sigmoid function to express the electric double layer.

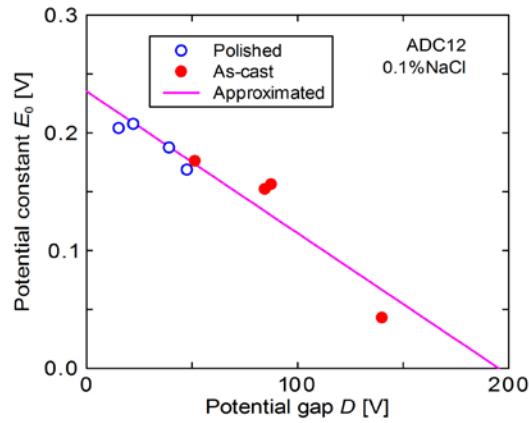
AMM016

Table 1 Constants obtained for as-cast surface

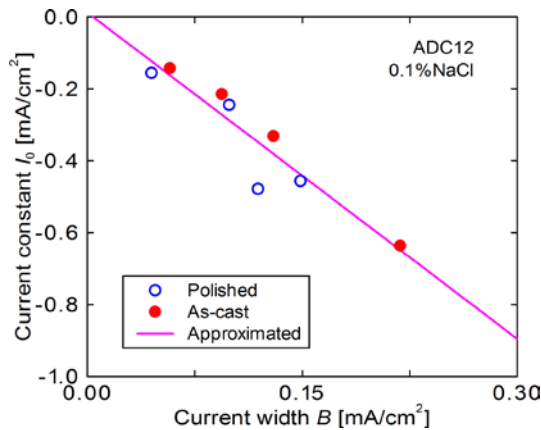
σ [MPa]	D [mV]	E_0 [mV]	B [$\mu\text{A}/\text{cm}^2$]	I_0 [$\mu\text{A}/\text{cm}^2$]	R [$\text{k}\Omega\text{cm}^2$]
0	627	-999	94	-215	0.0166
50	710	-1071	130	-332	0.0182
100	631	-996	58	-143	0.0242
150	577	-983	218	-637	0.0089

Table 2 Constants obtained for polished surface

σ [MPa]	D [mV]	E_0 [mV]	B [$\mu\text{A}/\text{cm}^2$]	I_0 [$\mu\text{A}/\text{cm}^2$]	R [$\text{k}\Omega\text{cm}^2$]
0	559	-975	45	-156	0.0144
50	571	-988	149	-456	0.0199
100	533	-962	99	-244	0.0141
150	523	-964	119	-478	0.0177



(a) Relationship between constants E_0 and D .



(b) Relationship between constants I_0 and B .

Fig. 7 Relationship between correlated constants.

By the least-square fitting, we obtained the coefficients as shown in Tables 1 and 2 for the as-cast and polished surfaces, respectively. From the correlation analysis, E_0 and D , and I_0 and B were dependent to each other, respectively, as shown in Fig. 7. Moreover, the difference between as-cast and polished surfaces was not recognized, so they were

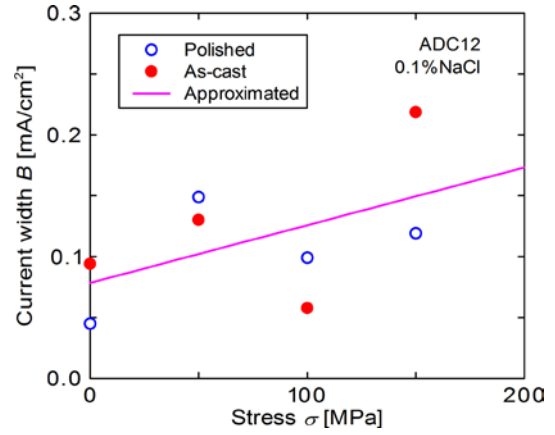


Fig. 8 Relationship between constant B and stress σ .

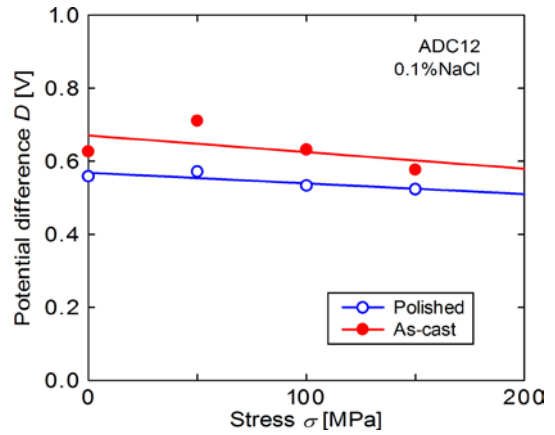


Fig. 9 Relationship between constant D and stress σ .

approximated by the linear least-square fitting for both surfaces as

$$E_0 = -676 - 0.535D, \quad (2)$$

$$I_0 = 12.2 - 3.03B. \quad (3)$$

The constant B could not be divided to the as-cast and polished surfaces as shown in Fig. 8, therefore it was also linearly approximated for both surfaces as

$$B = 78.5 - 0.474\sigma. \quad (4)$$

However, the constant D was clearly different between the as-cast and polished surfaces as shown in Fig. 9, so the constant D was individually approximated as

$$D = \begin{cases} 670 - 0.456\sigma & (\text{as-cast}) \\ 568 - 0.291\sigma & (\text{polished}) \end{cases} \quad (5)$$

The constant R was almost independent from the stress, therefore R was set to the mean value, that is, $0.0170 \text{ k}\Omega\text{cm}^2$ for the as-cast surface and $0.0165 \text{ k}\Omega\text{cm}^2$ for the polished surface. Consequently, the polarization

AMM016

curve can be determined by substituting the value of stress into Eqs. (1) to (5).

In the above formulation, the effect of stress was linearly approximated for simplicity, while the actual effect is nonlinear as shown in Fig. 9. The decrease of potential by the stress should be limited in some range within the elastic region as found in Fig. 6 obtained from the tensile tests. Moreover, a slight increase of stress was recognized in low level stress as shown in Figs. 5 and 9. Such kind of nonlinearity should be investigated in future work.

5. Concluding Remarks

The effect of stress on the electrochemical property of ADC12 high pressure die cast aluminum alloy in the corrosive environment of sodium chloride solution was experimentally investigated. The polarization curves of the as-cast and polished surfaces were measured under some levels of constant tensile stress. The variation of potential during the tensile test was also observed. The findings are summarized below.

- (1) The spontaneous potential decreased as the applied stress increased.
- (2) The polished surface had a lower spontaneous potential which meant a lower resistance to corrosion in comparison with the casting skin due to the exposed silicon phases.
- (3) The potential began to decrease at a low stress in elastic region, and became constant before reaching at the proof stress. This decrease appeared on the polished surface easier than the casting skin.
- (4) For the numerical simulation of electrostatic field for the corrosion associated with the stress variation, the formula of polarization curve

depending of the stress was proposed and their constants were determined based on the experimental results.

6. Acknowledgement

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7. References

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