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Electrochemical characteristics of Al−Mg and Al−Mg−Si alloy in sea water

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Abstract: Among Al alloys, particularly 5000 series Al−Mg and 6000 series Al−Mg−Si often used as marine materials have excellent corrosion resistance, low melting point, and thereby showing recycling availability when compared to other metals. Variety experiments were conducted to select the most suitable material for marine environments. All electrochemical experiments were conducted in natural seawater. The corrosion test was performed in many methods such as anodic/cathodic polarization and Tafel analysis using multi-channel potentio/galvanostat WMPG−1000. As results, anodic and cathodic polarization behaviors indicate the characteristics of passive state and concentration polarization by reduction reaction in dissolved oxygen, which shows excellent electrochemical behaviors. Tafel analysis results show no significant difference but 5052-O alloy of various alloy materials indicates the lowest corrosion current density. Therefore, 5052-O Al alloy presents most anti-corrosion material in marine environment.
Key words: Al alloy; ship; electrochemical characteristics; corrosion

1 Introduction

Recently, as FRP regulation is being reinforced, light-weighted Al alloy as the new eco-environmental material is getting the spotlight in the ship construction industry [1−5]. Especially, this material is widely used in fishing boat, coast-guard cutters and warship; leisure boat made of recycling materials; and high speed Wig-in-ground-effect craft which takes a category of an intermediate configuration between ship and aircraft [6]. Researches have proceeded gently to improve the corrosion resistance by heat treatment of Al alloy and addition of various ingredients to extend the life of Al alloy ship [7−9]. Still, there is a possibility that erosion and cavitation take place by corrosion and high speed under severe environment of the sea. As Al alloy is introduced as a ship material that substitutes FRP, corrosion has been prevented by continuous studies on corrosion protection of Al alloy under the marine environment. Also, it is an important task to prevent marine accident by a hole generation in the ship's hull due to a lack of knowledge on painting and corrosion protection method. Especially, the Al alloy materials should be carefully selected by considering corrosion resistance, durability, strength and weldability under the marine environment. Al alloy used as ship materials are mostly 5000 series Al−Mg and 6000 series Al−Mg−Si alloy [10]. Also, they are popular in various fields as materials to reduce environmental load. They are possible to be used for high speed purpose by its light weight due to the high specific strength compared to the steel ship [11]. Thus, in this study, the electrochemical characteristics were evaluated by selecting 5000 series Al−Mg (5052-O, 5083-O, 5083-H321, 5083-H116 and 5456-H116) used in the ship's hull that is directly touched by sea water and 6000 series Al−Mg−Si alloy(6061-T6) used in upper structure of the ship.

2 Experimental

5052-O, 5083-O, 5083-H321, 5083-H116 and 5456-H116 Al-Mg alloy maintains proper strength and has excellent corrosion resistance and molding possibility. Also, 6061-T6 Al alloy is obtained by heat treatment of 6061 alloy, which has excellent mechanical strength, corrosion resistance and molding possibility, requires light weight and high strength, so that its applicability is very high. The electrochemical experiment specimen of 1cm^2 is polished with emery

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paper 2000, washed with acetone and distilled water, and dried with dryer. Using Ag/AgCl as reference electrode and platinum electrode as counter electrode, the experiment was performed in the natural sea water solution. Experiment that measured spontaneous potential was performed for 86400 s to analyze the material's stabilizing time and corrosion characteristics under the sea water environment. Anodic and cathodic polarization experiment was performed at 2 mV scan rate in the sea water solution. It is repeated at least three times to secure the reproducibility and analyze the behavior. Also, Tafel analysis was performed by polarizing ±0.25 V based on open circuit potential to get average corrosion potential and average corrosion current density. Scanning electron microscopy (SEM) was used to compare the surface morphology of specimen to analyze corrosion degree.

3 Results and discussion

Figure 1 shows the natural potential in the sea water. 5052-O Al alloy indicates high potential at the beginning of immersion and −0.826 V to −0.77 V at approximately 10200 s. Then, it repeats some fluctuation and shows relatively stable potential of −0.807 V at the end of experiment. On the whole, fluctuation of potential are repeated, meaning that destroy and creation of protective film are repeated on the surface of specimen. Also, the potential of 5083-O Al alloy moves toward noble direction as soon as it is immersed, but potential moved toward active direction since oxidation film on the surface of specimen was destroyed by Cl^- ion in the sea water. The potential tends to increase regularly from 17000 s and reaches −0.742 V at the end of experiment. For 6061-T6 Al alloy, the potential sharply increases toward noble direction at the beginning of immersion and maintains stable potential, repeating ups and downs in a small degree within the range, from −0.704 V to −0.675 V. Potential at the end of experiment is −0.689 V, which is the noblest potential. For 5083-H321 Al alloy, potential sharply moves toward noble direction as soon as it is immersed, it shows similar tendency to other alloys. Then, the potential gradually tends to increase from 18300 s and shows −0.732 V at the end of experiment. Also, the initial potential of 5083-H116 Al alloy shows approximately −0.83 V. Then, the potential gradually increases and reaches −0.76 V at 2000 s. Within the range from −0.738 V to −0.734 V, the potential shows relatively stable. The potential range, at the end of experiment, is from −0.732 V to −0.719 V, indicating stable potential from the beginning to the end. 5456-H116 Al alloy indicates −0.81 V or more at the beginning of immersion, repeats ups and downs a little and tends to gradually increase from 13200 s. At the end of experiment, it shows −0.748 V. On the whole, 6061-T6 and 5052-O Al alloys indicate the most noble and active potential, respectively.

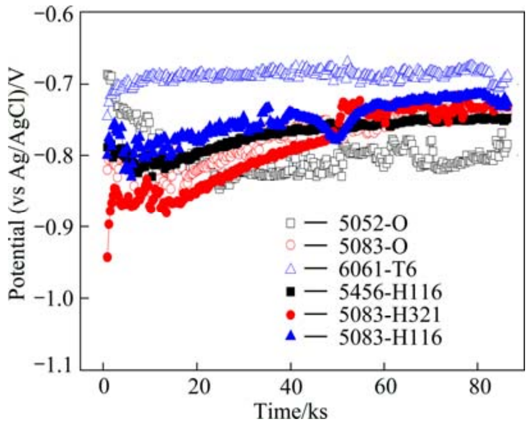

Fig. 1 Potential measurement for various Al alloys during 86400s in seawater

Figure 2 indicates the anodic polarization curve of various Al alloys in the sea water. 5052-O Al alloy indicates passive region that current density gently increases from open circuit potential, −0.8 V to −0.69 V. Above the range, current density increases sharply due to pitting caused by destroy of passive film. Thus, above the pitting potential, it is considered not only impossible to apply anodic protection method, but also weak for stress corrosion cracking in stress application. However, 5083-O Al alloy does not show clear range of passive region, unlike 5052-O alloy, and shows steady increase of current density, is not formed passive film until the end of experiment. Also, 6061-T6 Al alloys show open circuit potential of −0.783 V, and relatively low current density up to −0.663 V. Also, 6061-T6 Al alloy does not form passive film in anodic potential range, showing steady current density. 5456-H116 Al alloy indicates passive behavior from −0.87 V which is higher than the open circuit potential. Then, steady increase of current density is observed at pitting potential of −0.69 V. This range of passive region is approximately 0.18 V, showing remarkably broader than 5052-O and 6061-T6 alloys. 5083-H321 Al alloy shows relatively low current density of 1.815×10^{-6} -8.342×10^{-7} A/cm^2 corresponding to the potential of −0.82 V to −0.69 V. However, rapid increase of current density is observed above the range. Here, the range of passive region is shown as 0.13 V. 5083-H116 Al alloy indicates low current density, 4.04×10^{-8}–3.361×10^{-6}A/cm^2 up to −0.679 V as soon as it is immersed. Within this range, the current density increases very slightly. Besides, the range that shows passive behavior is 0.27 V, where passive behavior is observed the most clearly among other Al alloys. Pitting potential is −0.679 V and corrosion current density rapidly increases above the potential. As a result, anodic polarization behavior on various Al alloys is observed passive behavior. The pitting takes place due to passive film is being destroyed, and rapid increase of current density is being observed [12,13]. Also, the result that compares the range of passive region at the anodic polarization experiment among six Al alloys, 5083-H116 alloy shows the widest passive region while 5083-O shows the narrowest region. Also, the potential region of passive range is observed at the minimum of 0.11 V to the maximum of 0.27 V.

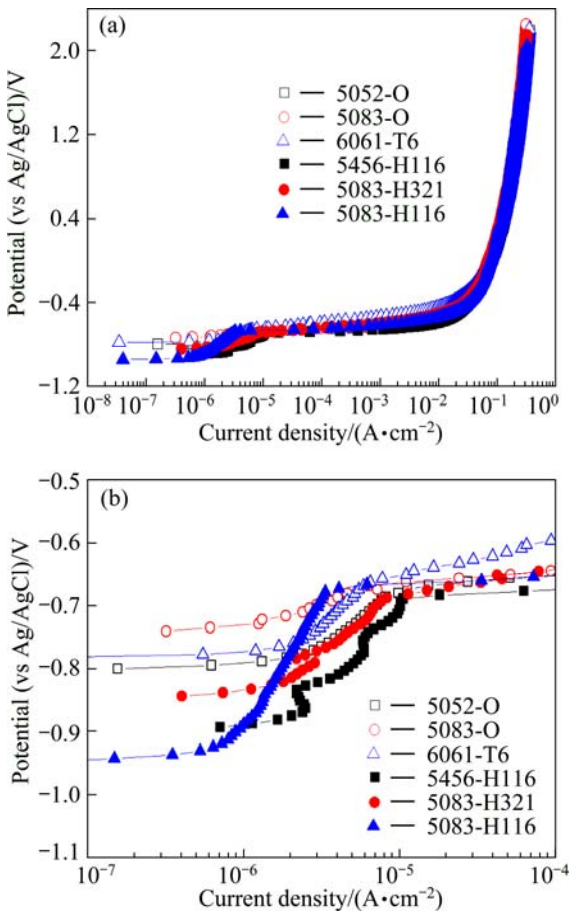

Fig. 2 Anodic polarization curves for various Al alloys in seawater

Figure 3 indicates the cathodic polarization behavior of various Al alloys. 5052-O Al alloy shows concentration polarization by dissolved oxygen reduction reaction and active polarization region by hydrogen gas generation as potential moves toward active direction [14−16]. The open circuit potential is −0.902 V, and from −0.95 V, the current density tends to be stagnant due to concentration polarization by dissolved oxygen reduction reaction. The range of concentration polarization corresponding to protection potential in cathodic polarization curve is −0.95 V to −1.43 V. Current density in this range is 5.366×10^{-6} to 7.753×10^{-5} A/cm^2, the

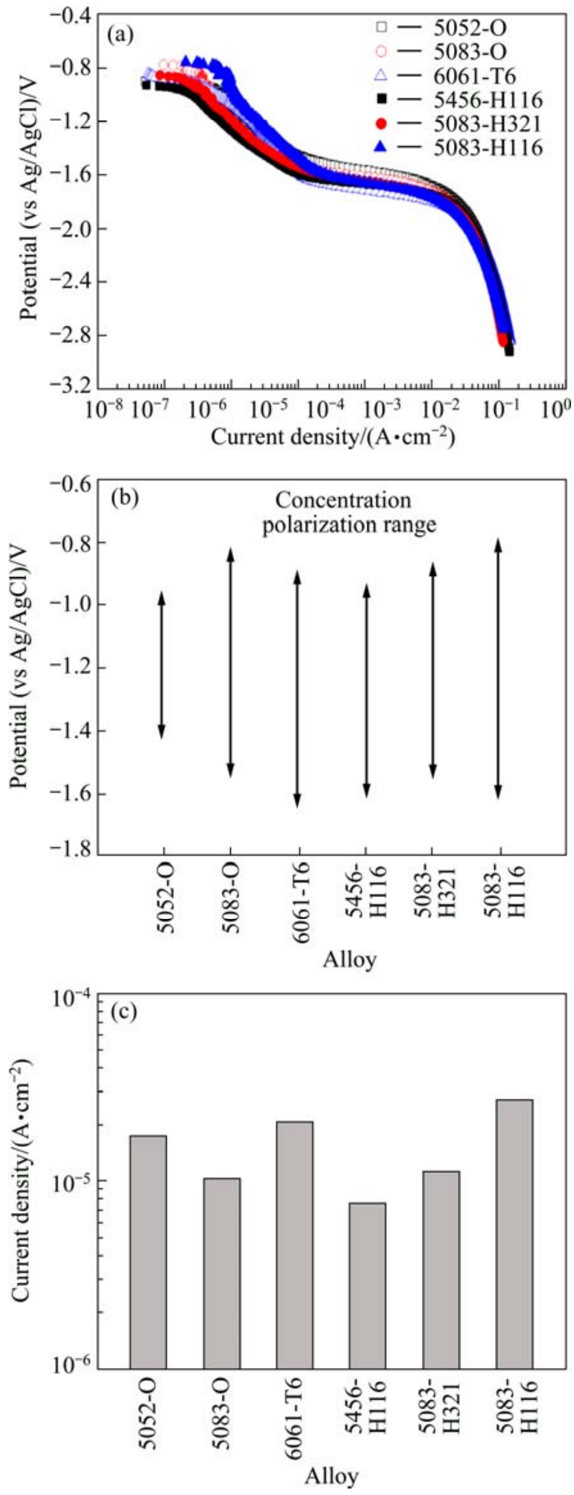

Fig. 3 Cathodic polarization curves (a, b) and comparison of current density at −1.2 V (c) for various Al alloys in sea water

passive region is observed at narrow range in the anodic polarization region. Thus, the cathodic protection method for 5052-O Al alloy is considered efficient since the current density is low and the range is wide. Also, turning point of concentration polarization and activation polarization is approximately −1.487 V, which stands for limit potential in applying cathodic protection method.

The potential range that shows concentration polarization at cathodic polarization in 5052-O alloy is −0.95 V to −1.487 V, which is approximately 0.54 V in range. For 5083-O Al alloy, cathodic polarization begins at −0.78 V (open circuit potential), the concentration and activation polarization tend to appear as potential move toward active direction after −0.804 V. Due to this concentration polarization behavior, the increase of current density is stagnated and the behavior continuously appears up to −1.551 V which is the turning point of activation polarization. The range of concentration polarization region in 5083-O alloy is from −0.804 V to −1.551 V, appearing through approximately 0.747 V in range. In 6061-T6 Al alloy, the concentration polarization takes place from −0.896 V, indicating stagnation of current density. The turning point of activation polarization is approximately −1.643 V. The range of concentration polarization is approximately 0.747 V, which is protection potential region of 6061-T6 Al alloy. For 5456-H116 Al alloy, the turning point of concentration and activation polarization appears at approximately −1.615 V where the concentration polarization range is about 0.682 V. Thereafter, the current density sharply increased. For 5083-H321 Al alloy, concentration and activation polarization are observed as the potential moves toward active direction at open circuit potential, −0.859 V. The range of concentration polarization range is about 0.71 V. The turning point between two reactions appears approximately at −1.569 V. As the potential moves toward active direction, concentration and activation polarization tend to appear from −0.783 V to −1.609 V. Here, the current density is 2.927×10^{-4} A/cm^2 and the range of concentration polarization is approximately 0.85 V. The concentration polarization range appeared in the cathodic polarization experiment for six Al alloys are compared. The result presented potential range of minimum of 0.54 V to maximum of 0.85 V. 5083-H116 Al alloy with the widest range is considered stable when applying cathodic protection method in the sea water. Also, their current densities at −1.2 V that is the concentration polarization are compared and the result indicates that 5456-H116 Al alloy has the lowest value of 7.5662×10^{-6} A/cm^2, and 5083-H116 Al alloy has the highest value of 2.7057×10^{-5}A/cm^2. Current density in the concentration polarization range presents corrosion degree when applying cathodic protection. Thus, we may assume the life of structure or ship's hull constructed with Al alloy by comparing current densities. As a result, 5456-H116 Al alloy is considered to have the lowest value of corrosion damage under the condition, excluded external environmental factor when applying cathodic protection method under natural sea water condition.

Figure 4 indicates the polarization curves of 5456-H116 Al alloy at ±0.25V in the sea water. The Tafel analysis was repeated three times to ascertain reproducibility larabic numbers in the figure denoting each experiment. In anodic polarization range, passive behavior is shown as potential increases after open circuit potential and current density sharply increase due to pitting occurred in the specific potential. In the cathodic polarization curve, however, concentration polarization by dissolved oxygen reduction reaction is observed. The average value of corrosion potential and corrosion current density are −833.1 mV and 1.2×10^{-6} A/cm^2, respectively.

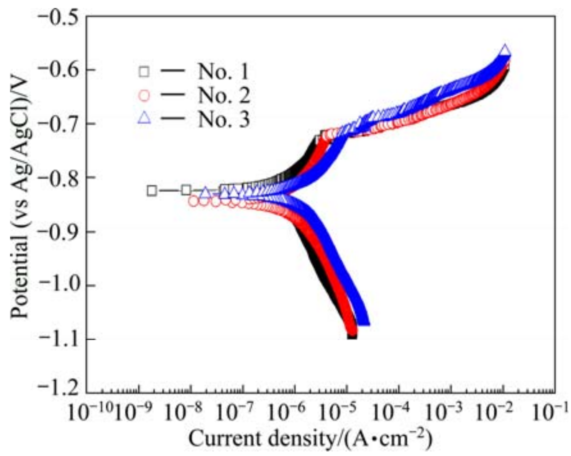

Fig. 4 Polarization curves for Tafel analysis of 5456-H116 Al alloy in sea water

The corrosion potential and corrosion current density are compared after Tafel analysis on various Al alloys as shown in Fig. 5. The analysis results of anodic and cathodic polarization behaviors indicate that 5083-H116 has the lowest potential that shows the broadest range in passive behavior and concentration polarization by dissolved oxygen reduction reaction. The specimen can be arranged in order of potential from high to low: 5083-H321, 6061-T6, 5456-H116, 5052-O and 5083-O. Thus, 5083-O specimen is considered the most stable alloy electrochemically in terms of galvanic cell formation. Since high corrosion current density means high corrosion rate, the higher value is the easier to corrode in the sea water. Thus, 5052-O alloy shows the best characteristics, indicating the lowest corrosion current density, while 5083-H321 is considered the worst one in the sea water since it shows the highest corrosion current density.

Figure 6 shows the surface of various Al alloy specimens observed by SEM after galvanostatic experiment for 3600 s in sea water. 5052-O Al alloy shows a lot of corrosion damages as current density increases. Damage in galvanostatic experiment at 1×10^{-6} A/cm^2 is found around the scratch created in polishing, but pitting is not observed. At current density of 1×10^{-5}

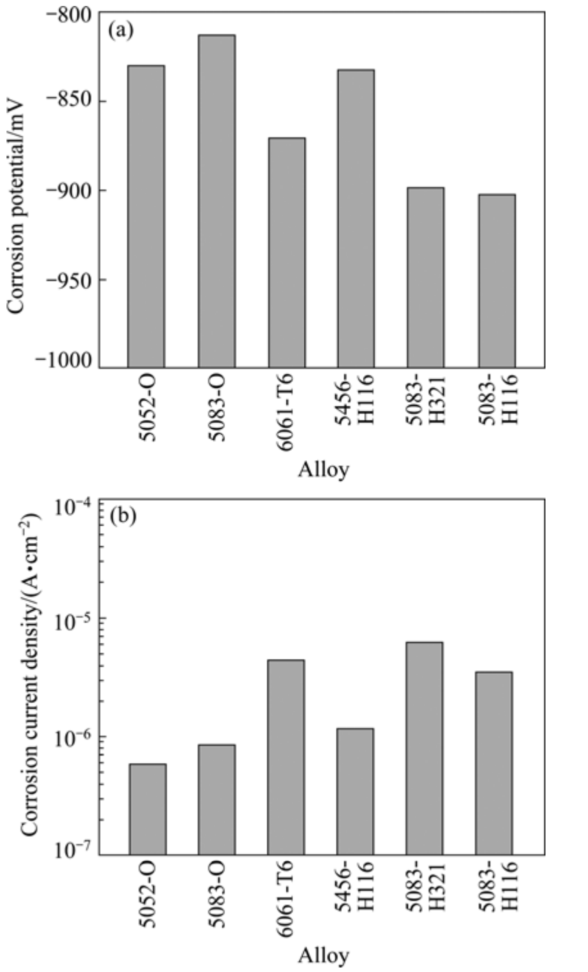

Fig. 5 Comparison of corrosion potential (a) and corrosion current density (b) after Tafel analysis for various Al alloys in sea water

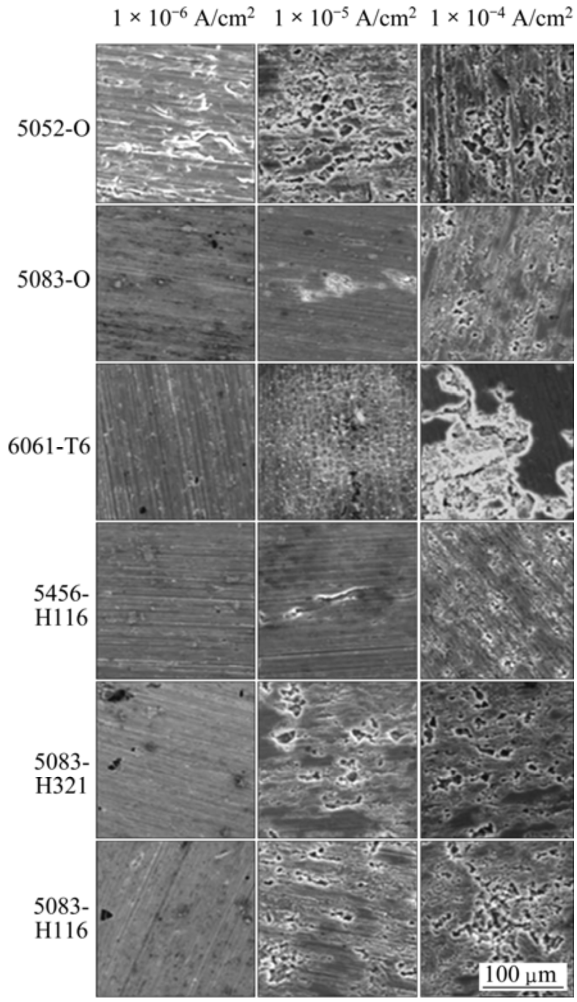

Fig. 6 Surface morphologies of various Al alloys after galvanostatic experiment

A/cm^2, pitting is generated by dissolution reaction; pitting and pitting are combined, and is corroded. However, there is no significant difference between 1×10^{-4} A/cm^2 and 1×10^{-5} A/cm^2, but the depth of pitting at 1×10^{-4} A/cm^2 increases. As a result, as current density increases, pitting is generated by active dissolution reaction at the stage of beginning, combined with each other, grow up and the depth of pitting tends to increase. In 5083-O Al alloy, only a little dissolution reaction is observed around scratch at current density of 1×10^{-6} A/cm^2 while the dissolution reaction created around the scratch gradually grows at current density of 1×10^{-5} A/cm^2. However, dissolution reaction around scratch at current density of 1×10^{-4}A/cm^2, presented mixed corrosion trend that pitting is sporadically generated. Overall, dissolution reaction generated around the scratch develops at the low current density and damage occurs while combining with pitting sporadically generated. For 6061-T6 Al alloy, a little dissolution reaction and only a bit of pitting appears at current density of 1×10^{-6}A/cm^2; both intergranular corrosion and pitting are observed at current density of 1×10^{-5} A/cm^2 at the same time; markedly deep corrosion is observed at grain boundaries at current density of 1×10^{-4} A/cm^2. For 5456-H116 Al alloy, no dissolution reaction or pitting appears at current density of 1×10^{-6} A/cm^2; a little dissolution reaction appears around the scratch at current density of 1×10^{-5} A/cm^2, showing relatively clean surface; a lot of dissolution reaction and a small pitting are observed around the scratch at current density of 1×10^{-4} A/cm^2. For 5083-H321 Al alloy, dissolution reaction does not appear but small pitting is sporadically observed at current density of 1×10^{-6} A/cm^2; pitting is generated, gradually increases in depth and width and partially a little dissolution appears around the scratch at current density of 1×10^{-5} A/cm^2; pitting mainly appears which is trends occurs seriously at current density of 1×10^{-4}A/cm^2. For 5083-H116 Al alloy, only a few pitting are observed at current density of 1×10^{-6}A/cm^2; dissolution reaction and pitting concurrently occurs around the scratch at the same time and tends to combine at current density of 1×10^{-5} A/cm^2. Also dissolution reaction and pitting concurrently occurs and tends to combine while pitting gradually grows at current density of 1×10^{-4} A/cm^2. This tendency tends to be noticeable in the grain boundary and corrosion tendency appears while pitting grows toward the depth direction. Overall, a little dissolution reaction and small pitting appear so that it is difficult to compare the corrosion level at current density of 1×10^{-6} A/cm^2. Remarkable damage is found in 5052-O and mostly similar tendency appears in other specimens. For 5000 series Al alloy, pitting is generated by dissolution reaction, corrosion is developed by combining pitting each other at current density of 1×10^{-5} A/cm^2. For 6061-T6 alloy, intergranular corrosion and pitting are observed at the same time. 5083-O and 5456-H116 Al alloys present a little damage at the highest current density of 1×10^{-4} A/cm^2, which is the current density applied for the galanostatic experiment.

4 Conclusions

1) The comparison results of corrosion characteristics by electrochemical experiment on various Al alloys in natural potential was measured. 6061-T6 Al alloy has the highest potential while 5052-O Al alloy has the lowest potential. Also, anodic polarization experiment indicated that a little difference in the passive behavior appeared on the metal surface with material.

2) The current density is sharply increased due to the generation of pitting with the increase of potential. The overall comparison of pitting and passive potential range indicated that 5083-H116 shows the highest resistance for pitting.

3) In cathodic polarization experiment, 5083-H116 Al alloy showed the most stable. Tafel analysis result indicate that 5052-O Al alloy has the lowest corrosion current density, meaning the lowest corrosion rate. Also, the result of galvanostatic experiment indicated large damage as the applied current increases.

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