Effect of Ga Content on Localized Corrosion of Al-9 mass%Mg Alloys in H₂SO₄-NaCl Solution[†]

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The effects of Ga content and aging treatment on localized corrosion characteristics of Al-9 mass%Mg alloys which contain a small amount of Ga were investigated by the measurements of polarization curves, potentiostatic corrosion tests and immersion corrosion tests. The scanning electron micrographs of precipitates of the secondary phase with aging treatment and the surface of the specimens corroded in NaCl containing 1×10^{-2} kmol/m³ H₂SO₄ solution at 303 K were also observed. The principal conclusions are as follows:

(1) The Al₃Mg₂ compounds of the secondary phase of Al-9 mass%Mg alloys aged at 453 K for 6.0 ks precipitate along the grain boundary irrespective of the specimens used. However, rodlet precipitates are observed even within the grain, and precipitate-free zones are formed along the grain boundary of the specimens aged at 453 K for 307.2 ks.

(2) The pitting potential E_{pit} of Al-9 mass%Mg alloys is shifted to a more basic potential with increasing NaCl concentration, Ga content in the alloys and aging time intervals, and thus the degradation of localized corrosion resistance were observed.

(3) The apparent anodic dissolution rates under the potentiostatic condition are enhanced with increasing Ga content in the alloys and aging time. The rates are increased in the order of super-saturated solid solution < the specimens aged at 453 K for 6.0 ks < the specimens aged at 453 K for 307.2 ks.

(4) The corrosion of super-saturated Al-9 mass%Mg alloys in H₂SO₄-NaCl solution is mainly pitting attack. However, the localized types of corrosion of the aged specimens are observed as intergranular and pitting attacks.

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I. Introduction

The Al-based alloys have various applications as industrial and lightweight structural materials by virtue of their excellent mechanical strength and corrosion resistance. The scope of their applications depends decisively upon the quality of the corrosion resistance, *i.e.* localized corrosion, especially stress corrosion cracking, pitting corrosion and intergranular corrosion. The localized corrosion at the grain boundary is greater in depth in a larger area than the corrosion rate and is therefore considered one of the most remarkable types of corrosion damage.

Meanwhile, the Al-Mg alloys as non-heat treatment type alloys have found wide applications as casting alloys. However, it has been reported that, in the alloys with Mg contents higher than 7 mass%, Al₃Mg₂ precipitation of a transition or an equilibrium phase is formed after heat treatment⁽¹⁾⁻⁽³⁾, which causes a considerable change in mechanical strength and corrosion resistance⁽⁴⁾⁻⁽¹⁰⁾.

In Japan, from the viewpoint of environmental prob-

lems and recycling of resources, the usage and production of Al-based alloys with recycled ingots and imported raw materials are being taken more and more into consideration. However, the complete removal of Ga in the recycled ingots is difficult not only technically but also economically. Further, in the imported materials a small amount of Ga is often found. This leads that an undesirable effect on mechanical properties and corrosion resistance of the alloys produced from these raw materials. At this moment, however, only a few reports are available dealing with this problem, and therefore, further investigations are necessary.

As a part of the study to determine the effect of Ga content on the corrosion resistance of Al alloys, the author and coworkers in a previous study measured the effect of Ga content on the corrosion behavior of Al-Ga solid solution alloys and Al-Mg alloy⁽¹¹⁾⁻⁽¹³⁾, as well as on the structure of the secondary phase that precipitates on heat treatment⁽¹⁴⁾⁽¹⁵⁾. They clarified that the presence of Ga seriously deteriorates the corrosion resistance and stress corrosion resistance of these alloys. In this investigation, in order to determine the effect of Ga content on the localized corrosion characteristics of Al-9 mass%Mg alloys which are used as casting alloys⁽¹⁶⁾, we measured the anodic polarization behavior of the specimens in a H₂SO₄-NaCl solution, carried out potentiostatic corrosion tests, and observed the structure and form of the corroded sur-

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faces of the aged specimens by SEM.

II. Experimental Procedure

1. Samples

For this investigation, Al-9 mass%Mg-X mass%Ga alloys, with the chemical compositions and Ga contents given in Table 1, were cast in the same manner as described in a previous paper⁽¹⁵⁾. After appropriate heat treatment and subsequent repeated treatments of cold rolling and annealing, these alloys were formed into a sheet of 1 mm thickness, out of which the specimens were cut to 20 mm × 20 mm size. The chemical composition of the specimens to be used was determined by emission spectrum analysis and atomic absorption spectrochemical analysis. The analysis showed a slight difference in Mg content by 0.3 mass% against the intended value of 9 mass%. The small amounts of impurities such as Fe, Mn and Si were confirmed. Further, the super-saturated solid solution specimens were prepared by quenching in ice water, after having been kept at a constant temperature of 703 K for 10.8 ks. The aged specimens were prepared at 453 K for a certain period of time till precipitation occurred. The two categories of precipitation treatment intervals were chosen to be 6.0 ks, as a typical example for the precipitation of secondary phase only along the grain boundary, and 307.2 ks, as an example for precipitation of the secondary phase both along the grain boundary and in the grain interior⁽¹⁵⁾.

In order to obtain the intermetallic compound Al₃Mg₂, Al of 99.99 mass% and the necessary amount of Mg were used. The Al was melted in a high-purity alumina crucible at 1023 K, and the surface of the crucible was covered with MgCl₂ flux. After addition of Mg, the compound was then melted and cast in a mold. The ingots were then homogenized at 703 K for 184.8 ks and were cut by a wire electric discharge machine to the size of 20 mm × 20 mm × 5 mm. The chemical composition was analyzed

with the atomic absorption spectrochemical analysis method. X-ray diffraction analysis was used to confirm the compound to be Al₃Mg₂. The Mg content of the prepared Al₃Mg₂ compound was 37.9 mass%, which is very close to the Mg content of 35.5 mass% in the stoichiometric compound. As impurities, small amounts of Fe and Mn were detected. In order to remove the residual stress resulting from the processing, the specimens were heat-treated at 685 K for 86.4 ks and then furnace-cooled before use.

2. Corrosion test solution

The H₂SO₄-NaCl mixed solution was used as the corrosion test solution which was made by adding an appropriate amount of NaCl to a solution of 1×10^{-2} kmol/m³ H₂SO₄.

3. Measuring methods

(1) Electrochemical measurement

The specimens used for the measurement of corrosion behavior were square wooden sheets of 20 mm × 20 mm. Prior to use, the specimens were polished with emery paper and buffed to a mirror finish, then de-greased with acetone, washed with water and alcohol and dried. Each of them was then sealed with epoxy resin except for an exposed surface of 10 mm × 10 mm which was to serve as an electrode.

The electrolytic cell for the electrochemical measurement consisted of a container of 4×10^{-4} m³ interior volume which was divided by a glass membrane into an H-shape. The cell was filled with the test solution which had been de-aerated with high purity Ar-gas and kept at constant temperature. The measurement of the polarization behavior was carried out by connecting a coulometer and a recorder to the potentiostat. As the reference electrode, an Ag/AgCl-3.3 kmol/m³ KCl electrode was used. The potential was given according to the NHE scale. All electrochemical measurements were carried out under Ar-gas flow.

(2) Potentiostatic corrosion test

The potentiostatic corrosion tests were carried out under the following standard conditions using the above-mentioned H-shaped cell.

- (i) Corrosion solution: mixture of 1×10^{-2} kmol/m³ H₂SO₄ + 5×10^{-1} kmol/m³ NaCl,
- (ii) Solution temperature: 303 K,
- (iii) Electrode surface area: 1×10^{-4} m²,
- (iv) Set potential: $E_{\text{pit}} + 0.04$ V,
- (v) Electricity: 4×10^4 C/m².

(3) Shape observation of precipitates of the secondary phase and corroded surface by a scanning electron microscope (SEM)

The micrographs of the precipitated particles of the secondary phase after aging treatment as well as the form of the corroded surface of each specimen after the corrosion test were observed by a scanning electron microscope (SEM).

Table 1 Chemical compositions of Al-9 mass%Mg-X mass%Ga alloys and Al₃Mg₂ intermetallic compound used.

Samples	Chemical composition (mass%)						
	Al	Mg	Fe	Mn	Ni	Sr	Ga
Al-9 mass%Mg alloy	bal.	8.84	0.01	0.006	—	0.001	0
Al-9 mass%Mg-0.05 mass%Ga alloy	bal.	9.30	0.01	0.007	—	0.006	0.04
Al-9 mass%Mg-0.1 mass%Ga alloy	bal.	8.97	0.01	0.009	—	0.006	0.09
Al-9 mass%Mg-0.2 mass%Ga alloy	bal.	8.78	0.01	0.008	—	0.008	0.19
Al ₃ Mg ₂ intermetallic compound	bal.	37.9	0.002	0.003	—	—	0

bal.: balance

—: not measured

III. Results and Discussion

1. Effect of Ga on the precipitation behavior and the form of the secondary phase after aging treatment

Figure 1 shows the results of the SEM observation of the precipitated form of the secondary phase in the alloys aged at 453 K. The micrograph of precipitated particles of the secondary phase differs remarkably according to different aging intervals. In the specimen with the precipitated treatment at 459 K for 6.0 ks, the precipitated particles of the secondary phase occur discontinuously along the grain boundary, the number of which, however, shows a decreasing tendency as the Ga content increases. On the contrary, in the specimens with precipitation treatment at 453 K for 307.2 ks, rodlet precipitates shorter than *ca.* 5 μm appear continuously along the grain boundary region. They were also seen within the grain interior. Around the grain boundary, a precipitate-free zone (PFZ) was observed, the width of which was narrower in the specimens containing Ga than in those without Ga.

Figure 2 shows a summarizing diagram of the effect of Ga content on the numbers of precipitates of the secondary phase along the grain boundary as well as on the width of the PFZ around the grain boundary after aging treatment. In the specimen with precipitation treatment at 453 K for 6.0 ks, the mean number of precipitates within a unit length of 10 μm in the grain boundary decreases with increasing Ga content, the precipitation of the secondary phase in the grain boundary being inhibit-

Fig. 2 Effect of Ga content on the mean number of precipitates of secondary phase to grain boundary and the mean width of P.F.Z. of Al-9 mass%Mg-X mass%Ga alloys aged at 453 K.

ed by the Ga component. In the specimens with precipitation treatment at 453 K for 307.2 ks, the precipitated particles of the secondary phase appeared not only along the grain boundary but also within the grain interior, and the PFZ was formed around the grain boundary. The mean width of the PFZ, on the contrary, became narrower with increasing Ga, and the precipitation of secondary phase in the grain interior was enhanced. Although the results of electron diffraction analysis are not shown, in the specimens aged at 453 K for 6 ks, the only precipitates which appeared were Al_3Mg_2 , regardless of

Fig. 1 Scanning electron micrographs of Al-9 mass%Mg-X mass%Ga alloys aged at 453 K for various time intervals.

the specimens, and Ga existed as a solid solution in the matrix. In the specimens treated for 307.2 ks, in addition to the Al₃Mg₂ compound, the Ga compounds such as Mg₂Ga and MgGa₂ were also confirmed⁽¹⁵⁾.

The effect of Ga on the precipitation behavior of the secondary phase of the above-mentioned Al-9 mass%Mg alloys can be summarized as follows: after a relatively short precipitation treatment of 6 ks, Ga existing as a solid solution in the matrix inhibits the diffusion of Mg into the grain boundary, thus decreasing the number of precipitated particles of the secondary phase in the grain interior. On the contrary, after a long precipitation interval of 307.2 ks, in the specimens containing Ga, the super-saturation of Mg around the grain boundary is greater than that of the specimens without Ga, and thus the precipitation of Al₃Mg₂ particles in the grain interior is enhanced, and the PFZ width becomes narrower as the Ga content in the alloys increases.

However, in consideration of the relatively low Ga concentration of less than 0.2 mass%, the proportion of the Ga compounds among the precipitates is small.

2. Effect of Ga on the anodic polarization characteristics of the specimens in H₂SO₄-NaCl solution

In order to clarify the effects of Ga and the aging treatment on the corrosion behavior of Al-9 mass% alloys, we measured the anodic polarization curves of the alloys in the H₂SO₄-NaCl solution.

Figure 3 shows typical examples of anodic polarization curves of the super-saturated alloys. The polarization behavior as expressed in the curves is almost identical in all the specimens. Starting from the rest potential, the anodic polarization shows a remarkable increase in the anodic current density, given as a log-value (I_a), near the rest potential as the potential rises, accelerating the anodic dissolution rate. In the potential range between *ca.* -0.78 to -0.54 V, the polarization occurs to a great extent. The anodic current density shows a limiting current density, and on the electrode the formation of a surface oxide film is observed. When the potential reaches a certain value, namely the pitting potential, the anodic current density increases rapidly, pits appear on the

specimen surface and pitting attack is enhanced. The pitting potential E_{pit} , however, decreases in accordance with the increase in Ga content in the alloys.

Although the anodic polarization curves of the aged samples are not shown in the figure, their behavior was similar to that of the super-saturated samples. However, with the prolongation of the aging interval, their pitting potential showed a less noble value than those of the super-saturated samples, regardless of the specimens used.

3. Effect of various factors on the pitting potential of the alloys

In order to understand the effects of various factors on localized corrosion behavior of the specimens used, we measured the pitting potential E_{pit} as the parameter for evaluation of the corrosion behavior.

Figure 4 shows the influence of NaCl concentration on the pitting potential of super-saturated specimens. In all samples, E_{pit} declines linearly with an increase in $\log(C_{NaCl})$. Compared at the same NaCl concentration, the sample containing 0.1 mass%Ga shows a less noble E_{pit} value by *ca.* 0.02 V than the sample without the Ga.

Figure 5 shows the effect of Ga on the E_{pit} of the super-

Fig. 4 Effect of NaCl concentration on the pitting potential E_{pit} of super-saturated Al-9 mass%Mg-X mass%Ga alloys in the 1×10^{-2} kmol/m³ H₂SO₄+X kmol/m³ NaCl solution at 303 K.

Fig. 3 Typical example of anodic polarization curves of super-saturated Al-9 mass%Mg-X mass%Ga alloys in the 1×10^{-2} kmol/m³ H₂SO₄+ 5×10^{-1} kmol/m³ NaCl solution at 303 K.

Fig. 5 Effect of Ga content on the pitting potential E_{pit} of super-saturated Al-9 mass%Mg-X mass%Ga alloys in the 1×10^{-2} kmol/m³ H₂SO₄+ 5×10^{-1} kmol/m³ NaCl solution at 303 K.

Fig. 6 Effect of aging treatment on the pitting potential E_{pit} of Al-9 mass% Mg-X mass% Ga alloys in the 1×10^{-2} kmol/m³ H₂SO₄ + 5×10^{-1} kmol/m³ NaCl solution at 303 K.

saturated alloy samples. The E_{pit} values shift to a less noble region as the Ga content in the alloys increases. This tendency was identical to that of the aged specimens.

Figure 6 illustrates the influence of the precipitates of the secondary phase on the pitting potential. In the specimens with Al₃Mg₂ precipitated particles of the secondary phase after the aging treatment, the values of E_{pit} shifted to a less noble region regardless of the specimens, as aging time advanced, in other words, as the amounts of the precipitates of the secondary phase increased. Thus, the localized corrosion resistance of the specimens was deteriorated as the Ga content and the amounts of the precipitated particles of the secondary phase in the alloys increased.

4. Effect of various factors on the anodic dissolution rate and on corrosion types

In order to study the influence of various factors on the anodic dissolution rate and corrosion types, we carried out immersion corrosion tests, potentiostatic dissolution tests, as well as observation of the form at the corroded surface by means of SEM.

A typical example of the anodic current density-time curves of the super-saturated samples as a result of potentiostatic corrosion tests at a constant $E_{pit} + 0.04$ V is shown in Fig. 7. The values of E_{pit} of the samples are different, and thus the values of $E_{pit} + 0.04$ V of the samples were taken as -0.56 V for the 0 mass% Ga alloy, -0.519 V for the 0.05 mass% Ga alloy, -0.526 V for the 0.1 mass% Ga alloy and -0.544 V for the 0.2 mass% Ga alloy. When the anodic polarization starting from the rest potential at the potential sweeping rate $dE/dt = 1 \times 10^{-3}$ V/s was first allowed to continue till the said potential value was reached, and the potential was then maintained at a constant value, the anodic current density-time curves obtained were divided in two stages. In the first stage, the anodic current density shows little dependence on the retention time and the values remain almost constant, which corresponds with the induction period for pit nucleation. Whereas in the second stage,

Fig. 7 Anodic current density-time curves of super-saturated Al-9 mass% Mg-X mass% Ga alloys in the 1×10^{-2} kmol/m³ H₂SO₄ + 5×10^{-1} kmol/m³ NaCl solution at 303 K under a constant potential of $E_{pit} + 0.04$ V.

the anodic current density shows a linear increase in relation to the retention time, which corresponds with the occurrence and the growth period of pitting corrosion⁽¹⁷⁾. In the super-saturated samples, the induction period of the first stage becomes shorter as the Ga concentration in the alloys increases. The slope of the linear part of the current density-time curve in the second stage is steeper when the Ga content is greater, and the anodic dissolution rates are accelerated in dependence on the Ga content. A similar tendency was observed with the aged samples.

Based on this result, we further measured the effects of various factors relating to the corrosion rate, by finding the apparent anodic dissolution rate constant γ from the grade of the linear portion of the second stage of the anodic current density-time curve diagram.

Figure 8 shows the effects of the Ga content and aging treatment on the apparent anodic dissolution rates. With

Fig. 8 Effects of Ga content and aging treatment on the apparent anodic dissolution rates of Al-9 mass% Mg-X mass% Ga alloys in the 1×10^{-2} kmol/m³ H₂SO₄ + 5×10^{-1} kmol/m³ NaCl solution at 303 K under a constant potential of $E_{pit} + 0.04$ V.

both the super-saturated specimens and the aged specimens, the anodic dissolution rates increased with the increase in Ga content of the alloys as well as to the increase in the numbers of precipitated particles of the secondary phase that occurred through aging treatment. Their influence is especially remarkable with the specimens with Ga existing as a solid solution.

We observed the form of the corroded surfaces of the specimens by SEM after the corrosion tests, in order to clarify the effects of the Ga content and the precipitated particles of the secondary phase on the corrosion form of the alloys used.

Figure 9 illustrates the results of the form observation of the corroded surface of the specimens containing 0.2 mass%Ga after the anodic dissolution tests under the given corrosion conditions of a constant potential $E_{\text{pit}} + 0.04$ V. The values of $E_{\text{pit}} + 0.04$ V are taken as -0.544 V for the super-saturated alloy sample, -0.564 V for the sample aged at 453 K for 6 ks and -0.572 V for the sample aged at 453 K for 307.2 ks. The super-satu-

rated specimens, are mainly attacked by pitting. In the aged specimens, when the secondary phase precipitated only along the grain boundary, pitting and intergranular attacks occurred discontinuously. When further precipitates appeared both along the grain boundary and in the grain interior, the obtained corrosion image indicated that both pitting corrosion and intergranular corrosion occurred simultaneously. A similar tendency was observed in the specimens without Ga.

In Fig. 10, all results of the observations of the corroded surfaces are shown, after the specimens were placed in the immersed corrosion tests under the given conditions for 172.8 ks. In the case of the super-saturated specimens, the corrosion form consisted mainly of pitting. In the specimens without Ga, a few relatively large-sized pores were observed in the surface oxide film. On the contrary, with the specimens containing 0.2 mass%Ga, numerous small-sized pores were observed. In the case of the specimens with the precipitation treatment time of 6 ks, in other words, when the precipitated particles of the

Fig. 9 Scanning electron micrographs of surface of Al-9 mass%Mg-0.2 mass%Ga alloy corroded in the 1×10^{-2} kmol/m³ H₂SO₄ + 5×10^{-1} kmol/m³ NaCl solution at 303 K under a constant potential of $E_{\text{pit}} + 0.04$ V up to 4×10^4 C/m².

Fig. 10 Scanning electron micrographs of surface of Al-9 mass%Mg-X mass%Ga alloys corroded in the 1×10^{-2} kmol/m³ H₂SO₄ + 5×10^{-1} kmol/m³ NaCl solution at 303 K for 172.8 ks.

secondary phase appeared only along the grain boundary, despite the formation of a surface oxide film on all the specimens, the corrosion profile obtained indicates that the localized types of corrosion such as pitting and intergranular corrosion also occurred. In the case of the specimens with 0.2 mass%Ga content, the numbers of small pores in the grain interior obviously increased as compared with Ga-free specimens.

Further, with the specimens aged for 307.2 ks, *i.e.*, with the precipitated particles of the secondary phase in both the grain boundary and the grain interior, a corrosion image showing a simultaneous progress of pitting and intergranular attacks was obtained irrespective of the specimens. Especially the precipitation of the secondary phase within the interior enhances localized corrosion immensely, and with the specimens containing Ga, intensive deterioration of the surface oxide film was recognized.

5. Electrochemical behavior of galvanic couple of the precipitates of the secondary phase and the matrix of the specimens

The corrosion behavior of the specimens used in this investigation, as already described, is affected by the precipitation of the Al_3Mg_2 particles of the secondary phase through aging treatment, so that the pitting and the intergranular corrosion progress at the same time and the corrosion rate is greatly accelerated. This phenomenon is thought to be caused by the electrochemical interaction of a galvanic coupling occurring between the precipitated particles of the secondary phase and the matrix. Therefore, we carried out measurements of the electrochemical behavior of the galvanic coupling. When the galvanic coupling was performed using the Al_3Mg_2 intermetallic compound and Al-9 mass%Mg-X mass%Ga alloys, the potential of the Al_3Mg_2 intermetallic compound which indicated a less noble rest potential polarized and shifted to a noble potential region, acting as an anode. At the same time, that of Al-9 mass%Mg-X mass%Ga alloys showing a noble rest potential also polarized and the potential shifted to a less noble region, with the alloy acting as a cathode. Eventually the potentials of both alloys remain at the same level after 1.8 ks.

Figure 11 shows the potential of the galvanic coupling as function of Ga content. In the same diagram, the rest potential of the Al_3Mg_2 intermetallic compound and that of Al-9 mass%Mg-X mass%Ga alloys are also given. The rest potential of the Al_3Mg_2 alloys remains constant at *ca.* -0.98 V throughout all the measurements, whereas the rest potential of Al-9 mass%Mg-X mass%Ga alloys acting as a cathode shifted to a less noble potential region as the Ga content in the alloys increases. The galvanic coupling potential decreases slightly with the increase in Ga content, but this potential is close to the level of the rest potential of the Al_3Mg_2 compound, which indicates that the corrosion reaction in this system is controlled by the cathode.

Furthermore, we measured the anodic polarization curve of the Al_3Mg_2 intermetallic compound and the

Fig. 11 Effect of Ga content on the galvanic coupling potential of Al-9 mass%Mg-X mass%Ga alloys and Al_3Mg_2 compound in the 1×10^{-2} kmol/m³ $\text{H}_2\text{SO}_4 + 5 \times 10^{-1}$ kmol/m³ NaCl solution at 303 K.

cathodic polarization curves of Al-9 mass%Mg-X mass%Ga alloys.

Figure 12 shows typical examples of the anodic polarization curve of the Al_3Mg_2 intermetallic compound and the cathodic polarization curves of Al-9 mass%Mg-X mass%Ga alloys. On the anodic polarization curve of the Al_3Mg_2 intermetallic compound, the anodic current density $\log(I_a)$ around the region of the rest potential increases markedly as the potential rises, indicating enhancement of the anodic dissolution. The cathodic polarization behavior of Al-9 mass%Mg-X mass%Ga alloys shows similar curves for both specimens. The cathodic current density $\log(I_c)$ increases as the cathodic potential rises. On the electrode, the reduction of H^+ ions to H_2 gas proceeds. However, the cathodic polarization of the samples is decreased in those containing 0.2 mass%Ga in comparison to the samples without Ga, and the $\log(I_c)$ value at the same overvoltage is higher in the latter.

Figure 13 shows a cathodic current density $\log(I_c)$ as function of Ga content in the alloys, at a constant potential of -0.9 V. In the super-saturated samples, the cathodic current density $\log(I_c)$ at the constant potential of -0.9 V increases with the increase in Ga content.

Fig. 12 Anodic and cathodic polarization curves of Al_3Mg_2 compound or Al-9 mass%Mg-X mass%Ga alloys in the 1×10^{-2} kmol/m³ $\text{H}_2\text{SO}_4 + 5 \times 10^{-1}$ kmol/m³ NaCl solution at 303 K.

Fig. 13 Effect of Ga content on the cathodic current density $\log(I_c)$ of Al-9 mass%Mg-X mass%Ga alloys in the 1×10^{-2} kmol/m³ H₂SO₄ + 5×10^{-1} kmol/m³ NaCl solution at 303 K under a constant potential of -0.9 V.

Thus, the Ga component enhances the reductive reaction of H⁺ to H₂ gas.

Based upon the measurements of the electrochemical behavior of the galvanic coupling as well as upon the results of the observation of the corroded surface by means of SEM, we examined the effect of Ga on the deterioration of the localized corrosion resistance of the specimens used. In the alloys in which particles of Al₃Mg₂ as the secondary phase precipitated after aging treatment, the anodic dissolution of Al₃Mg₂ particles along the grain boundary and in the grain interior was enhanced, due to the interaction of the galvanic coupling occurring between the precipitated particles and the matrix. Furthermore, the Ga existing as a solid solution in the matrix enhances the reduction of H⁺ to H₂ gas, and thus promoting the localized corrosion.

Also, it is considered that, in the specimen with the precipitate of the secondary phase, the inhomogeneity of the surface is intensified by the precipitated particles. The surface oxide film is covered mainly by microscopic cracks and defect points, which again contribute to the increase in the active points for pit occurrence, thus lowering the pitting potential, increasing pits, and accelerating the corrosion rate. Tuck *et al.*⁽¹⁸⁾ reported that, in the case of corrosion of Al-Mg-Zn-Cu alloys in an acidic solution containing NaCl, the pitting occurred around the grain boundary where the Mg and Zn concentrations were high as well as in the region where MgZn₂ particles of the secondary phase precipitated. They further reported that the surface oxide film formed in these regions had numerous microscopic defect points that served as active points for the pit occurrence, thus causing enhancement of the pitting dissolution.

On the other hand, in the super-saturated solid solution samples, the pit-resistance deteriorates as the pitting potential falls, thus leading to the augmentation of the pit dissolution rate. The cause of this is the decrease in the protection of the surface oxide film, which contributes to continuation of activation on the sample surface,

to the lowering of the pitting potential, and to the acceleration of the pitting dissolution. In regard to this question, Carroll *et al.*⁽¹⁹⁾ conducted an interesting study in which, on the corroded surface of Al-Ga solid solution alloys, the concentration of the Ga becomes higher, as the corrosion of the Al compound advances, contributing to continuation of the activation of the sample surface. They further reported that the characteristics of the surface oxide film also changed, so that the adsorption of halogen ions became easier, which again led to the deterioration of pitting corrosion resistance.

IV. Conclusions

In order to determine the effect of Ga on the localized corrosion behavior of Al-9 mass%Mg alloys which are used as casting alloys, we carried out measurements of the anodic polarization behavior of the specimens in the H₂SO₄-NaCl solution and corrosion tests as well as observations of the form of the corroded surface by SEM.

The important results are summarized as follows:

(1) In the specimens aged at 453 K for 6.0 ks, the particles of secondary phase precipitated along the grain boundary. The numbers of precipitates diminished as the Ga content in the alloys increased. With the specimens aged for 307.2 ks, the precipitated particles of the secondary phase were observed both along the grain boundary and in the grain interior, and a PFZ was recognized. However, the width of the PFZ decreased in accordance with the increase in Ga content. In the case of the specimens containing Ga, the precipitation of the secondary phase within the grain interior was enhanced.

(2) The pitting potentials of the super-saturated solid solution specimens decreased as the concentration of NaCl and that of Ga in the alloys increased, leading to the deterioration in pitting corrosion resistance, and the pitting growth rates increased substantially with increasing Ga content.

(3) The pitting potentials of the aged alloys decreased with increasing number of the precipitated particles of the secondary phase as well as with increasing Ga content in the alloys, regardless of the specimens used, thus leading to the deterioration of localized corrosion resistance and the augmentation of the corrosion rates. The reason for augmentation of the corrosion rate after aging treatment is the electrochemical interaction of the galvanic coupling produced between the precipitated particles of the secondary phase and the matrix.

(4) In the case of galvanic coupling occurring between the Al₃Mg₂ particles of the secondary phase and the matrix, the Al₃Mg₂ with a less noble potential functions as the anode, whereas the matrix with a noble potential functions as the cathode. The corrosion reaction of the galvanic coupling is controlled by the cathode. The corrosion of super-saturated Al-9 mass%Mg alloys in H₂SO₄-NaCl solution is mainly pitting attack. However, the corrosion types of the aged specimens are observed as intergranular and pitting attacks.

REFERENCES

- (1) M. Conserra and M. Leoni: *Metall. Trans.*, **6A** (1975), 189.
- (2) C. Panseri, T. Federighi and S. Cerasara: *Trans. Metall. Soc. AIME*, **227** (1963), 1122.
- (3) H. Gordir and K. Detert: *Z. Metallk.*, **52** (1961), 321.
- (4) K. Higashi, T. Ohnishi, G. Nakatani and I. Okamura: *J. Japan Inst. Light Metals*, **30** (1980), 560.
- (5) I. Nagaoka and T. Sunano: *J. Japan Inst. Metals*, **47** (1983), 147.
- (6) H. Kanmatus, M. Okito and T. Oki: *J. Japan Inst. Light Metals*, **36** (1986), 333.
- (7) J. C. Scully: *Corrosion Sci.*, **15** (1975), 207.
- (8) K. Toma, Y. Ugai and Y. Takeuti: *J. Japan Inst. Light Metals*, **31** (1981), 157.
- (9) T. Takemoto and I. Okamoto: *J. Japan Inst. Light Metals*, **33** (1983), 315.
- (10) T. Inoue, T. Sinoda and T. Oki: *J. Japan Inst. Light Metals*, **38** (1988), 47.
- (11) T. Mae, H. Nomura, J. Ohkubo, H. Notoya and K. Arai: *J. Japan Inst. Metals*, **55** (1991), 405.
- (12) T. Mae, H. Nomura, M. Hibino, S. Sunada, S. Sanuki and K. Arai: *J. Japan Inst. Metals*, **56** (1992), 438.
- (13) H. Hibino, T. Mae, S. Toriyama, S. Sunada and K. Arai: *J. Japan Inst. Metals*, **58** (1994), 913.
- (14) T. Mae, M. Ihara, H. Iotake, S. Toriyama, S. Sunada and K. Arai: *J. Japan Inst. Metals*, **58** (1994), 1304.
- (15) T. Mae, M. Ihara, K. Komura, S. Toriyama, S. Sunada and K. Arai: *J. Japan Inst. Metals*, **60** (1996), 282.
- (16) Y. Murakami and K. Kamei: *Hitetsu-zairyou-gaku, Asakura-syoten*, (1984), p. 64.
- (17) H. J. Engel and N. D. Stolice: *Z. Phy. Chem. N.F.*, **20** (1959), 113.
- (18) H. J. Raetz-Scheibe and C. D. S. Tuck: *Corrosion Sci.*, **36** (1994), 941.
- (19) C. B. Breslin and W. M. Carroll: *Corrosion Sci.*, **33** (1992), 1902.