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Effect of Additional Fe, Ni, Mn, Si and Cu on Corrosion Resistance of Aluminium Alloy Fin Stock for Autmotive Heat Exchangers

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The effect of additional Fe, Ni, Mn, Si and Cu on corrosion rate of aluminum alloy fin stock for automotive heat exchangers has been investigated in terms of size, density and chemical composition of intermetallic compounds. In addition, the results were discussed with cathodic polarization behavior of intermetallic compounds. Corrosion rate increased with Fe and Ni addition in Al-1.0%Mn-1.5%Zn alloy, because Al_6(Mn,Fe) and/or Al-Ni-Fe compounds worked as effective cathode in the alloy. On the other hand, corrosion rate decreased with Mn addition more than 1.3% in Al-Mn-0.2%Fe-1.5%Zn alloys. This was explained that cathodic ability of Al_6(Mn,Fe) compound decreased with decreasing of Fe/Mn ratio in the compound. While, corrosion rate did not increase with Si addition in Al-1.5%Mn-0.2%Fe-1.5%Zn alloy in spite of increase of α-AlMnSi compound density, because the compounds did not work as effective cathode in the alloy. By contrast, corrosion rate drastically increased with Cu addition. This was because deposited Cu on the specimen surface during corrosion test worked as strong cathode in the alloy.

Keywords: *Sacrificial anode fin, Corrosion resistance, Cathodic polarization, Intermetallic compound, SWAAT*

1. Introduction

Recently, aluminum alloy fin stock for automotive heat exchangers become thinner without compromising corrosion and mechanical properties. To follow this trend, more corrosion resistance and higher strength is required. In this paper, the effect of additional Fe, Ni, Mn, Si and Cu which were main added element on corrosion rate of aluminum alloy fin stock were investigated by SWAAT and electrochemical measurements.

2. Experimental procedure

2.1 Specimen preparation

Fifteen alloys with various Fe, Ni, Mn, Si and Cu content were used. The chemical compositions of the alloys were listed in **Table 1**. Alloys were prepared by direct chill casting and hot rolling, then cold rolling, and intermediate annealing (633K for 3h). Finally these alloys were rolled to 0.06mm thickness at H14 temper. The sheets were heat treated at 873K for 3minute in high purity N_2 gas atmosphere simulated brazing and then cooled to 573K at the rate about 100K/minute, and air cooled with blower to room temperature, subsequently.

2.2 Corrosion test

Corrosion test were carried out by SWAAT (Sea Water Acidic Accelerated Test, 1 cycle is spray : 30min. +moistening : 90min.) according to ASTM G85 with the ASTM D1141 solution (SWAAT solution, bases: 3.5%NaCl+10mℓ/ℓCH_3COOH, pH 2.8~3), and mass loss were measured after removal corrosion product by boiling phosphoric acid and chromic acid mixed solution.

Table 1 Chemical composition of specimens (mass%)

Symbol	Mn	Fe	Si	Cu	Ni	Zn	Al
0Fe	1.03	tr.	tr.	tr.	tr.	1.47	bal.
0.1Fe	1.03	0.11	0.03	tr.	tr.	1.48	bal.
0.2Fe	1.01	0.22	0.03	tr.	tr.	1.46	bal.
0.4Fe	1.01	0.43	0.03	tr.	tr.	1.46	bal.
0.7Fe	1.00	0.75	0.04	tr.	tr.	1.46	bal.
0.2Fe-0.4Ni	1.03	0.23	0.04	tr.	0.43	1.49	bal.
0.2Fe-0.7Ni	1.03	0.23	0.05	tr.	0.76	1.51	bal.
0.5Mn-0.2Fe	0.46	0.23	0.06	tr.	tr.	1.46	bal.
1.5Mn-0.2Fe	1.51	0.22	0.06	tr.	tr.	1.49	bal.
0.06Si	1.51	0.22	0.06	tr.	tr.	1.49	bal.
0.3Si	1.47	0.21	0.31	tr.	tr.	1.46	bal.
0.5Si	1.45	0.21	0.50	tr.	tr.	1.47	bal.
1.0Si	1.56	0.21	0.95	0.01	tr.	1.53	bal.
1.0Si-0.15Cu	1.45	0.22	1.02	0.15	tr.	1.48	bal.
1.0Si-0.30Cu	1.44	0.19	0.98	0.32	tr.	1.47	bal.

2.3 Polarization measurement

Cathodic polarization measurements were carried out in aerated SWAAT solution and 3.5%NaCl solution at 313K stirring. The polarization curves were potentio-dynamically measured with a scanning rate 0.5mV/s. A saturated calomel electrode (SCE) and platinum were used for the reference electrode and counter electrode, respectively. Prior to mesurements, surface was etched alkaline degreaseing in 5%NaOH solution at 323K for 5minute, and neutralized in 30%HNO_3 solution at room temperature for 1 minute and then was washed in deionized water. In addition, α-AlMnSi ($Al_{15}Mn_3Si_2$[1]), Al_6Mn, Al-Mn-Fe compounds were prepared, and cathodic polarization characteristics were measured too, for discussed the effect of intermetallic compound on cathodic polarization characteristics of material.

2.4 Concentration analysis of intermetallic compound

To investigate the chemical composition of intermetallic compounds, the quantitative analysis were carried out on the compounds over 1 μ m of average diameter, and semi-quantitative analysis were performed by TEM-EDS on the compounds less than 1 μ m of average diameter.

3. Results and discussion

3.1 Effect of additional Fe and Ni on corrosion rate [2]

Relation between additional Fe and Ni, and corrosion rate of Al-1.0%Mn-1.5%Zn alloy were shown in **Figure 1**. Corrosion rate increased with Fe and Ni addition in the alloy. Al_6(Mn,Fe) and/or Al-Ni-Fe compounds worked as effective cathode in the alloy formed in matrix (**Figure 2**), and cathodic current density of the alloy increased (**Figure 3**).

3.2 Effect of Mn content on corrosion rate [2]

The influence of Mn content on corrosion rate of Al-Mn-0.2%Fe-1.5%Zn alloys are shown in **Figure 4**. Mn affect different from Fe. Corrosion rate decreased with increasing of Mn content in spite of increasing of Al_6(Mn,Fe) compound density as shown in **Figure 5**. It could explain that cathodic ability of Al_6(Mn,Fe) decreased with decreasing of Fe/Mn ratio in the compound (**Figure 6**), and the cathodic current density of the alloy was decreased in the alloy as shown in **Figure 7**. Effect of Fe/Mn ratio in Al_6(Mn,Fe) on the cathodic current dencity at −900mV vs SCE of the alloy which

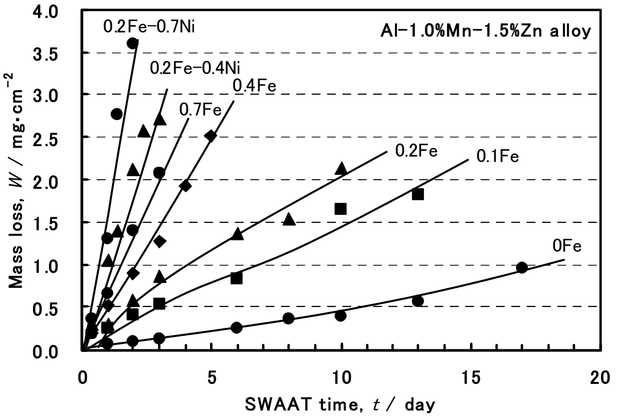

Fig.1 Effect of Fe and Ni contents on the corrosion rate in Al-1.0%Mn-1.5%Zn alloy.

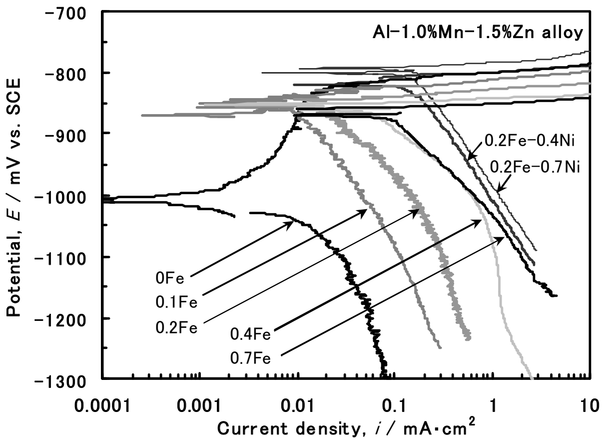

Fig.3 Effect of Fe and Ni contents on the polarization behavior of Al-1.0%Mn -1.5%Zn alloy in aerated SWAAT solution at 313K.

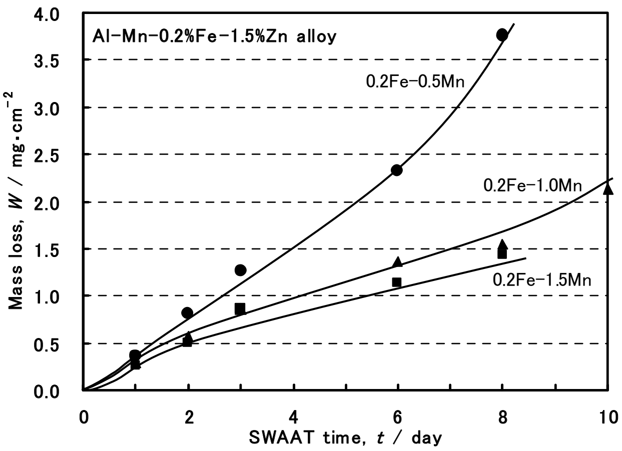

Fig.4 Effect of Mn content on corrosion rate for Al-1.0%Mn-Fe-1.5%Zn alloys.

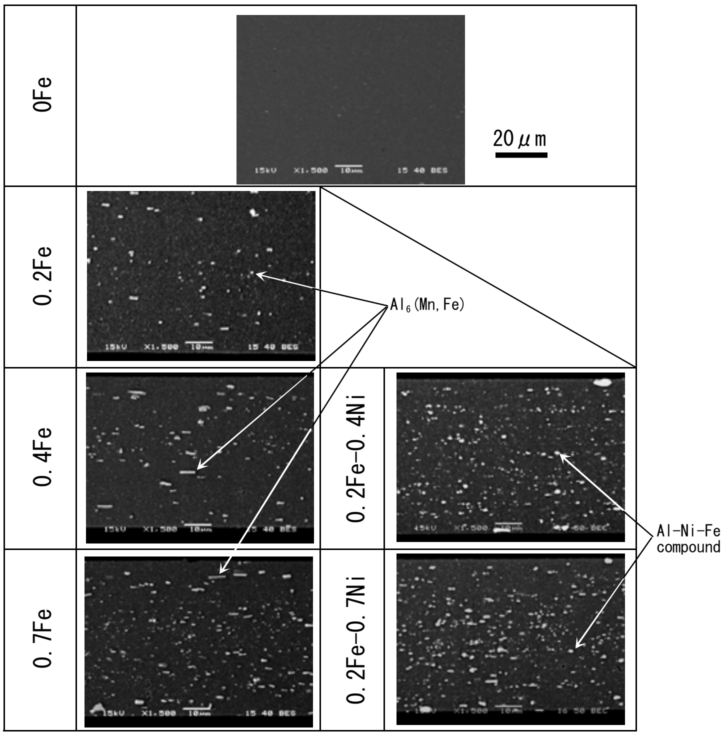

Fig.2 SEM micrograhg showing intermetallic compounds distribution by cross section in Al-1.0%Mn-Fe-Ni-1.5%Zn alloy.

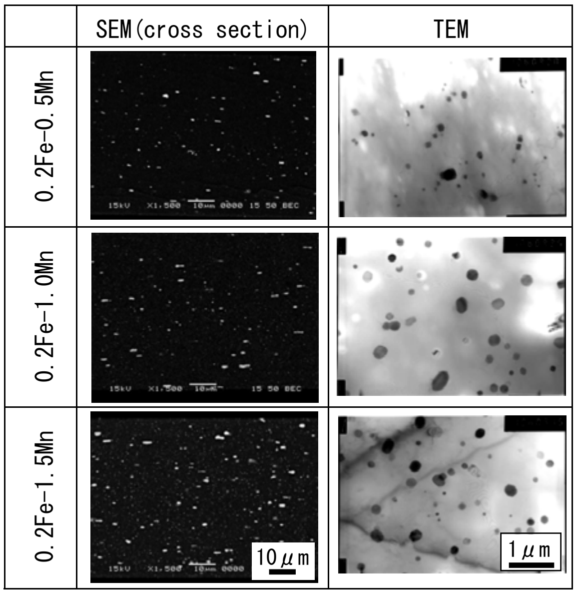

Fig.5 SEM and TEM micrographs showing size and density of intermetallic compounds in Al-Mn-0.2%Fe-1.5%Zn alloy.

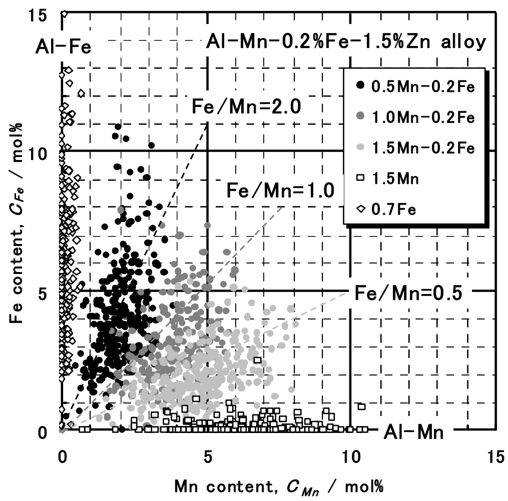

Fig.6 Effect of Mn content on the Fe/Mn raio of $Al_6(Mn,Fe)$ in Al-Mn-0.2%Fe-1.5%Zn alloy.

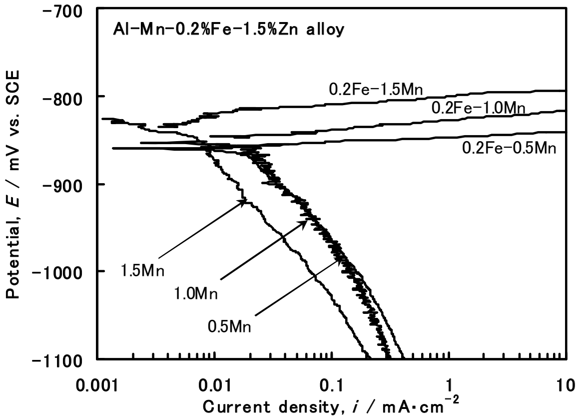

Fig.7 Effect of Mn content on the polarization behavior of Al-Mn-0.2%Fe-1.5%Zn alloy in aerated SWAAT solution at 313K.

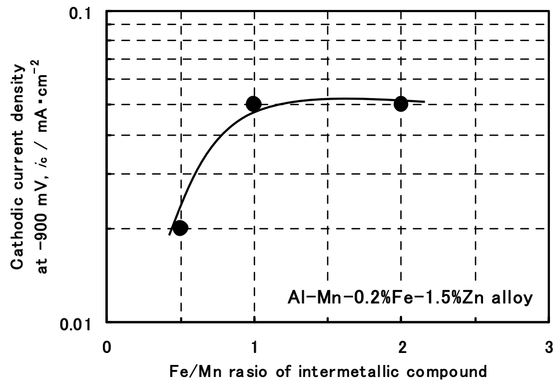

Fig.8 Cathodic current density at −900mV in aerated SWAAT solution at 313K vs. Fe/Mn ratio of $Al_6(Mn,Fe)$ for Al-Mn-0.2%Fe-1.5%Zn alloy.

corrosion potential were shown in **Figure 8**.

Cathodic current density of the alloy became small when Fe/Mn ratio in the compounds became less than 1.0 (which equals to Fe/Mn ratio of additive amount in the alloy became less than 0.15, and, this value is available by additional Mn over 1.3% in the alloy included 0.2% Fe which industrially produced aluminum contained).

3.3 Effect of Si content on corrosion rate [3]

Relation between Si content and corrosion rate of Al-1.5%Mn-0.2%Fe-1.5%Zn alloy were shown in **Figure 9**. Intermetallic compound, especially fine α-AlMnSi, density increased with Si addition (**Figure 10**), but the cathodic current density did not increase as shown in **Figure 11**. So, the cathodic polarization characteristics of α-AlMnSi were shown in **Figure 12** (for the purpose of comparison, the measurement results of Al_6Mn, it is noted that this compound did not deteriorate corrosion resistance[4], and Al-Mn-Fe compound, which conversely deteriorated corrosion resistance, were shown in this figure. The cathodic current density of Al_6Mn was small, it almost equaled to pure Al. Therefore, this compound did not work as effective cathode in the alloy. While, the cathodic current density of α-AlMnSi was slightly bigger than Al_6Mn, but this behavior was almost same to Al_6Mn.

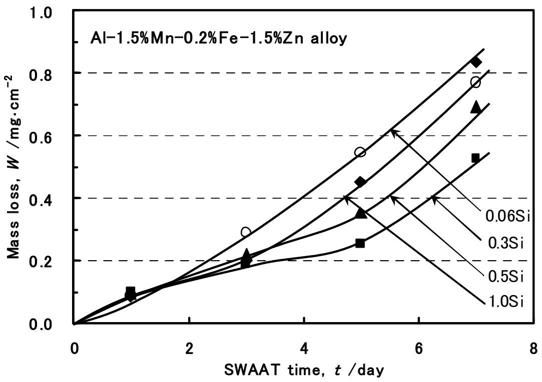

Fig.9 Effect of Si content on corrosion rate of Al-1.5%Mn-0.2%Fe-1.5%Zn alloy.

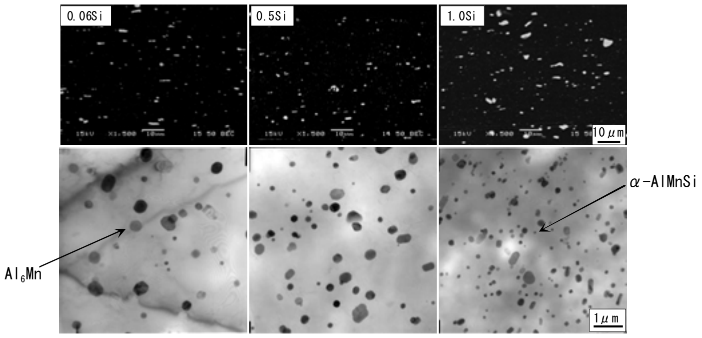

Fig.10 Micrographs showing size and density of intermetallic compounds for Al-1.5%Mn-0.2%Fe-Si-1.5%Zn alloy.

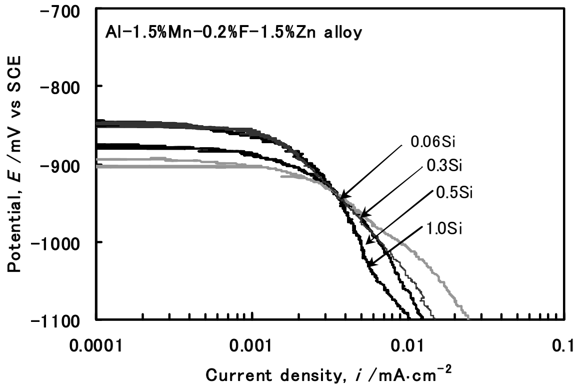

Fig.11 Effect of Si content on cathodic polarization behavior of Al-1.5%Mn-0.2%Fe-Si-1.5%Zn alloy in aerated 3.5%NaCl solution at 313K.

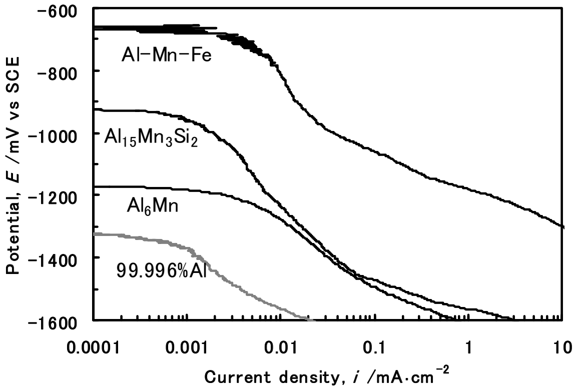

Fig.12 Cathodic polarization curves of $Al_{15}Mn_3Si_2$, Al_6Mn, and AlMnFe compounds and pure aluminum in aerated 3.5%NaCl solution at 313K.

And so it was likely that the cathodic ability of α-AlMnSi is also weak. On the other hand, the cathodic current density of Al-Mn-Fe compound included Fe was bigger than both compounds and pure Al, and so worked as effective cathode in the alloy. The reason, why the cathodic current density did not increase and corrosion rate did not increase, was that the increase of α-AlMnSi density did not contribute to cathodic current density of the alloy.

3.4 Effect of Cu content on corrosion rate [3]

The corrosion rate of Cu added alloys were shown in **Figure 13**. The corrosion rate drastically increased with Cu addition. Corrosion resistance of Cu additive alloy depends on existence condition of Cu[5]. So, microstructure of the alloy were investigated, the compounds included Cu was not observed in the alloy. Therefore, Cu contributed to corrosion resistance as solid solution. The cathodic polarization behavior of Cu additive alloy was shown in **Figure 14**. The cathodic current density did not increase that much with additional Cu. This result did not correspond to the result of corrosion test.

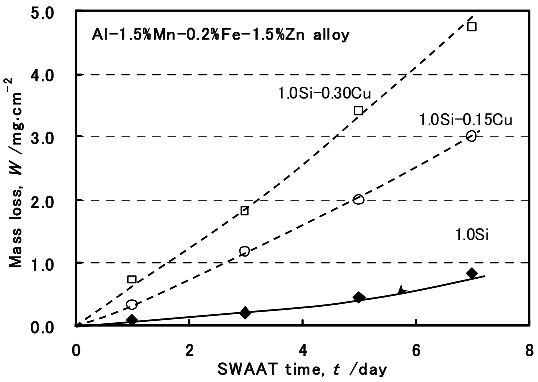

Fig.13 Effect of Cu content on corrosion rate of Al-1.5%Mn-0.2%Fe-1.0%Si-1.5%Zn alloy.

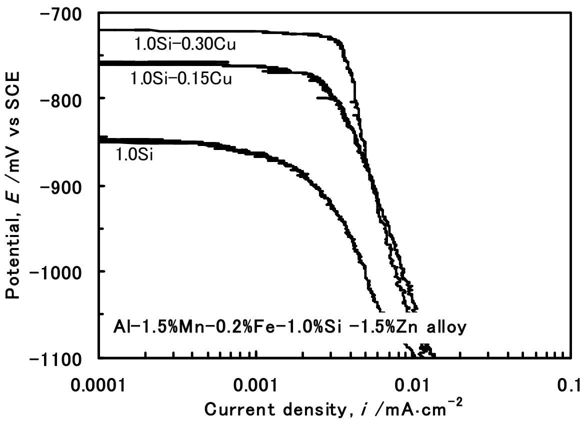

Fig.14 Effect of Cu content on the cathodic polarization curve of Al-1.5%Mn -0.2%Fe-1.0Si-1.5%Zn alloy in aerated 3.5%NaCl solution at 313K.

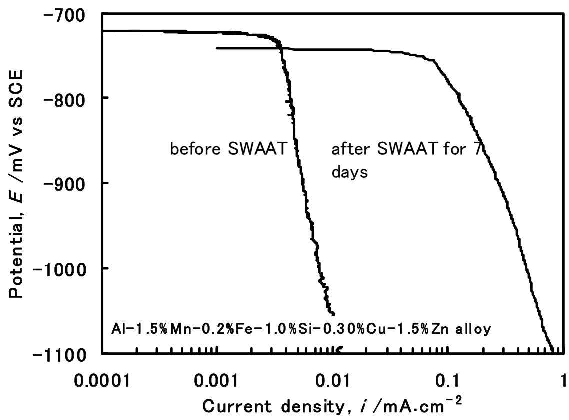

Fig.15 Cathodic polarization curves of Al-1.5%Mn-0.2%Fe-1.0%Si-0.30% Cu-1.5%Zn alloy before and after SWAAT for 7 days in aerated 3.5%NaCl solution at 313K.

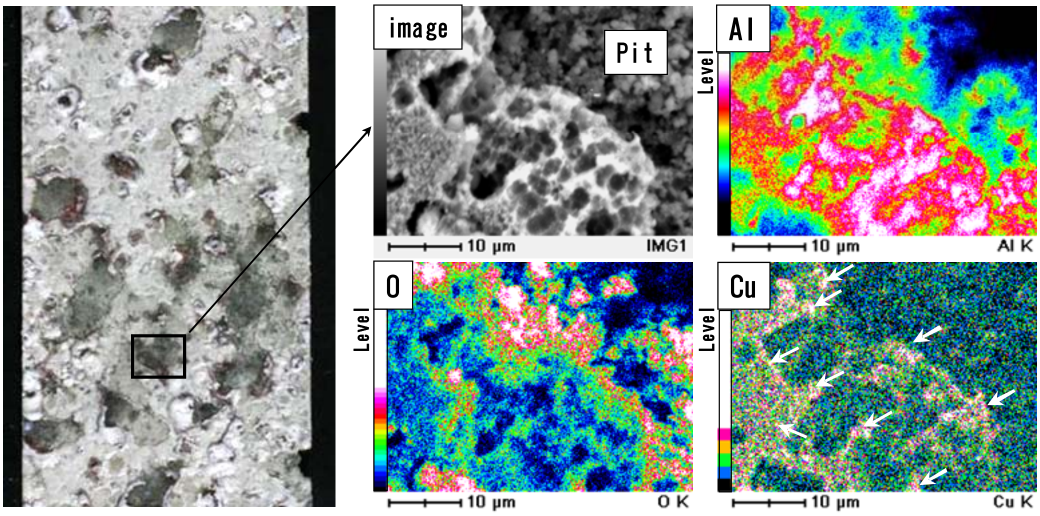

Fig.16 Surface observation and EDS mappings after SWAAT for 3 days on Al-1.5%Mn-0.2%Fe-1.0%Si-0.30%Cu-1.5%Zn alloy. Deposited Cu was indicated arrowed line in Cu mapping image.

However, cathodic current density after SWAAT drastically increased as shown in **Figure 15**. And, **Figure 16** showed that, the metallic Cu was observed at corrosion pits neighborhood of the specimen surface after SWAAT. Therefore, the increasing of corrosion rate in Cu additive alloy attributed to the deposited Cu on surface during corrosion test which worked strong cathode in the alloy.

4. Conclutions

The effect of additional Fe,Ni,Mn,Si and Cu on corrosion rate of Al-Mn-Zn system alloy were investigated. The following results were obtained.

1) Corrosion rate increased with Fe and Ni addition in Al-1.0%Mn-1.5%Zn alloy, because Al_6(Mn,Fe) and Al-Ni-Fe compounds worked as effective cathode in the alloy.
2) Corrosion rate decreased with Mn more than 1.3% in Al-Mn-0.2%Fe-1.5%Zn alloy, because cathodic ability of Al_6(Mn,Fe) decreased with decreasing of Fe/Mn ratio in the compound.
3) Corrosion rate did not increase with Si addition in Al-1.5%Mn-0.2%Fe-1.5%Zn alloy in spite of increasing of α-AlMnSi density , because this compounds did not work as effective cathode in the alloy.
4) Corrosion rate drastically increased with Cu addition in Al-1.5%Mn-0.2%Fe-1.0%Si-1.5%Zn alloy, because deposited Cu on the specimen surface during corrosion test worked as strong cathode in the alloy.

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