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Effect of Additional Cu and Mg in Al-Mn-Si Alloy on Intergranular Corrosion Susceptibility After Heat-treatment at 473K.

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ABSTRACT
Effect of additional Cu and Mg in Al-Mn-Si alloy on intergranular corrosion susceptibility has been investigated by SWAAT after brazing at 873K and heat-treatment at 473K. Intergranular corrosion occurred for Al-Mn-Si-Cu alloy after heating for 1 to 100 hours, while pitting corrosion was observed for Al-Mn-Si-Cu-Mg alloy. In the case of former alloy, precipitates including Cu were observed at grain boundaries, but they did not occurred at inner grain after heating. As a result, the potential difference between neighborhood of grain boundaries and inner grain became larger Therefore, selective dissolution occurred at neighborhood of grain boundaries which was lower solution of Cu. In the case of latter alloy, fine precipitates including Cu were observed not only at grain boundary but also at inner grain even after shorter heat treatment at 473K. As a result, the proof stress became remarkably higher by precipitation hardening and the potential of inner grain became less noble. It follows from these arguments that decreasing intergranular corrosion susceptibility of Al-Mn-Si-Cu-Mg alloy, were caused by smaller potential difference between neighborhood of grain boundaries and inner grain. In conclusion, additional Mg in Al-Mn-Si-Cu alloy improved not only strength but also corrosion resistance after heat-treatment at higher temperature such as 473K.

Keywords: Al-Mn-Si-Cu-Mg alloy, intergranular corrosion, pitting corrosion, pitting potential

1. INTRODUCTION
Recently, environment of heat exchanger for automobiles become severe and the cases used at high temperature are increasing. It is said in particular that material used for the Inter-Cooler(Charged Air Cooler) and CO_2 refrigerant heat exchanger, reached to temperature around 473K. Metallurgic change, such as solution and precipitation of additional elements, occurs to the materials after exposed to such high temperature, and it is assumed that corrosion resistance of brazing sheet used for heat exchanger change by progress of time. For example, it is known that brazing sheet which added Cu in core alloy for the purpose of increasing strength, compounds including Cu precipitates at grain boundaries. And Cu-SDZ(solute depleted zone) is formed at neighborhood of grain boundaries. Because of this, intergranular corrosion susceptibility of the core increase[1-3]. In this case, if the brazing sheet thickness is more than 1mm and there are added Zn in filler, these materials can maintain corrosion resistance due to its filler corroded uniformly[4]. However, in the case of the thin brazing sheet, because the corrosion reaches core easily and penetration occurs early, it is necessary to decrease intergranular corrosion susceptibility of core. Therefore, in this report, influence on intergranular corrosion susceptibility after heat-treatment, have been investigated in more detail regarding the materials added Cu and Mg in Al-Mn-Si alloy assumed core of brazing sheet[5].

2. EXPERIMENTAL
2.1 Sample preparation
Direct chill cast slabs of laboratory scale were prepared which is based on 99.7% pure aluminum and additional elements. Chemical compositions of the alloys used for this investigation were shown in **Table 1**. These alloys were rolled to thickness 0.5mm by hot-rolling and cold-rolling, and annealed at 673K for 3h. These annealed sheets were risen to 873K and kept 3min in N_2 gas atmosphere simulating brazing and cooled down by cooling speed 50K/min. Additionally, it was heat-treated at 473K for 0.5 to 1000h, assuming the use at the high temperature.

Table 1 Chemical composition of specimens. (mass%)

alloy	Mn	Si	Mg	Cu
Al-1.2%Mn-0.75%Si	1.26	0.74	0.00	0.00
Al-1.2%Mn-0.75%Si-0.1%Mg	1.25	0.74	0.10	0.00
Al-1.2%Mn-0.75%Si-0.3%Mg	1.25	0.73	0.29	0.00
Al-1.2%Mn-0.75%Si-0.5%Cu	1.26	0.74	0.00	0.49
Al-1.2%Mn-0.75%Si-0.75%Cu	1.26	0.74	0.00	0.75
Al-1.2%Mn-0.75%Si-0.5%Cu-0.1%Mg	1.25	0.76	0.10	0.49
Al-1.2%Mn-0.75%Si-0.75%Cu-0.3%Mg	1.25	0.76	0.30	0.74

2.2 Corrosion test
Sea water acetic acidified spray test (SWAAT:ASTM G85-85) which was the accelerated corrosion test which simulate outside corrosion environment, were carried out.

2.3 Electrochemical polarization measurement
Anodic polarization measurements were carried out to measure pitting potential of each material. The polarization measurement carried out with reference electrode of Saturated Calomel Electrode (SCE), by the scanning rate 0.5mV/s, in 2.67%$AlCl_3$ water solutions of 313K. The test solutions were deaerated enough by the bubbling high purity N_2 gas.

3. RESULTS

3.1 Strength measurement after heat-treatment
The measurement result of the 0.2% proof stress both after brazing and heat-treatment at 473K, was shown in **Figure 1**. In the case of Al-1.2%Mn-0.75%Si alloy and Cu additive alloy, variation of the proof stress by the heat-treatment at 473K after brazing was comparatively small. On the other hand, in the case of Al-1.2%Mn-0.75%Si-0.3%Mg alloy, proof stress reached to 100MPa after heat-treatment at 473K for 10h by age hardening. Furthermore, Al-1.2%Mn-0.75%Si-0.75%Cu-0.3% Mg alloy, proof stress reached to 180MPa after heat-treatment at 473K for more than 1h. It is assumed that proof stress was remarkably increased by age hardening. In addition, proof stress decreased by overage after heat-treatment at 473K for 1000h. However, actual heat exchangers are exposed at 473K only short time considering the life of automobiles. Therefore, the possibility of overaging is very small, and these strength improvements are effective in actual use.

3.2 Corrosion test
Cross sectional observation of localized corrosion after SWAAT 72h of each material were shown in **Figure 2**. In the case of Al-Mn-Si alloy and Mg additive alloy, the remarkable localized corrosion

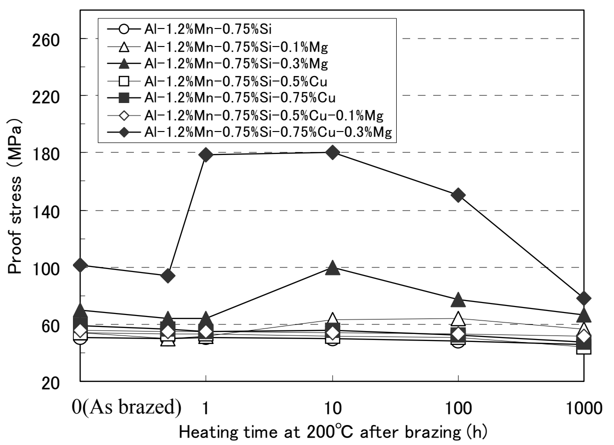

Fig.1 Variation of the 0.2% proof stress with heating time.

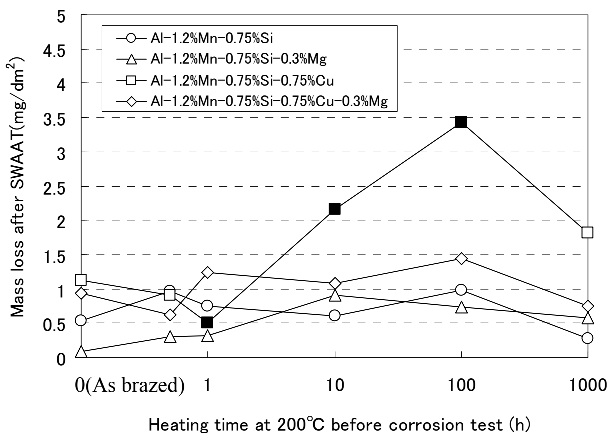

Fig.3 Mass loss and corrosion form after SWAAT 72h.
Black mark : intergranular corrosion

was not observed at either heat-treatment. Contrary, in Al-Mn-Si-Cu alloy, remarkable intergranular corrosion occurred after heating for 10h. On the other hand, in the case of Al-Mn-Si-Cu-Mg alloy, while intergranular corrosion slightly occurred, pitting corrosion occurred even if it was heat-treated 473K after brazing. Mass loss and corrosion form after SWAAT of each material were shown in **Figure 3**. (in addition, materials which obvious intergranular corrosion occurred, were shown by black mark). In Al-1.2%Mn-0.75%Si alloy and Al-1.2%Mn-0.75%Si -0.3%Mg alloy, the remarkable increase of the mass loss did not occur by the heat-treatment at 473K for 0.5 to 1000h. In Al-1.2%Mn-0.75%Si-0.75%Cu alloy, remarkable intergranular corrosion occurred by the heat-treatment at 473K for 1 to 100h and mass loss significantly increased at heat-treatment for more than 10h, because the falling down of grains occurred. Furthermore, in the case of heat-treatment time of 1000h, intergranular corrosion was inhibited and the mass loss was decreased. In contrast, in the case of the alloy added both Cu and Mg, the remarkable increase of mass loss did not occur. Because, intergranular corrosion did not occur by the heat-treatment at 473K for 0.5 to 1000h in this alloy. These results well accorded with the corrosion observation results which were shown in Figure 2.

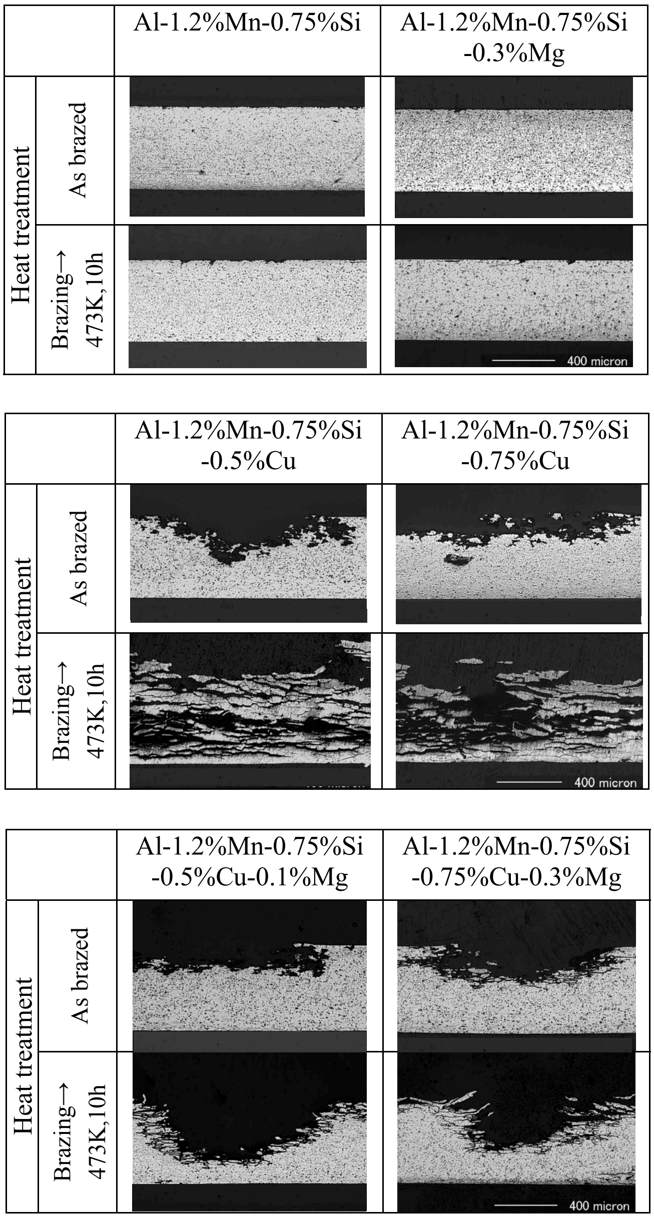

Fig.2 Cross section observation of localized corrosion after SWAAT 72h.

4. DISCUSSION

4.1 Solid and precipitation of additional elements

Electric conductivity of each material was shown in **Figure 4**. Electric conductivity of all materials became higher with increase of heat-treatment time after brazing and it showed that precipitation progressed. In particular, electric conductivity of Al-1.2%Mn-0.75%Si-0.75%Cu-0.3%Mg alloy became higher by the heat-treatment for more than 1h. Contrary, the variation of the electric conductivity of Al-1.2%Mn-0.75%Si-0.75% Cu alloy was comparatively small in the range of heat-treatment time from 1 to 100h. And the electric conductivity became higher at 1000h. EPMA analysis of each material after brazing and heat-treatment at 473K for 100h was shown in **Figure 5**. The colorbar in the figure expresses each elemental concentration level, and concentration is the highest at white part, and the lowest at black part. In addition, the analized point is the rolling direction section and thickness direction central part of the materials. As for Al-1.2%Mn-0.75%Si alloy, Si-SDZ (solute depleted zone) was obeserved. In the case of Al-1.2%Mn-0.75%Si-0.3%Mg alloy, Mg-SDZ was observed and high concentration point of the Mg was observed.

It is confirmed that these Mg-SDZ and the high concentration point of Mg are not observed as brazed material. Therefore, it is supposed that intermetallic compounds including Mg were precipitated by the heat-treatment at 473K and Mg solution of the neighborhood with it decreased, and so Mg-SDZ was formed. In addition, precipitation of the intermetallic compound occurred at grain boundaries and formation of SDZ occurred at neighborhood of the grain boundaries. In Al-1.2%Mn-0.75%Si-0.75%Cu alloy, Si-SDZ and Cu-SDZ were observed. In addition, the high concentration point that seemed to be intermetallic compound including Cu was observed at the Cu-SDZ. Contrary, in the case of the alloy which added both Cu and Mg, Cu-SDZ is unclear. In addition, high concentration point of Mg and Mg-SDZ is hardly confirmed. The formation of Si, Cu or Mg-SDZ, was observed around grain boundaries by the heat-treatment at 473K for 100h for the all materials as written above. But it is only Al-1.2%Mn-0.75%Si-0.75%Cu alloy that remarkable intergranular corrosion occurred by corrosion test. TEM bright-field images in grain of Al-1.2%Mn-0.75%Si-0.75%Cu alloy and Al-1.2%Mn-0.75%Si-0.75%Cu-0.3%Mg alloy with heat-treatment at 473K for 10h were shown in **Figure 6**. In the alloy which added both Cu and Mg, the needle shaped intermetallic compound (compound No. 1) was confirmed as shown in the figure. An example of the EDS analysis of these needle shaped intermetallic compounds was shown in **Figure 7**. These needle shaped intermetallic compounds were Al-Mg-Si-Cu. From the above result, the precipitates (including Cu) were not observed in grain by the alloy which added only Cu in Al-Mn-Si alloy. But in the case of the alloy which added both Cu and Mg, the fine precipitation (including Cu which gives big influence for electric potential) occurred in grain by the heat-treatment at 473K for the short time[6-8]. For reason mentioned above, electric conductivity and proof stress of the alloy which added both Cu and Mg became higher. Those results were shown in Figure 4 and Figure 1. Based on EPMA analysis and TEM observation results, schematic representation of metallurgical structure around grain boundaries, were shown in **Figure 8**.

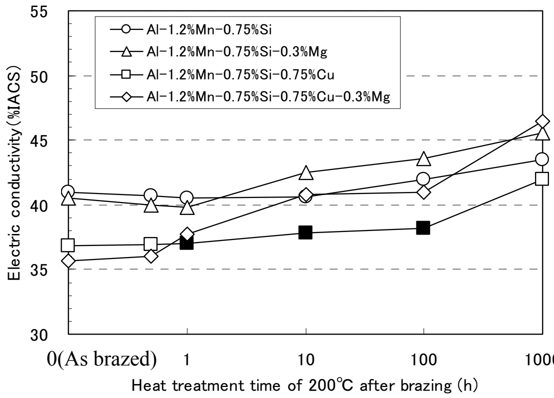

Fig.4 Variation of electric conductivity with heating time.
Black mark : intergranular corrosion

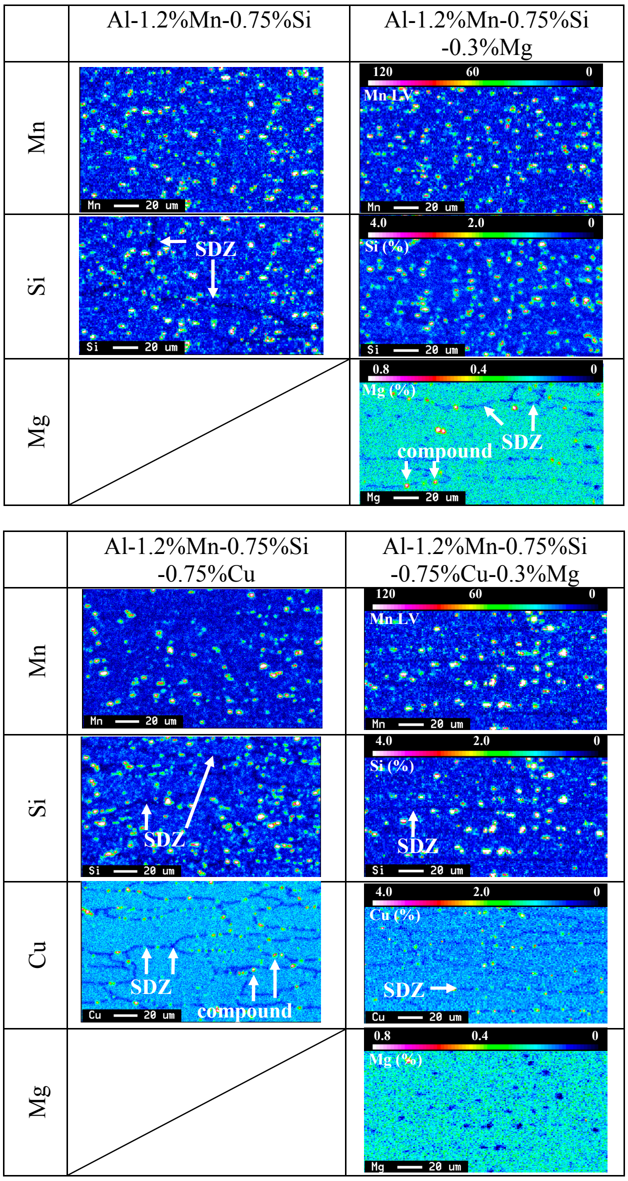

Fig.5 EPMA analysis after heating for 100h at 473K.

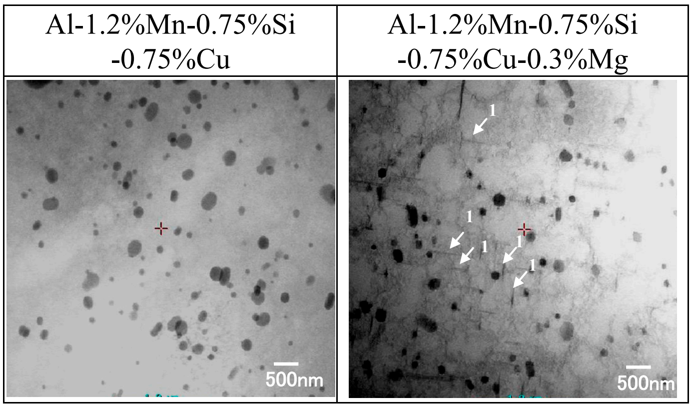

Fig.6 TEM bright field images of matrix in grain.(Observation [001])
Heating for 10h at 473K after brazing

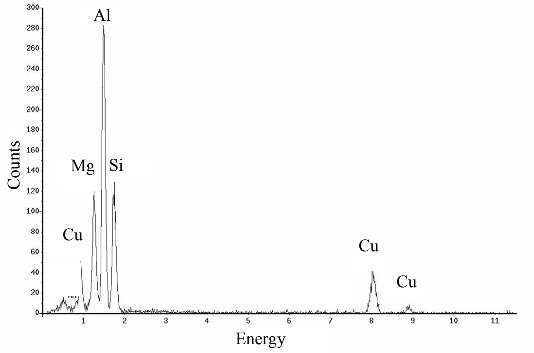

Fig.7 Example of EDS analysis result of needle shape compound.

It is concluded that all materials maintains high solution on as brazed material, but precipitation including Si, Cu or Mg occurred at grain boundaries, and SDZ of each element is formed around grain boundaries by the heat-treatment at 473K. In the case of the alloy which added both Cu and Mg, fine precipitates including Cu were observed not only at grain boundary but also at inner grain even after shorter 473K heating time. It is concluded that potential difference between SDZ and inner grain gives great influence to intergranular corrosion susceptibility[9-10].

4.2 Potential difference between SDZ and inner grain

Anodic polarization measurements were carried out to clarity relations between the formation of SDZ and intergranular corrosion susceptibility. It is known that the lowest potential is measured as pitting potential[11]. Therefore, in the case of material which was formed SDZ, the electrochemical potential of SDZ that was less noble than inner grain was measured, because Si and Cu solution were lower. It was shown in Figure 8. In addition, approximately the potential of inner grain is measured by the polarization measurement as brazed materials without the formation such as SDZ. Variation of pitting potential on materials with heat treatment was shown in **Figure 9**. As for Al-1.2%Mn-0.75%Si alloy, potential difference(⊿E) between neighborhood of grain boundaries and inner grain was about 13mV. Although, Si-SDZ formed by heat-treatment, the selective corrosion of SDZ (that is the intergranular corrosion) was not observed in SWAAT.

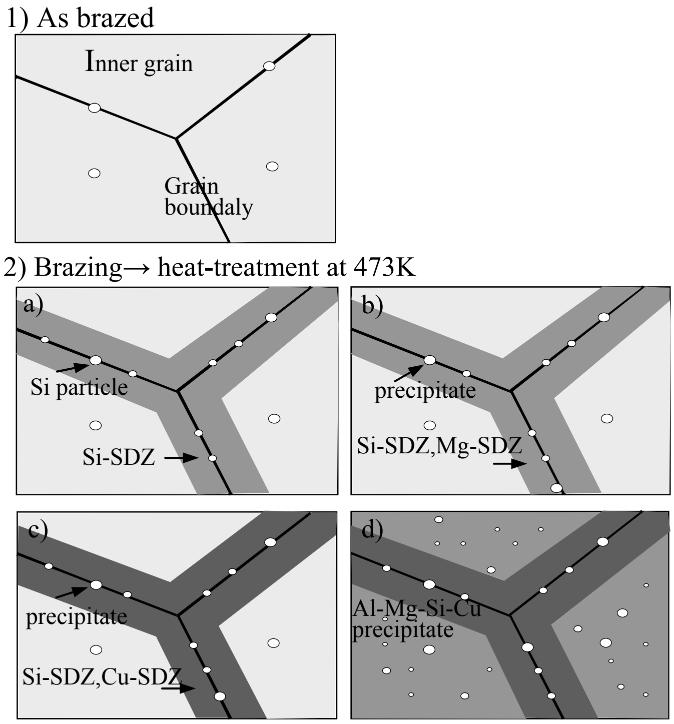

Fig.8 Schematic representation of metallurgical structure around grain boundary.
a)Al-1.2%Mn-0.75%Si alloy
b)Al-1.2%Mn-0.75%Si-0.3%Mg alloy
c)Al-1.2%Mn-0.75%Si-0.75%Cu alloy
d)Al-1.2%Mn-0.75%Si-0.75%Cu-0.3%Mg alloy

Because potential difference was comparatively small. In addition, as for Al-1.2%Mn-0.75%Si-0.3%Mg alloy, potential difference was small too. As for Al-1.2%Mn-0.75%Si-0.75%Cu alloy, potential difference was about 41mV. It is supposed that intergranular corrosion was observed in SWAAT because potential difference became bigger. On the other hand, as for the alloy which added both Cu and Mg, potential difference became 35mV, when it was measured by the same method. However, the precipitates of compound including Cu which gives great influence to electrochemical potential, were observed inner grain (Figure 6, Figure 8). Therefore, by the heat-treatment at 473K, the electrochemical potential inner grain of this alloy became less noble than as brazed and it is thought that true ⊿E considerably small than measured value. Thus, it is concluded that intergranular corrosion did not occur in SWAAT.

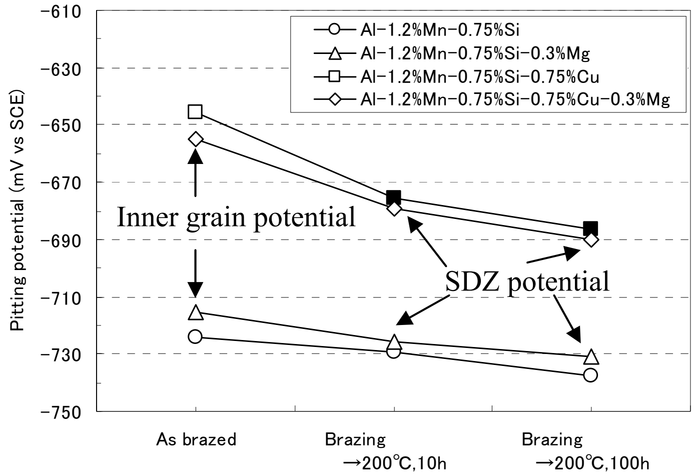

Fig.9 Variation of pitting potential on materials with heat treatment.
Black mark : intergranular corrosion

5. CONCLUSION

1) By the heat-treatment at 473K after brazing, remarkable intergranular corrosion occurred on Al-Mn-Si-Cu alloy. On the other hand, pitting corrosion occurred on Al-Mn-Si-Cu-Mg alloy.
2) In the case of Al-Mn-Si-Cu alloy, although the precipitates of the compounds including Cu were observed at grain boundaries, they were not observed inner grain. Therefore, potential difference(⊿E) between SDZ and inner grain became comparatively larger, and it is concluded that the selective corrosion of SDZ (that is the intergranular corrosion) occurred.
3) In the case of Al-Mn-Si-Cu-Mg alloy, the fine precipitates including Cu were observed not only at grain boundary but also at inner grain by 473K heat-treatment for the short time. Therefore, by age hardening, proof stress became higher remarkably and electrochemical potential inner grain became less noble. In addition, intergranular corrosion susceptibility of Al-Mn-Si-Cu-Mg alloy decreased compared with Al-Mn-Si-Cu alloy, because potential difference(⊿E) became comparatively small.

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