Evaporate Phenomena of Mg in Vacuum Brazing of Aluminum

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ABSTRACT   The aim of this work is to examine how the distribution of Mg_2Si particles in the brazing metal affect the magnesium evaporate behavior. We studied them with a thermo-gravimeter, and we get the results show the following. In the brazing metal having a high numerical density of Mg_2Si particles from 2 to 4 μ m, the magnesium evaporation proceeds so stably that the growth of oxide film is suppressed across the fusion and flowing out of the brazing metal. By this reason, it seems possible to control the deterioration in brazeability especially in case that the degree of vacuum is lowered.
      Keywords: *vacuum brazing, magnesium evaporation behavior, thermobalance*

1. INTRODUCTION

Aluminum brazing is frequently carried out using a brazing sheet that consists of a core metal of 3000 series aluminum alloy group and a brazing metal clad thereon of 4000 series aluminum alloy group in general. In vacuum brazing without using flux, Al-Si alloys with a small addition of magnesium are used for brazing metal also. When heated for brazing, magnesium contained in the brazing metal also. When heated for brazing, magnesium contained in the brazing metal begins to evaporate slowly and reducing aluminum oxide films on the brazing metal but also gettering of the in-furnace oxidizing gas (H_2O, O_2) [1]. In the brazing metal, magnesium exists in the form of Mg2Si particles and the distribution of their size and number varies depending on the processing parameters of brazing metal [2]. So, it is considered that even if heating for brazing is made under the same conditions in design and manufacturing of the products to be brazed, the difference in metallographic structure of the brazing metal may alter the magnesium evaporation behavior, that is, the magnesium evaporation, so as to produce a powerful effect on the vacuum brazeability [3,4]. How magnesium evaporates when the brazing sheet is heated in a vacuum has been studied also by means of mass spectrometric measurement and the like [5,6]. However, mass spectrometry is a method of gas analysis in an atmosphere, and thus it is difficult to directly compare the difference between the materials. In the present study, therefore, we prepared brazing metals with different distribution of Mg_2Si particles, compared their difference in magnesium evaporation behavior from the weight variations when heated for brazing and reviewed their effect on the vacuum brazeability.

2. EXPERIMENTAL

2.1 Specimens

The chemical compositions of the core and brazing metals for brazing sheet employed in the present study are shown is Table 1. Each of the core metal of 3003 aluminum alloy and the brazing metal of 4104 aluminum alloy used was out of the ingots industrially produced. Homogenizing treatment was applied to the core metal at the temperature of 873K for three hours and to the brazing metals at the temperature of 733K for three hours and 813K for three hours so as to modify the metal structure. Then, the brazing metals were clad on both sides of the core metal at the cladding ration of 15% on a single side. The clad sheet was reduced down

Table 1 Chemical composition of specimen (mass%)

	S i	F e	C u	M n	M g	B i	A l
3003	0. 23	0. 50	0. 14	1. 12	——	——	Bal.
4104	10. 3	0. 41	0. 08		1. 21	0. 08	Bal.

from 72mm to 1mm thickness through hot and cold rolling processes and finally annealed at the temperature of 633K for three hours to be finished to the specimen condition. In this case, the initiating temperatures of hot rolling was set at the same level as the brazing metal homogenizing temperatures.

2.2 Testing Procedure

The metallographic structure of brazing metals was observed by catching the image of back scattered electrons in a scanning electron microscope. The image of back scattered electrons differ in contrast according to the difference in composition of the particles crystallized or precipitated the brazing metal. We made, therefore, an image analysis of the Mg_2Si particles in the photograph image of back scattered electrons in order to obtain the circle equivalent diameter and the per-unit area number of particles existing in the image for comparing their distribution.

In measurement of the weight variations in each specimen when heated for brazing, we used thermo-gravimetric apparatus. In this measurement it is possible to heat the specimens in a vacuum atmosphere below 1.3×10^{-2}Pa. Magnesium evaporation behavior was evaluated by obtaining the weight variation ratio (the ratio of weight variations to the magnesium weight in the brazing metal). In temperature rising, they were degassed and kept at 578K before being heated at the rate of 15K/min. to the desired temperature.

As for the brazeability, we adopted the joint clearance filling test method as shown in Fig.1. The brazeability was evaluated by measuring the fillet length developed when heated for brazing in an atmosphere different in degree of vacuum.

The thickness of oxide films formed on the surface of brazing sheet when heated for brazing was measured by means of ESCA after the samples were heated to the desired temperature in the atmosphere of 6.7×10^{-3}Pa and then quenched by nitrogen gas.
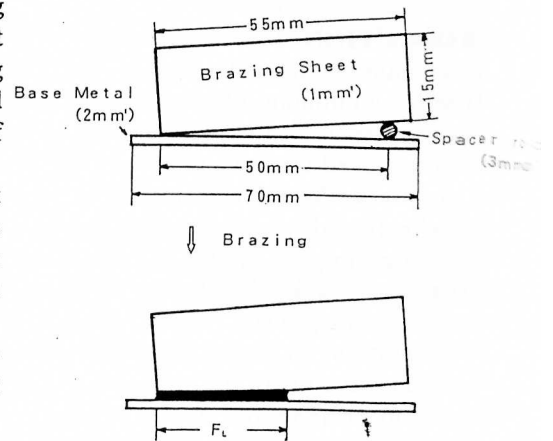

Fig.1 Shape and size of joint clearance filling test. F_L is filled length.

3. TESTING RESULTS

3.1 Metallographic Structure

The image of reflection electrons in brazing metals is shown in Fig.2. Using the EDX analysis technique, we identified that, in this figure, the black particles were those of Mg_2Si and the white particles were those of Si or those of Al-Fe-Si alloy system.

From the image analysis of Mg_2Si particls, we found a numerical density, that is, the ratio in number of particles different in grain size to the number of particles existing per unit area. The results are shown in Fig.3. In the case of specimens which were homogenized at the higher temperature, there are seen a large number
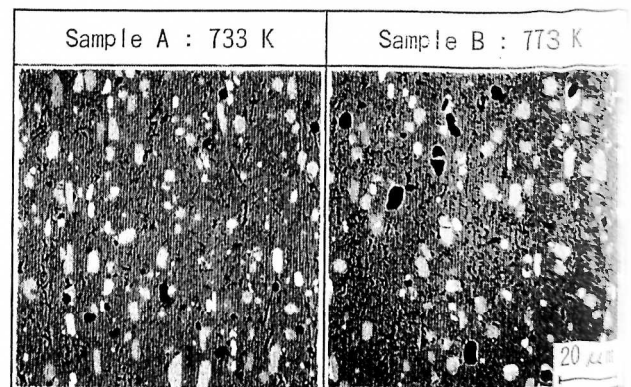

Fig.2 Image of reflection electrons in brazing metals

of coarse Mg2Si particles above 5 μ m and fine Mg2Si particles below 1 μ m. Whereas, in the case of specimens which were heattreatmented at the lower temperature, there is seen a higher numerical density of particles ranging from 2 μ m to 4 μ m. Hereat, however, the "grain size of 1 μ m" means the Mg2Si particles of analyzable grain size above 0.4 μ m but below 1 μ m and the "grain size of 2 μ m" does the Mg2Si particles of grain size larger than 1 μ m but less than 2 μ m.
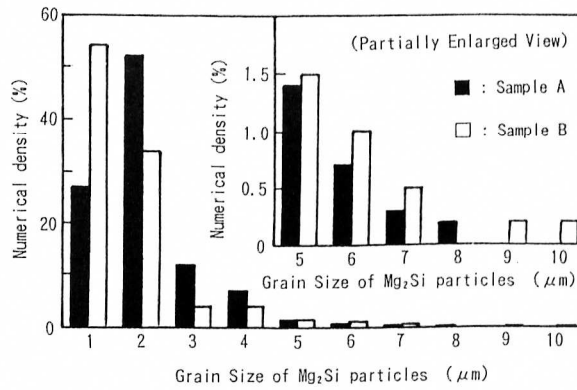

Fig.3 Grain size distribution of Mg2Si particles

3.2 Magnesium Evaporation Behavior When Heated for Brazing

The weight variation ratio of specimens when heated for vacuum brazing is shown in Fig.4. In general magnesium is said to start its evaporation slowly at about 673 K in a vacuum, but a decrease in weight was observed at about 793 K in the actual measurement. Then, the weight variation rate increases at about 823 K, since magnesium evaporation becomes active along with temperature rising. Furthermore, when the temperature reaches the Al-Si eutectic point (850 K) and the brazing metals are molten down and liquefied, the residual magnesium evaporates rapidly and almost 100% of the magnesium content in brazing metals ends its evaporation at 873 K.

Fig.4 Thermo-gravimetric variation ratio

You can find the difference in brazing metal structure in this magnesium evaporation behavior. Although the weight loss initiating temperatures are about the same, in comparison of the temperature when the weight variation occurs rapidly, that of Specimen A is about 10 K lower than that of Specimen B. In the amount of weight loss at each temperature also, that of Specimen A is more than that of Specimen B. At the eutectic temperature of 850 K the weight variation rates are different: about 80% in Specimen A against about 40% in Specimen B. After this, the weight loss proceeds to about 90% at 853 K and comes to an end 873 K in Specimen A but it continues gradually up to 873 K in Specimen B.
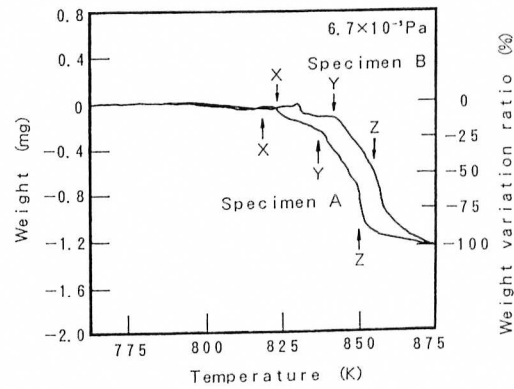
3.3 Vacuum Brazeability

The results of an evaluation of brazeability are shown in Fig.5. In each of the specimens, the fillet lengths gets shorted and the vacuum brazeability declines as the degree of vacuum decreases. In the case of high degrees of vacuum, the difference in brazeability between the both specimens is within a range of scattering and shows about the same value. However, when the degree of vacuum is lowered, the fillet length is
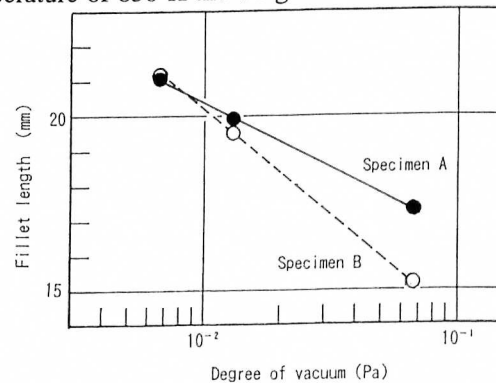

Fig.5 Vacuum Brazeability

Specimen A gets longer than that in Specimen B. This shows that the brazeability is more stable in Specimen A.

4. CONSIDERATIONS
4.1 Magnesium Evaporation Behavior Analyzed by Thermobalance

In a thermobalance, its measuring mechanism is based on the moving element which is strained by the mass change in specimens, so that the higher the thermobalance is in sensitivity, the more the analytical result is affected by various factors. Especially for the device used in the present study, the balance area is in a vacuum atmosphere, and thus it is susceptible to the thermal effect induced by the actions of buoyancy, convection and hot molecular flow which are generated along with temperature rising or evacuation [7]. It is necessary, therefore, to consider these effects in case of interpretation of the date. According to the graph in Fig.4, we outline our findings of the weight variation behavior in each specimen as follows.

Along with temperature rising, magnesium evaporates and each specimen decreases in weight. Nevertheless, around the eutectic temperature of Mg_2Si and Al (828 K), there is seen a small weight increase (indicated by an arrow X). This is attributable to the fact that an increase in apparent weight is induced by the action of buoyancy generated by the increased pressure inside the chamber in action of buoyancy generated by the increased pressure inside the chamber in a rapid evaporation of magnesium in the brazing metal.

In the neighborhood of 833 K, there is seen a point of inflection towards weight decrease (indicated by an arrow Y). For the factor causing this inflection point, two cases are supposed. One is the case where exist a quantity of Mg_2Si particles of grain size being apt to melt and evaporate at such a temperature. Another is the case where works the equilibration between the actual weight loss caused by a rapid magnesium evaporation and the apparent weight increase induced by the action of buoyancy. Hereat, in view of the fact that it is difficult to think the possible existence of such an inflection point from the grain size distribution as shown in Fig.3 and the fact that the temperature indicated as the inflection point is inapplicable to any of the eutectic temperatures analogized from the constituents in the brazing metal, the latter seems to be the right factor. In other words, it is considered that the inflection point arisen in case that the equilibrium inside the chamber leaned towards the weight loss superiority due to the gradual declining buoyancy induced by the evacuation within the chamber.

When heated up to the Al-Si eutectic temperature, the brazing metals are liquefied. The dispersion in liquid phase progressed so faster as compared in solid state that the residual magnesium evaporates rapidly (indicated by an arrow Z). It appears, therefore, that the weight loss rate at this temperature reaches to 100%. However, since it takes a little time for the whole of each specimen to be molten down, the magnesium evaporation is prolonged and the weight loss ends barely at 873 K. Especially in Specimen B, the amount of residual magnesium at 850 K is more than that in Specimen A and its effect also seems to work more strongly.

4.2 Mg_2Si Grain Size Distribution and Magnesium Evaporation Behavior

Fig.4 shows the fact that the magnesium evaporation initiating temperature, namely, the temperature at which the specimens start to lose in weight is not almost unaffected by the difference in material. However, regarding the temperature at which the weight loss emergent remarkably Specimen A is about 10 K lower. It is considered that this temperature difference is attributable to the difference in Mg_2Si grain size. In Fig.3, Mg_2Si particles of 1 μ m are more contained in Specimen B but Mg_2Si particles ranging from 2 to 4 μ m are more contained in Specimen A. It is considered, therefore, that Mg_2Si particles of grain size 1 μ m contribute to the process from the initiation of evaporation to the start of a remarkable weight loss, and Mg_2Si particles of grain size above 2 to 4 μ m do to the remarkable weight loss. Since Mg_2Si articles of large grain size remain

unmolten up to high temperatures, the amount of residual magnesium at 850 K is more in Specimen B, where exist more Mg$_2$Si particles above 5 μ m, than in Specimen A. From the above considerations, we can assume a model of thermo-gravimetric variation as shown in Fig.6 concerning the magnesium evaporation behavior when heated for brazing. In case that the Mg$_2$Si particles existing in the brazing metal are of uniform size ranging from 2 to 4 μ m, a remarkable weight loss begins around the eutectic temperature of Mg$_2$Si and Al (828 K) and all of the residual magnesium complete their evaporation at the Al-Si eutectic temperature of 850 K.

Fig.6 Thermo-gravimetric variation (model)

However, depending on the heat treatment conditions, along with the enrichment of coarse Mg2Si particles above 5 μ m and fine Mg$_2$Si particles below 1 μ m, the amount of residual magnesium at 850 K increases as the temperature at which a remarkable weight loss begins to shift towards the high temperature size.

Also it appears that fine Mg$_2$Si particles below 0.4 μ m and solid solute magnesium, which can be involved in this time analysis, exist in the brazing metal. It is supposed that these contribute to the initial magnesium evaporation through their behavior similar to that of Mg$_2$Si particles of 1 μ m.

4.3 Vacuum Brazeability and Magnesium Evaporation Behavior

As shown in Fig.5, Specimen B shows a better brazeability than Specimen A in the region of high vacuum. With the decrease in degree of vacuum, however, Specimen A in its turn becomes better in brazeability. We consider the reason why it turns so, in connection with the magnesium evaporation behavior as follows.

Fig.7 shows the magnesium evaporation behavior in case that the degree of vacuum is low. In both the specimens, the magnesium evaporation begins almost simultaneously around 823 K. This seems attributable to the fact that the magnesium evaporation was suppressed u to around the eutectic temperature of Mg$_2$Si and Al under the high pressure inside the chamber. Immediately

Fig.7 Thermo-gravimetric variation ratio

after the magnesium evaporation started, unlike when heated in a high vacuum, a weight loss arises more sharply in Specimen B than Specimen A. This seems attributable to the more existence of Mg2Si particles of 1 μ m in Specimen B. These particles induced a great deal of magnesium evaporation which removed the oxidizing gas within the chamber, brought about a rapid decrease in pressure and the resultant buoyancy caused a decrease in apparent weight loss. On the other hand, in Specimen A, the weight loss arises slowly along with temperature rising. The behavior is about the same as that in the region of high vacuum and almost unaffected by the atmosphere.

Fig.8 shows the results of the measurement of oxide films on the brazing sheet at each temperature. In Specimen A, the oxide film grows thicker gradually at 773 K, reaches the maximum thickness in the neighborhood of 828 K and turns thinner again at 873 K. On the other hand, in Specimen B, the oxide film grows rapidly at 813 K, reaches the maximum thickness at 853 K and then turns thinner. These oxide film formation behavior between both specimens. In other words, in Specimen B, there exist a lot of Mg$_2$Si particles of 1 μ m, the magnesium evaporation arises
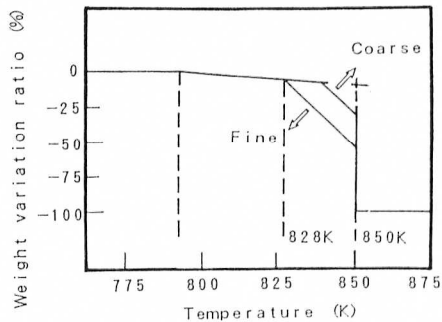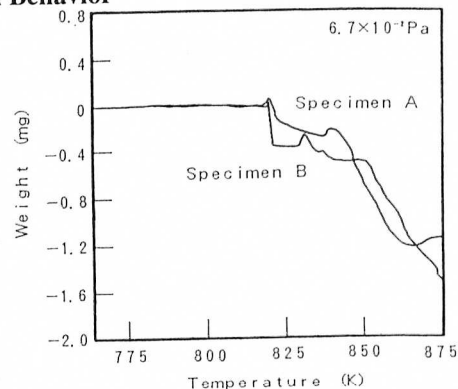
gradually at low temperatures, and thus the growth of oxide film is suppressed by the action of gettering. However, in the process up to 850 K where Mg_2Si particles above 5 μ m are molten down and evaporated, the action of gettering declines for a while and the oxide film grows rapidly. On the other hand, in Specimen A, there exist less fine Mg_2Si particles, so that a certain amount of oxide film grows but its rapid growth is hindered by the continual magnesium evaporation. In both the specimens, the oxide film is 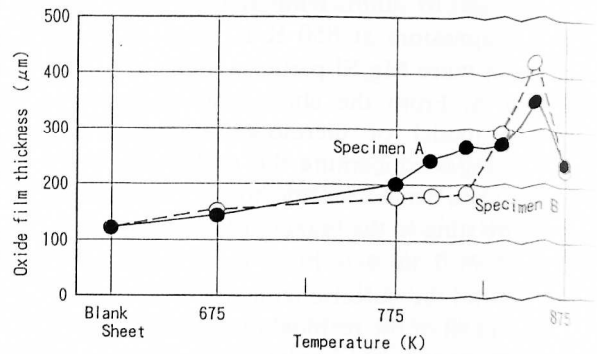broken and thinned by the action of fusion and flow in the brazing metal. The above oxide film growing behavior well agrees with the results of magnesium evaporation behavior as shown in Fig.7, and it appears to be liable to form the oxide film to make the difference in material conspicuous in case that the degree of vacuum is low.

Fig.8 Thickness of oxide films when heated for brazing

In the region of high vacuum, therefore, as compared to Specimen A, Specimen B shows good brazeability because the evaporated magnesium remains unmolten up to high temperatures and by this reason gettering is performed to the full immediately before brazing. In Specimen B however, the oxide film grows thicker than in Specimen A across the Al-Si eutectic temperature at which the brazing metal is molten down and flowed out, and thus it is considered that the brazeability comes worse than that in Specimen A in case that the degree of vacuum is lowered.

In order to get a good brazeability, the brazing parameters and the constituents of brazing metal are often modified [9], but it is considered that a much better brazeability can be obtained by controlling the magnesium evaporation behavior in the aspect of brazing metal structure.

5. CONCLUSION

The magnesium evaporation behavior when heated for brazing and the vacuum brazeability were evaluated using the materials of different distribution of Mg_2Si particles in the brazing metal. The results show the following matters.

(1) Fine Mg_2Si particles below 1 μ m are molten down and evaporated at low temperatures, but coarse Mg_2Si particles above 5 μ m remain unmolten up to high temperatures. Therefore, the state of distribution of Mg_2Si particles in the brazing metal influences the magnesium evaporation behavior when heated for brazing.

(2) In the brazing metal having a high numerical density of Mg_2Si particles from 2 to 4 μ m, the magnesium evaporation proceeds so stably that the growth of oxide film is suppressed across the fusion and flowing out of the brazing metal. By this reason, it seems possible to control the deterioration in brazeability especially in case that the degree of vacuum is lowered.

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