論　文

Influence of the Mg and Bi Content on Brazeability of MONOBRAZE™ Material under Flux-Free Brazing Conditions*

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In the conventional brazing, the clad materials with the filler layer and the flux coating have been used to get good brazeability. However, an innovative Al-Si based single-layer brazing material (MONOBRAZE material) has been developed recently which does not need filler layer by supplying molten filler from the inside of the material during brazing. In addition, a new flux-free brazing technique has also been developed. In the flux-free brazing, Mg and Bi are added to break the oxide film and to improve the wettability of molten filler, respectively. However, it is not clarified how these elements work on the brazeability of MONOBRAZE material in flux-free brazing. Therefore, in this study the effect of Mg and Bi content on the brazeability of MONOBRAZE material was investigated. From the result, it was found that MONOBRAZE material was applicable for flux-free brazing by adding Mg. Mg was considered to break the oxide film into fine particles and Bi was considered to assist the destruction of oxide film. From this cause, a new aluminum substrate surface was exposed which allow molten filler to move on the surface and contribute to the formation of the fillet.

Keywords: *flux-free brazing, MONOBRAZE, in-situ observation, oxide film*

1. Introduction

1.1 Conventional brazing technology

Aluminum brazing has been applied to connect a lot of components of automobile heat exchanger efficiently. Basically, filler alloy (Al-Si alloy; 9-13mass%Si) is cladded on core alloy (Al-Mn alloy) and it works as molten filler at temperature over 577℃ to connect with other components, while core alloy does not melt[1]. In order to achieve the good bonding, flux is sprayed on the filler alloy surface to remove the oxide film during brazing.

There are several methods of aluminum brazing such as vacuum brazing, inert gas brazing, VAW brazing and CAB brazing. Currently, NOCOLOK® brazing is a mainstream of aluminum brazing[2] which use non-corrosive flux to remove the oxide film.

1.2 MONOBRAZE material

In recent years, an innovative Al-Si based single layer brazing material (MONOBRAZE material) has been developed which does not need a filler layer by supplying a molten filler that consists of Si around 2.5mass% from the inside of the material during brazing[3]. From the thermodynamics calculation by JMatPro® as shown in **Fig. 1**, it was clear that the fraction of liquid phase of 2.5mass% Si is 17mass% at the temperature 600℃, while that of 10mass% Si

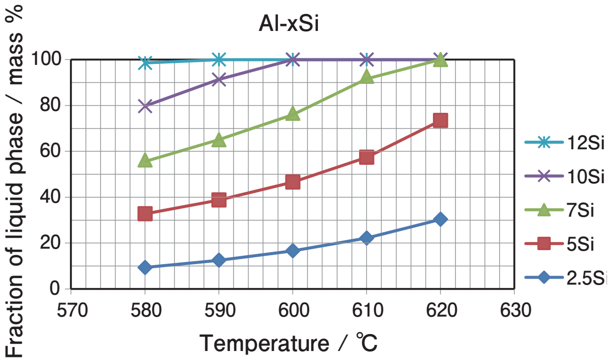

Fig. 1 The fraction of the liquid phase at different Si contents calculated by JMatPro.

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[*] The main part of this paper has been published in MATEC Web of Conferences, **326**, 08003 (2020).

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(4045 aluminum alloy) is 100%. Due to the less amount of liquid phase, the alloy with 2.5mass% Si maintains its structural strength, while the liquid phase, generated at mainly grain boundary and Si particles, works as a connecting molten filler sufficiently.

1.3 Flux-free brazing technology

To minimize the manufacturing cost, a new brazing technique without using flux has been developed. Under a vacuum or inert gas atmosphere, it is known that Mg works to destroy the aluminum oxide film during brazing when using a Mg-containing aluminum alloy[4), 5)]. Also, adding Bi is known to improve the brazeability by increasing the wettability of the molten filler[4)]. There are reports about brazeability of clad materials using flux-free brazing[4), 5)], but it has not ever surveyed whether flux-free brazing can be applicable to MONOBRAZE material. Therefore, in this study, the effect of the Mg and Bi contents on the brazeability of the MONOBRAZE material during flux-free brazing was investigated.

2. Experiment procedures

2.1 Material

2.1.1 Chemical composition

The chemical composition of the MONOBRAZE material is shown in **Table 1**. In this paper, the concentration of elements means mass concentration (denoted "%" as abbreviation). As the base composition, the MONOBRAZE material contained 2.5% Si.

For No.2, 0.05% Mg was added with no added Bi. For No.3 and No.4, 0.025% and 0.05% Mg was added with 0.02% Bi, respectively.

2.1.2 Manufacturing condition

The manufacturing condition of the MONOBRAZE materials was shown in **Table 2**. Each sample was cast by a continuous casting process into a plate with the thickness of 6 mm. The plate was annealed at 420℃ for 2 hours, rolled down to the thickness of 0.2 mm, and finally annealed again at 370℃ for 2 hours. Grain recrystallization of the entire plate was confirmed. Moreover, in order to remove the oxide film that formed during the manufacturing processes, the material was dipped in 2% nitric acid / 1% hydrofluoric acid at room temperature for 90 sec.

Table 1 The chemical composition of MONOBRAZE material.

No.	Chemical composition (mass %)					
	Si	Fe	Mn	Zn	Mg	Bi
No.1	2.5	0.2	1.1	1.5	0	0
No.2	2.5	0.2	1.1	1.5	0.05	0
No.3	2.5	0.2	1.1	1.5	0.025	0.02
No.4	2.5	0.2	1.1	1.5	0.05	0.02

2.2 Brazing process

In this study, the sample temperature was raised to the target temperature of 600 ℃ for 5 min., then cooled to room temperature as shown in **Fig. 2**. Brazing was performed under a nitrogen gas atmosphere.

2.3 Evaluation of brazeability

2.3.1 In situ observation of surface during brazing

In order to investigate how the fillet would be formed during brazing, the T-joint sample was brazed up to 600℃ in a chamber, then cooled to room temperature while continuously taking a video of the surface of horizontal plate (No.1 and No.2) from the top side over the vertical plate (3003, t1.0 mm) as

Table 2 The manufacturing condition of MONOBRAZE material under flux-free brazing condition.

Process	Condition
Casting	Continuous casting (CC)
Intermediate annealing	420℃ for 2h
Cold rolling	0.20 mm
Final annealing	370℃ for 2h
Etching	2% nitric acid and 1% hydrofluoric acid at room temperature for 90 sec

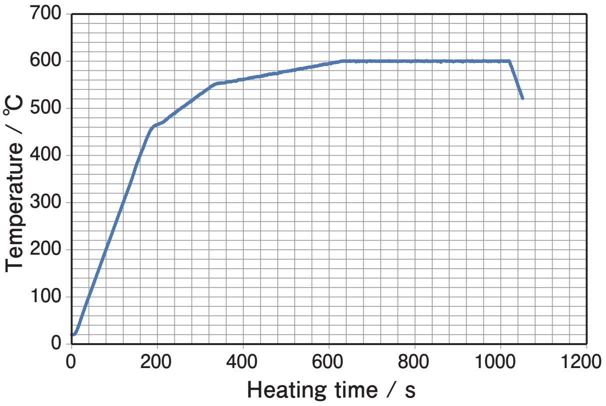

Fig. 2 Brazing heat profile.

shown in **Fig. 3**. Since sample No.1 was used as a reference of conventional brazing, NOCOLOK flux was sprayed on the surface of No.1 before assembling the T-joint specimen. After brazing, the cross section of the bonding part between vertical and horizontal plates was observed using a microscope.

2.3.2 Evaluation of bonding ratio of miniature-core sample

To evaluate the brazeability of the MONOBRAZE material under flux-free brazing condition, the bonding ratio between the fin and plate of a miniature-core sample was measured. **Fig. 4** shows a schematic diagram of the miniature-core sample. Samples No.1 to No.4 were used as plates to sandwich the corrugated fin stock (t0.08 mm, H14 temper). The chemical composition of the fin stock was shown in **Table 3**. The fin pitch was adjusted to 3 mm, and the number of connecting points between fin and plate was 12 per a miniature-core.

After brazing the miniature-core sample, the fin was peeled off and the lengths of the remaining fillets were measured as shown in **Fig. 5**. The bonding ratio was then calculated by equation (1).

$$\text{Bonding ratio} = \sum_{b=1}^{12} \frac{l_b}{l} \times 100 \tag{1}$$

3. Results

3.1 T-joint sample

Fig. 6 shows images of the surface of T-joint samples that were taken by a video camera. At a temperature <570℃, molten flux was observed on sample No.1 (0Mg-0Bi). Stripe patterns formed by rolling can be seen on the surface of No.2 (0.05Mg-0Bi). At a temperature over 600℃, web-like patterns and small dots, which did not appear at the temperature <570℃, could be seen on the surface of No.2. These patterns were also seen on the surface of No.1 although less visible probably due to coverage of the molten flux. Web-like patterns and small dots were considered to correspond to melt sites of the grain boundary and precipitated Si particles.

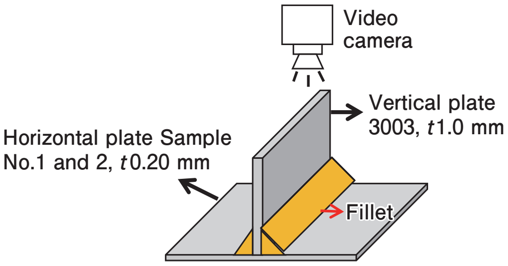

Fig. 3 T-joint sample set up for observation of molten filler alloy.

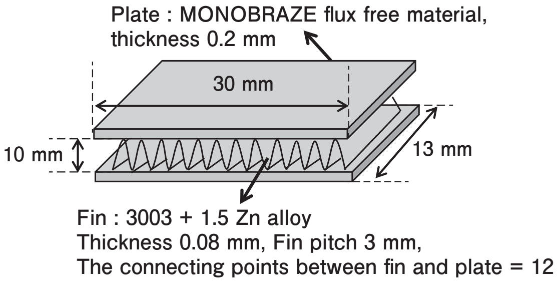

Fig. 4 The schematic diagram of the miniature-core sample.

Table 3 The chemical composition of alloy 3003+1.5Zn.

Alloy name	Chemical composition (mass %)				
	Si	Fe	Mn	Zn	Cu
3003 + 1.5 Zn	0.25	0.3	1.25	1.5	0.1

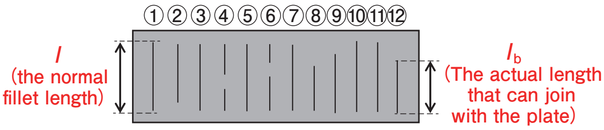

Fig. 5 The schematic of the miniature-core sample.

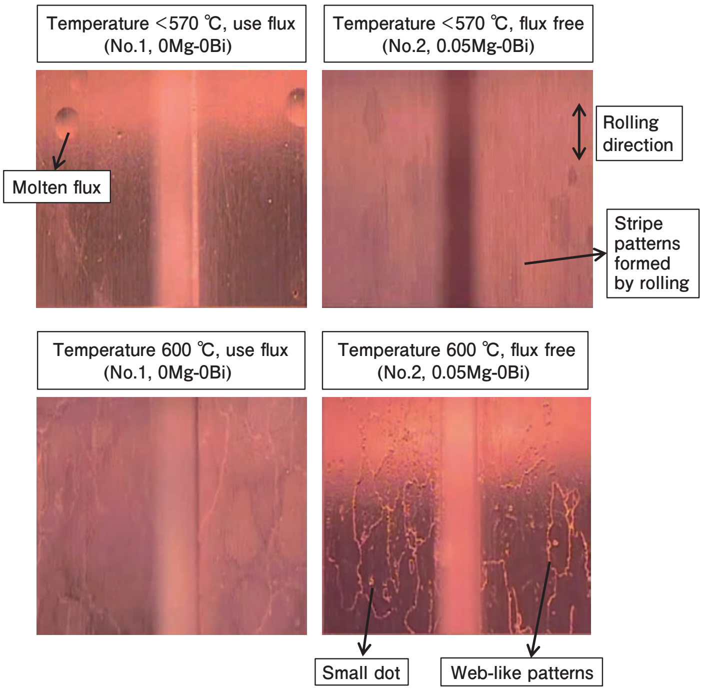

Fig. 6 Surface of T-joint sample during brazing at temperature <570℃ and 600℃.

Fig. 7 shows the cross section of a T-joint specimen. It is clear that the vertical plate and horizontal plate were bonded with filler. From the result, there was no difference in the size of the fillet between the conventional brazing and MONOBRAZE flux free brazing. Moreover, no void was seen for the specimen using MONOBRAZE flux free brazing, while some voids were found in the specimen with conventional brazing using flux.

3.2 Bonding ratio of miniature-core sample

Fig. 8 shows the result of the bonding ratio for different Mg and Bi contents. When Mg was not added, there was no bonding without flux (No.1). However, when 0.05% Mg was added (No.2), the bonding ratio increased from 0% to 86%. From comparing No.2 and No.4, the addition of 0.02% Bi was considered to increase bonding ratio. When comparing No.3 and No.4, it is clear that the increase of Mg content has positive effect on the increase of bonding ratio.

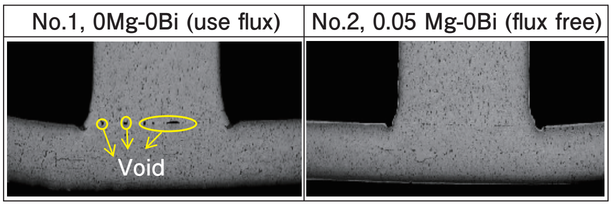

Fig. 7 Cross section photomicrograph at bonding part after brazing.

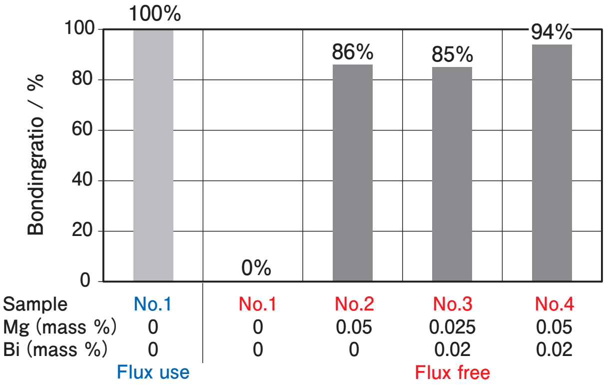

Fig. 8 The result of bonding ratio.

4. Discussion

4.1 The effect of Mg and Bi on the destruction of oxide film of plates (MONOBRAZE material itself)

Since the breazeability of a material during flux-free brazing is considered to be closely related to the condition of the oxide film during brazing, the thickness of the oxide film during brazing was investigated by an XPS analysis. To estimate the thickness of the oxide film, the width at half maximum (WHM) of oxygen from the depth profile was measured. **Fig. 9** shows the WHM of oxygen obtained from samples with different Bi contents which were heated to the target temperature. Based on the result of the XPS analysis, there was a tendency that the thickness of the oxide film gradually increased as the brazing temperature increased, and there was no significant difference in the thickness of the oxide film between 0% Bi and 0.02% Bi at the melting temperature 580℃.

In addition, the transformation of the oxide film on the surface of MONOBRAZE material during brazing was also observed by SEM. **Fig. 10** shows the secondary electron images of surface of samples No.1 (0Mg-0Bi), No.2 (0.05Mg-0Bi) and No.4 (0.05Mg-0.02Bi) which were suddenly cooled at each temperature (550 and 580℃) during heating to 600℃. When focusing on the surface of No.2 at 580℃, fine white particles can be seen on the entire surface, whereas no particles seen on No.1. This tendency became more remarkable with the addition of 0.02%Bi, clearly showing separated areas of fine white particles and black region.

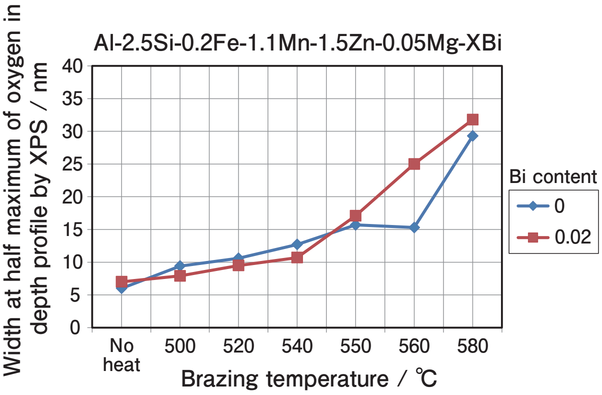

Fig. 9 The relation between the thickness of the oxide film and Bi content during brazing.

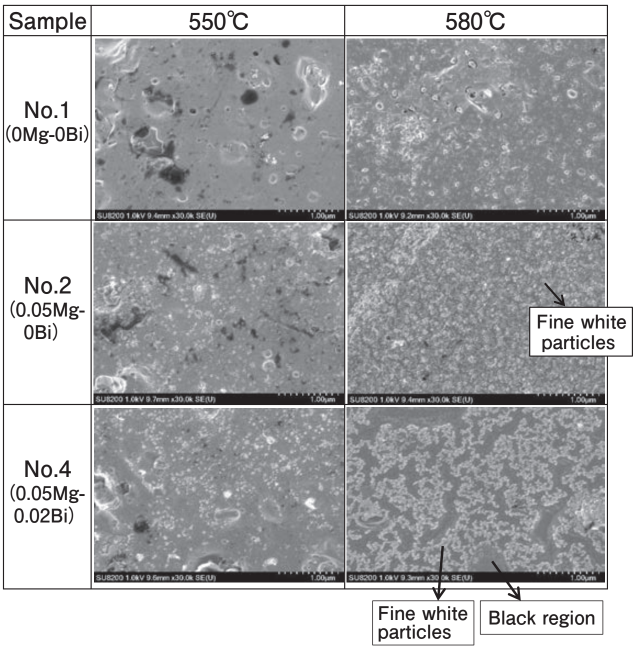

Fig. 10 The secondary election images of MONOBRAZE material under flux-free brazing condition surface during brazing process.

According to Yamayoshi et al.[3], this is the result of the oxide film broken into complex oxide particles by the following reduction reaction;

$$Mg + 4/3Al_2O_3 \rightarrow MgAl_2O_4 + 2/3Al$$

When this reaction happens, the molten filler was considered to move on the surface of the MONOBRAZE material toward bonding part.

4.2 The effect of Mg condensed in the fillet on the destruction of oxide film of fin stocks

To acheive a good bonding between a plate and a fin stock, the oxide film of fin stock is necessary to be destructed as well. Therefore, in order to clarify the effect of Mg content on the destruction of the oxide film of fin stock, the concentration of Mg inside the molten filler during brazing was calculated by JMatPro as shown in **Fig. 11**. At the temperature of 590℃, the material was considered to be partially melted and the molten filler was supposed to have a contact with the fin stock. From Fig. 11, the Mg concentration in the molten filler was estimated to be about 0.20%. This is 4 times higher than added Mg content. This highly concentrated Mg was considered to attack the oxide film of fin stock, resulting in formation of the fillet. This theory was in good accordance with our experiment result that the addition of 0.05% Mg increased the bonding ratio.

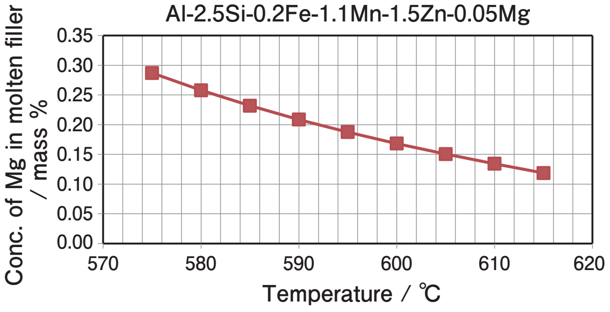

Fig. 11 Concentration of Mg in molten filler of Al-2.5Si-0.2Fe-1.1Mn-1.5Zn-0.05Mg calculated by JMatPro.

However, the result in this study was considered not sufficient to explain the characteristics of the oxide film changes with the Bi content. Therefore, the relation of the oxide film and the characteristics of Bi in terms of the chemical composition and crystal structure will be investigated in a future study.

5. Conclusions

In this research, the influence of the Mg and Bi contents on the brazeability of the MONOBRAZE material under flux-free brazing conditions was investigated. Followings are conclusions in this study.

1. The MONOBRAZE material is applicable for flux-free brazing by adding Mg.
2. Mg is considered to break the oxide film into fine particles.
3. Bi is considered to assist the destruction of oxide film.

Based on the above result, a new aluminium substrate surface was exposed which allows molten filler to move on the surface and contribute to the formation of the fillet.

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