

Influence of the Mg and Bi content on brazeability of MONOBRAZE material under flux-free brazing conditions

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Abstract. 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 element works 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 is found that MONOBRAZE® material is applicable for flux-free brazing by adding Mg. Mg is considered to break the oxide film into fine particles and Bi is 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.

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 clad on core alloy (Al-Mn alloy) and it works as molten filler at temperature over 577°C to connect with other components, while core alloy does not melt¹. 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 brazing² 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 brazing³. From the thermodynamics calculation by JMatPro® as shown in Fig.1, it is clear that the fraction of liquid phase of 2.5mass% Si is 17mass% at the

temperature 600°C, while that of 10mass% Si (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 filler⁴. 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.

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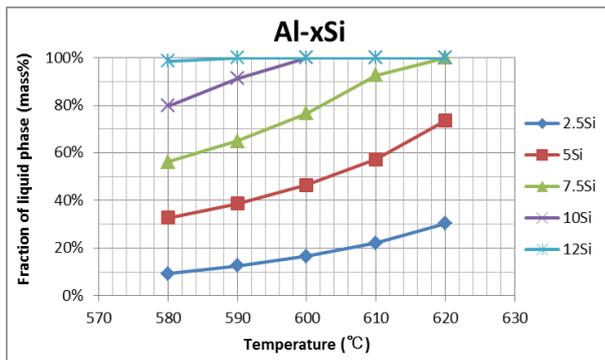


Fig. 1. The fraction of the liquid phase at different Si contents calculated by JMatPro®

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.

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

Table 2. 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

2.1.2 Manufacturing condition

The manufacturing condition of the MONOBRAZE® materials is shown in Table 3. Each sample was casted by a continuous casting process into a plate with the thickness of 6 mm. The plate was annealed at 420°C for 2 hours, rolled down to the thickness of 0.2 mm, and finally annealed again at 370 °C 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 3. The manufacturing condition of MONOBRAZE® material under flux-free brazing condition

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

2.2 Brazing process

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

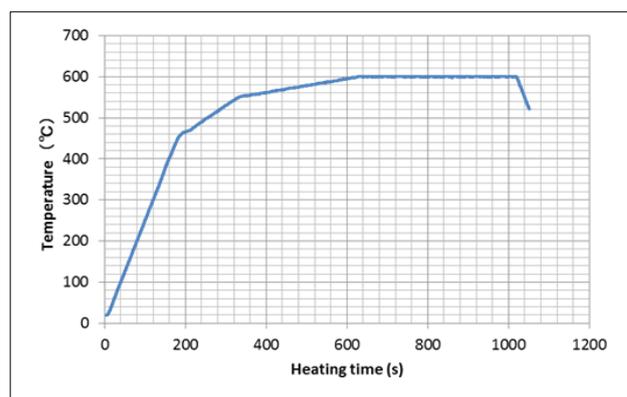


Fig. 2. Brazing heat profile

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°C 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 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.

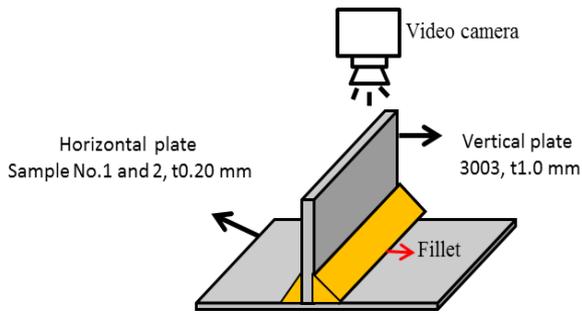


Fig. 3. T-joint sample set up for observation of molten filler alloy

2.3.2 Evaluation of bonding ratio of miniature-core sample

To evaluate the brazability of the MONOBRAZE® material under flux-free brazing condition, the bonding ratio between the fin and tube of a miniature-core sample was measured. Figure 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 is shown in Table 2. The fin pitch was adjusted to 3 mm, and the number of connecting points between fin and tube was 12 per a miniature-core.

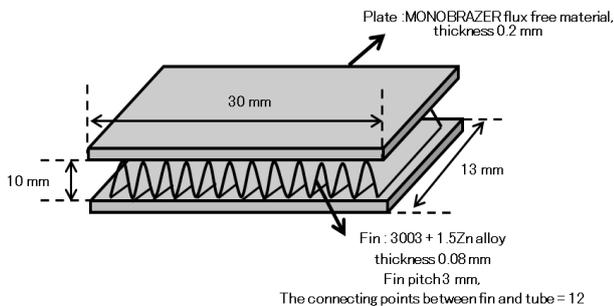


Fig. 4. The schematic diagram of the miniature-core sample

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).

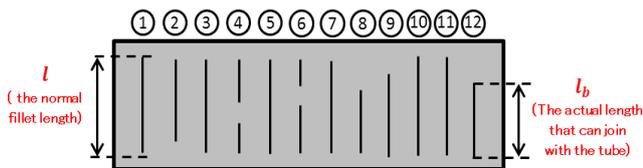


Fig. 5. The schematic of the miniature-core sample

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

3 Results

3.1 T-joint sample

Figure 6 shows images of the surface of T-joint samples that were taken by a video camera. At a temperature <570°C, 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°C, web-like patterns and small dots, which did not appear at the temperature <570°C, 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 are considered to correspond to melt sites of the grain boundary and precipitated Si particles.

Figure 7 shows the cross section of a T-joint specimen. It is clear that the vertical plate and horizontal plate were joined 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.

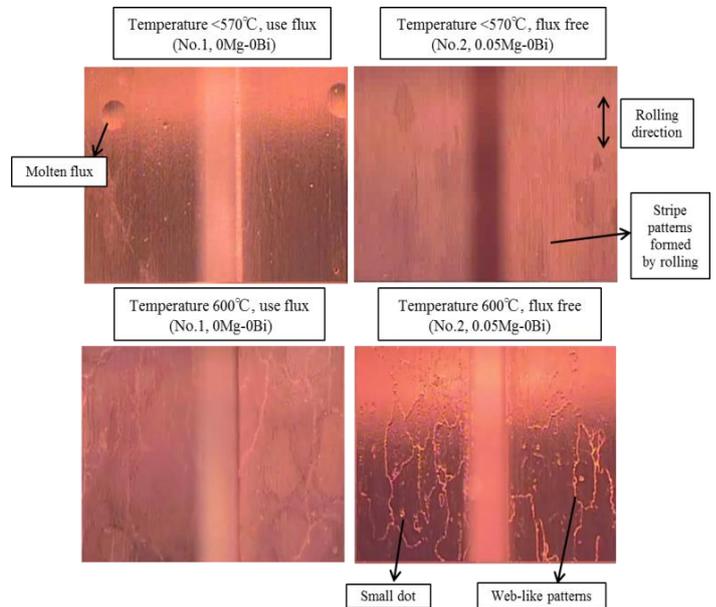


Fig. 6. Surface of T-joint sample during brazing at temperature <570°C and 600°C

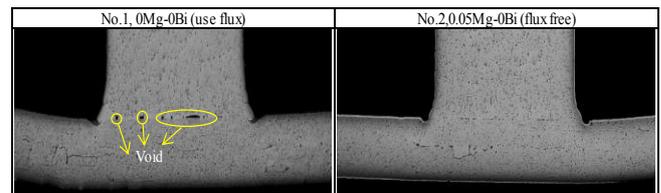


Fig. 7. Cross section photomicrograph at bonding part after brazing

3.2 Bonding ratio of miniature-core sample

Figure 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.

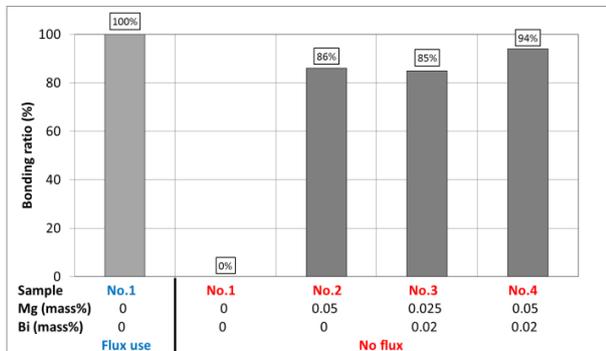


Fig. 8. The result of bonding ratio

4 Discussion

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

Since the brazeability 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. Figure 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°C.

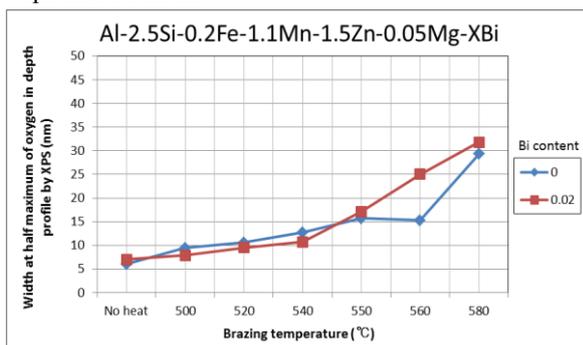
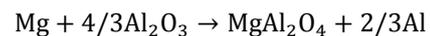


Fig. 9. The relation between the thickness of the oxide film and Bi content during brazing

In addition, the transformation of the oxide film on the surface of MONOBRAZE® material during brazing was also observed by SEM. Figure 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°C) during heating to 600°C. When focusing on the surface of No.2 at 580°C, 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.

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



When this reaction happens, the molten filler is considered to move on the surface of the MONOBRAZE® material and allowing flux free brazing.

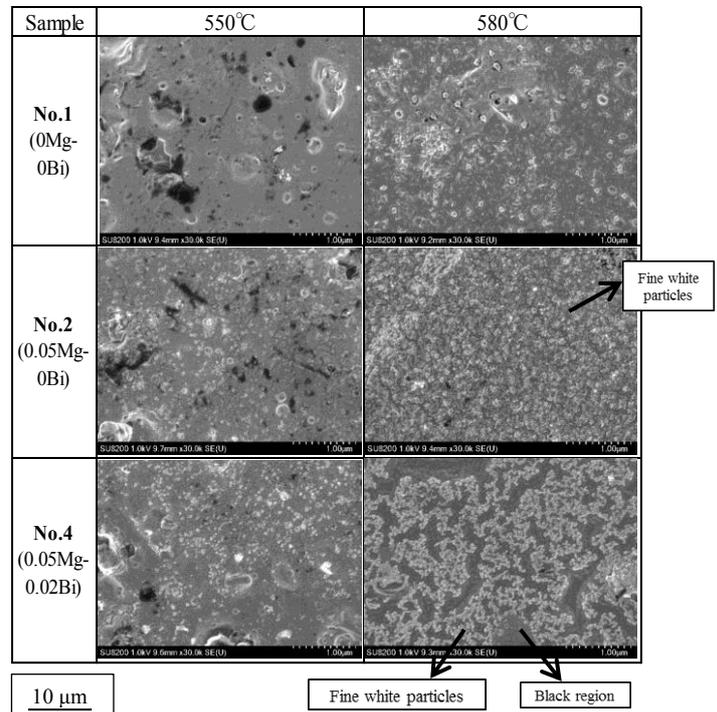


Fig. 10. The secondary electron images of MONOBRAZE® material under flux-free brazing condition surface during brazing process

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

To achieve a good bonding between a plate and a fin stock, the oxide film of fin stock is necessary to be destroyed 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 in the liquid phase of Al-2.5Si-0.2Fe-1.1Mn-1.5Zn-0.05Mg was calculated by JMatPro® as shown in Fig.11. At the temperature of 590°C, the material is considered to be partially melted

and the molten filler is supposed to have a contact with the fin stock. From Fig.11, the Mg concentration in the molten filler is estimated to be about 0.20%. This is 4 times higher than added Mg content (0.05%). This highly concentrated Mg is considered to attack the oxide film of fin stock, resulting in formation of the fillet. This theory is in good accordance with our experiment result that the addition of 0.05% Mg increased the bonding ratio.

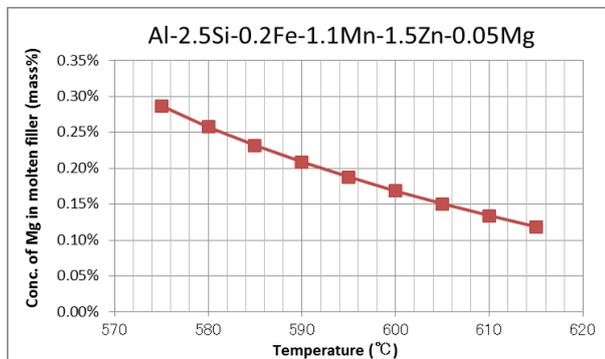


Fig. 11. Concentration of Mg in molten filler of Al-2.5Si-0.2Fe-1.1Mn-1.5Zn-0.05Mg calculated by JMatPro®

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.

Base 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.

6 References

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