UACJ Technical Reports, Vol.2 (2015), pp. 80-90

論　文

# Reaction Behavior of Mixtures of Non-Corrosive Flux and Non-Corrosive Flux Containing Zn during Brazing*

Hidetoshi Kumagai** and Naoki Yamashita**

The reaction behaviors of a non-corrosive flux (the NC-flux), non-corrosive flux containing Zn ($KZnF_3$) and their mixture during brazing were investigated. Regarding the mixture of the NC-flux and $KZnF_3$, a behavior different from the single-component flux was observed. $KZnF_3$ in the flux mixture was completely consumed above 500°C, and pure Zn was detected at 500°C. It was considered that this behavior of the flux mixture was due to the reactions of $KZnF_3$ with $Al_2O_3$ and the reduction of ZnO by $KAlF_4$.

***Keywords:*** *aluminum brazing, non-corrosive flux, chemical reactions*

## 1. Introduction

Aluminum automotive heat exchangers are generally manufactured by controlled atmosphere brazing (CAB) using a non-corrosive flux (the NC-flux), such as the potassium aluminum fluorides of $KAlF_4$, K2$AlF_5$ and $K_3AlF_6$. Recently, a non-corrosive flux containing Zn (the Zn-flux), such as the potassium zinc fluoride of $KZnF_3$ is also being widely used. The significant feature of the Zn-flux is that the Zn diffusion layer into the aluminum multi-port extrusion tube is for protection from the corrosion perforation formed during brazing. Therefore, the application of this flux removes the requirement of the conventional process of Zn arc spraying onto the aluminum multi-port extrusion tube, and also reduces the manufacturing cost. Furthermore, it also allows applying the mixture of both the NC-flux and the Zn-flux.

The reactions of the Zn-flux versus the oxygen concentration and the moisture during brazing are more sensitive than those of the NC-flux. Therefore, it is difficult to make good brazing joints without defects like discoloration by applying the Zn-flux. Since the mechanism of the reactions of the Zn-flux has not been widely reported, this paper describes the reaction mechanism of the NC-flux, the Zn-flux and their mixture during brazing.

## 2. Experimental Procedure

### 2.1 Brazing of single substance and mixture of fluxes

**Table 1** shows the specimens, and **Fig. 1** shows the relationship between the oxygen concentration in a furnace and the material temperature during brazing. $KZnF_3$ was added and mixed with the NC-flux at 0%, 50% and 100% fractions. These fluxes were dispersed in an organic solvent, then brushed on 3003 alloy sheets (25 mm × 25 mm, O temper). After drying, these were brazed at the maximum temperature of 400°C, 500°C and 600°C in the brazing furnace with

**Table 1** Specimens for brazing and XRD analysis. (mg)

| Sample name | Amount of flux | | |
|---|---|---|---|
| | NC-flux ($KAlF_4$) | $KZnF_3$ | Total |
| Z0 | 4 | 0 | 4 |
| Z100 | 0 | 4 | 4 |
| Z50 | 2 | 2 | 4 |

* The main part of this paper was published in the proceedings of the 12th Vehicle Thermal Management systems (VTMS12), England, May, 10-13, 2015.

** No. 4 Research Department, Research & Development Division, UACJ Corporation

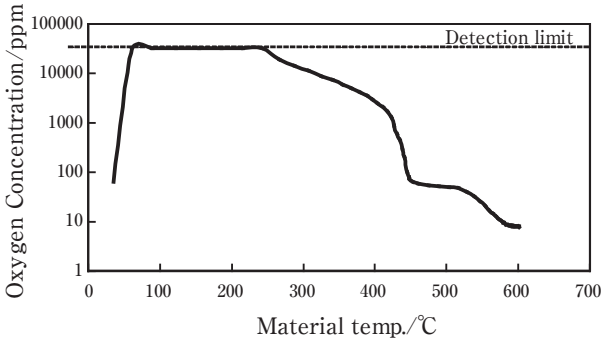



**Fig. 1** Relationship between oxygen concentration in furnace and material temperature during brazing.

$N_2$ atmosphere. The oxygen concentration in the brazing furnace is over 2500 ppm below 400°C, 50-2500 ppm in the range of 400-500°C, and below 50 ppm in the range of 500-600°C. The specimens after brazing were analyzed by X-ray diffraction (XRD). Regarding the Z50 brazed at 500°C, observations by scanning electron microscopy (SEM) and elemental analysis by energy dispersive X-ray spectrometry (EDX) were carried out.

### 2.2 Additional examinations

#### 2.2.1 Validation of chemical reactions

**Table 2** shows the specimens for thermogravimetric and the differential thermal analysis (TG-DTA) and XRD analysis. The after estimated chemical reactions could be validated by TG-DTA. The specimens in the Pt pan were heated at the rate of 20°C/min and the flow rate of the argon gas or the air was 300 ml/min. All of the specimens were analyzed by TG-DTA. P1, P2 and P3 were analyzed by the XRD after the TG-DTA.

#### 2.2.2 Further validation for reduction of ZnO

Regarding the reduction of ZnO, a further validation was determined. The mixture of the NC-flux and ZnO (75:25) was brazed at the maximum temperature of 600°C. The mixture of approx. 2.7 mg was dispersed in an organic solvent and dropped onto the center of the A3003 alloy sheet (50 mm × 50 mm, O temper). After drying, the specimen was brazed under the same condition as **2.1**. The specimen after brazing was analyzed by the XRD.

**Table 2** Specimens for TG-DTA and XRD analysis.

| Sample name | Blend ratio (%) | | | | Flow gas species |
|---|---|---|---|---|---|
| | NC-flux ($KAlF_4$) | $KZnF_3$ | $Al_2O_3$ | ZnO | Ar |
| P1 | – | 50 | 50 | – | Atmospheric air |
| P2 | – | 100 | – | – | Ar |
| P3 | 50 | – | – | 50 | Ar |
| $KZnF_3$ | – | 100 | – | – | Ar |
| NC-flux | 100 | – | – | – | Ar |

## 3. Results and Discussion

### 3.1 Brazing of single substance and mixture of flux

#### 3.1.1 Z0 (NC-flux: 100%, $KZnF_3$: 0%)

**Fig. 2** shows the appearance of the specimens after brazing and **Fig. 3** shows the XRD patterns of Z0 after brazing. At the maximum temperature of both 400°C and 500°C, the appearance of the specimen after brazing had a white color and powdery that was the same as the specimen before brazing. In the XRD patterns, $KAlF_4$ and $K_3AlF_6$ were detected. At the maximum temperature of 600°C the appearance of the specimen had a transparent color and melt-solidified. It was considered that the flux had normally melted. In the XRD patterns, $KAlF_4$ and $K_3AlF_6$ were detected. The intensity of the diffraction peaks for $K_3AlF_6$ increased with the elevating maximum temperature of brazing. The reason why $K_3AlF_6$ was detected at such the low temperature of 400°C was considered to be due to the oxygen concentration below 500°C during brazing being high, i. e., 50-2500 ppm or more. It means that the atmosphere in the brazing furnace contained not only $O_2$, but also $H_2O$. Therefore, $KAlF_4$ brazed in a bad atmosphere reacted with $H_2O$ to form $K_3AlF_6$ following the chemical reaction equations (1)-(3) [1), 2)].

$$KAlF_4 \rightarrow KF + AlF_3 \quad (1)$$

$$2AlF_3 + 3H_2O \rightarrow Al_2O_3 + 6HF\uparrow \quad (2)$$

$$2KF + KAlF_4 \rightarrow K_3AlF_6 \quad (3)$$


(a) 400℃ (b) 500℃ (c) 600℃

**Fig. 2** Appearance of Z0 after brazing at various temperatures.

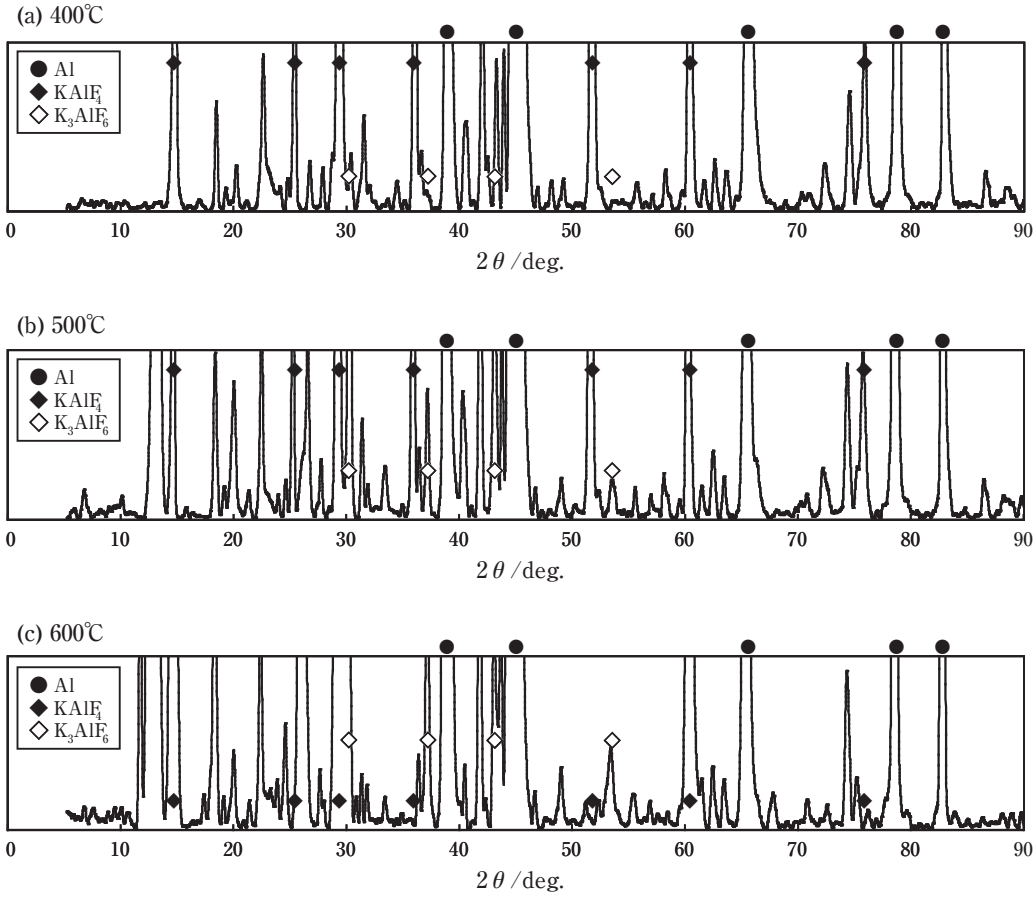



**Fig. 3** XRD patterns of Z0 after brazing at various temperatures.

### 3.1.2 Z100 (NC-flux: 0%, $KZnF_3$: 100%)

**Fig. 4** shows the appearance of the specimens after brazing and **Fig. 5** shows the XRD patterns of Z100 after brazing. At the maximum temperature of 400°C, the appearance of the specimen after brazing had a white color and powdery that was the same as the specimen before brazing. In the XRD patterns, $KZnF_3$ and slight almost of ZnO were detected. At the maximum temperature of 500°C, the appearance of the specimen had a white color and powdery. In the XRD patterns, $KZnF_3$, $K_3AlF_6$ and ZnO were detected. At the maximum temperature of 600°C, the appearance of the specimen had a transparent color and melt-solidified as well as Z0. It was considered that the flux had normally melted. In the XRD patterns, $KAlF_4$ and $K_3AlF_6$ were detected, but $KZnF_3$ and ZnO were not detected. $KZnF_3$ generally reacts with the aluminum at approx. 555°C following the chemical reaction equation (4) to form $KAlF_4$, $K_3AlF_6$ and Zn [3].


(a) 400℃ (b) 500℃ (c) 600℃

**Fig. 4** Appearance of Z100 after brazing at various temperatures.

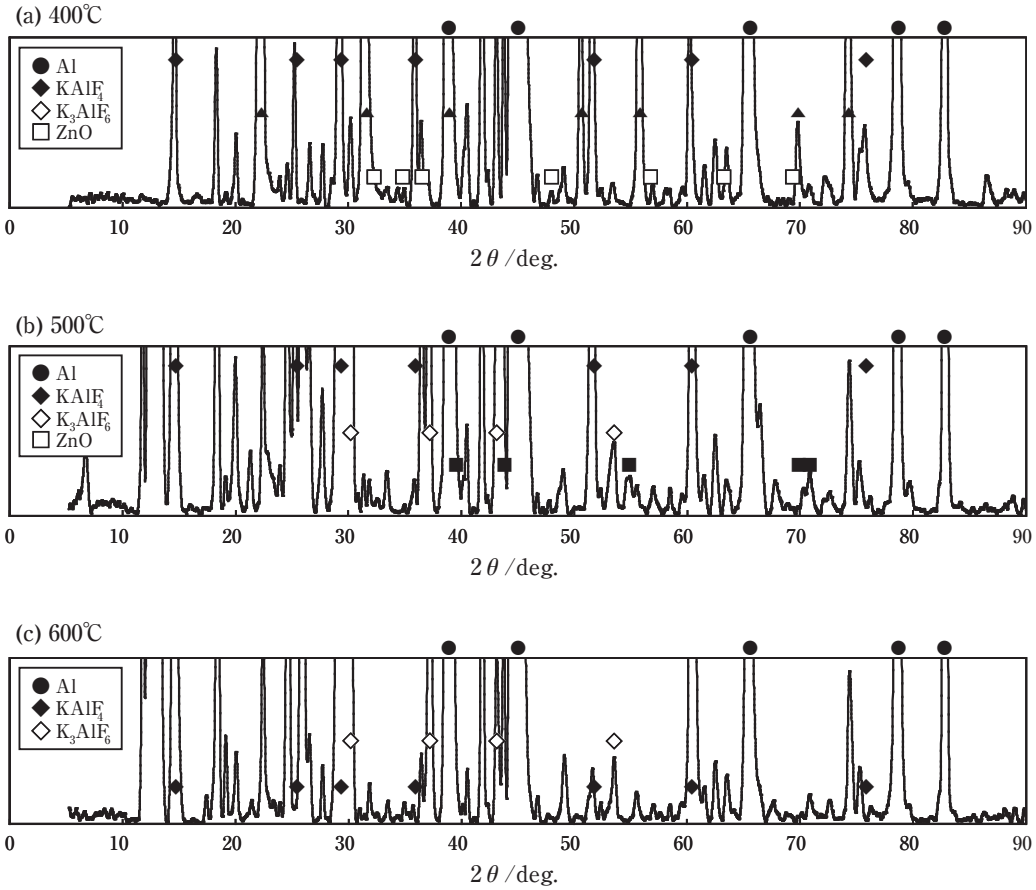



**Fig. 5** XRD patterns of Z100 after brazing at various temperatures.

$$6KZnF_3 + 4Al \rightarrow 3KAlF_4 + K_3AlF_6 + 6Zn \quad (4)$$

Below 500 °C, however, eq. (4) could not occur. Therefore, it was estimated that chemical reaction equations (5)-(7) could occur.

$$6KZnF_3 + 2Al_2O_3 \rightarrow 3KAlF_4 + K_3AlF_6 + 6ZnO \quad (5)$$

$$KZnF_3 \rightarrow KF + ZnF_2 \quad (6)$$

$$ZnF_2 + H_2O \rightarrow ZnO + 2HF\uparrow \quad (7)$$

Eq. (5) is the reaction of $KZnF_3$ with the oxide film on the aluminum, and eq. (7) is the reaction of $KZnF_3$ with $H_2O$ in the brazing atmosphere. Although the amount of $K_3AlF_6$ was too low to detect in the XRD patterns at the maximum temperature of 400°C, it was considered that $KAlF_4$ formed by eq. (5) reacted with KF formed by eqs. (1) and (6) to form $K_3AlF_6$ as well as Z0. It was considered that most of the $KZnF_3$ not in contact with the surface of the aluminum base

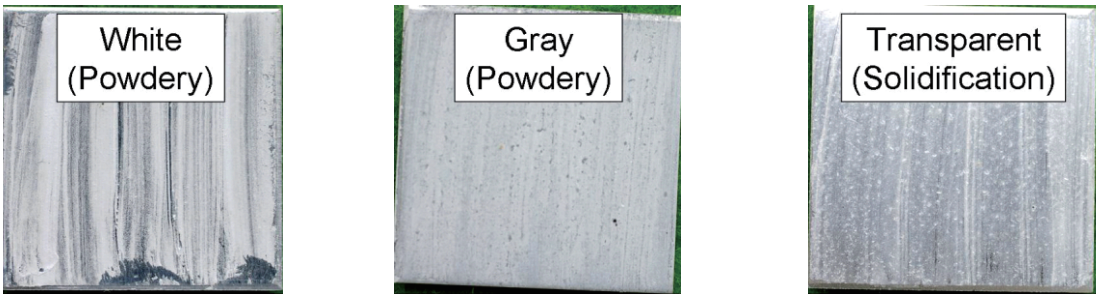
material could not have reacted and therefore remained, because eq. (5) occurred on the surface of the aluminum base material. Furthermore, it was considered that eqs. (6) and (7) also occurred on the $KZnF_3$. However, ZnO was not detected at 600°C. It was considered that the following chemical reaction equation (8) could occur.

$$3KAlF_4 + 3ZnO \rightarrow K_3AlF_6 + Al_2O_3 + 3Zn + 3F_2 \uparrow \quad (8)$$

Above 500°C, eq. (4) occurred at approx. 555°C, i. e., the formed $KAlF_4$ and $K_3AlF_6$ were melted at approx. 562°C. Finally, Zn diffused into the aluminum base material.

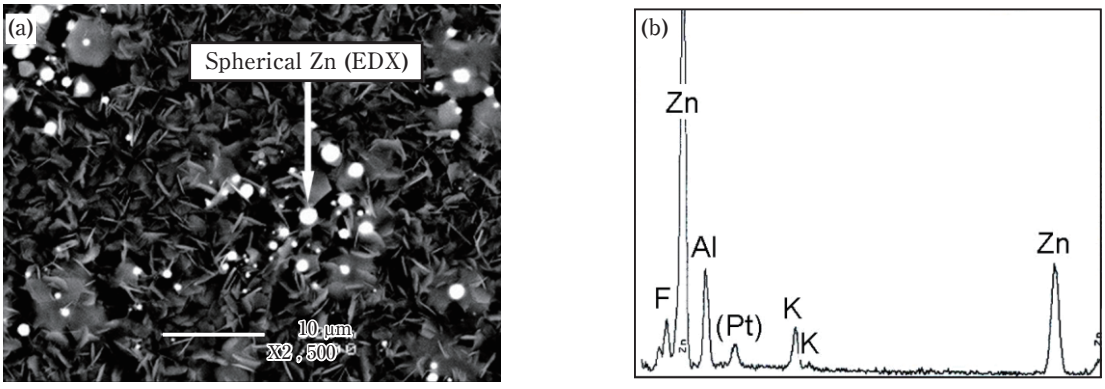
### 3.1.3 Z50 (NC-flux: 50%, $KZnF_3$: 50%)

**Fig. 6** shows the appearance of the specimens after brazing, **Fig. 7** shows the XRD patterns of Z50 after brazing and **Fig. 8** shows the SEM image and EDX analysis at the maximum temperature of 500°C. At the maximum temperature of 400°C, the appearance of the specimen after brazing had a white color and powdery that was the same as the specimen before brazing. In the XRD patterns, $KAlF_4$, $KZnF_3$ and a slight ZnO were detected. At the maximum temperature of 500°C, the appearance of the specimen had a slight gray color and powdery. In the XRD patterns, $KAlF_4$, $K3AlF_6$ and Zn were detected, but $KZnF_3$ and ZnO were not detected. At the maximum temperature of 600°C, the specimen had a transparent color and melt-solidified as well as Z0 and Z100. It was considered that the flux had normally melted. Below 400°C, it was considered that chemical reactions, eqs. (1)-(3) and (5)-(7), occurred as well as Z100. At the maximum temperature of 500°C, ZnO was not detected in the XRD patterns and spherical Zn was observed by the SEM and the EDX analysis. The shape of the spherical Zn indicates that there was melted Zn. Therefore, it was considered that eq. (8) occurred. On the other hand, as the reason why $KZnF_3$ was completely consumed at 500°C, It was considered that eqs. (5)-(8) occurred. First, eqs. (6) and (7) occurred and




(a) 400℃ (b) 500℃ (c) 600℃

**Fig. 6** Appearance of Z50 after brazing at various temperatures.




(a) Composition image of SEM micrograph (b) EDX of spherical Zn

**Fig. 7** SEM micrograph and EDX of Z50 after brazing at 500°C.

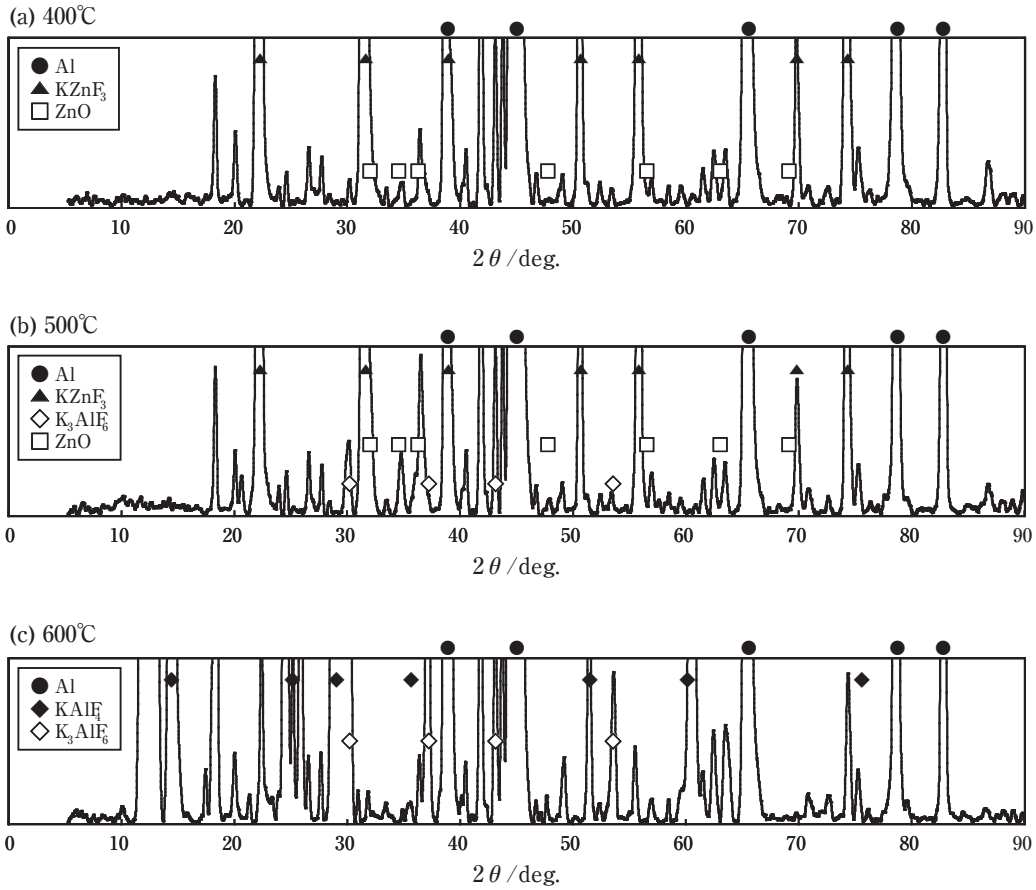



**Fig. 8** XRD patterns of Z100 after brazing at various temperatures.

ZnO was formed in all over Z50, then eq. (8) occurred in Z50 as the reaction between ZnO formed by eqs. (6) and (7) and $KAlF_4$ because $KAlF_4$ was included in Z50 as one of the components before brazing. Furthermore, eq. (5) occurred as the reaction between $KZnF_3$ and $Al_2O_3$ of both the oxide film and the product by eq. (8), then both eqs. (5) and (8) continuously occurred by means of the product of each equation as the reactant of the each equation respectively. Consequently, $KZnF_3$ had been completely consumed. As the reason why the spherical Zn was observed at 500°C, it was inferred that $KAlF_4$ and $K_3AlF_6$ prevented Zn diffused to the base material. Below 562°C, the unmelted $KAlF_4$ and $K_3AlF_6$ prevented Zn from diffusing into the aluminum base material, therefore, the melted Zn was spherically agglomerated. At the maximum temperature of 600°C, $KAlF_4$ and $K_3AlF_6$ had already melted. Therefore, Zn diffused into the aluminum base material.

### 3.2 Additional examination – Validation of chemical reactions

#### 3.2.1 P1 ($KZnF_3$: 50%, $Al_2O_3$: 50%, Flow gas: Ar)

**Fig. 9** shows the TG-DTA curves of P1 and $KZnF_3$ and **Fig. 10** shows the XRD patterns of P1 after the TG-DTA. For the validation of eq. (5), $KZnF_3$ and $Al_2O_3$ were mixed and heated in the flowing argon gas at the maximum temperatures of 388°C, 492°C, 593°C and 638°C. A clear endothermic peak was observed at around 628°C in the DTA curve of P1, and the weight loss started shortly after the onset of heating in the TG curve of both P1 and $KZnF_3$. In the TG curves, the starting temperature of the weight loss of P1 was equal to that of $KZnF_3$. Therefore, it was considered that the weight loss of P1 originated in $KZnF_3$ as a component of P1. However, the cause of the weight loss at such a low temperature was unclear. In the XRD patterns at the maximum temperature of 388°C and 492°C, $KZnF_3$, $Al_2O_3$ and ZnO were detected, and at the maximum temperature or 593°C, $KZnF_3$, $K_3AlF_6$, $Al_2O_3$ and ZnO

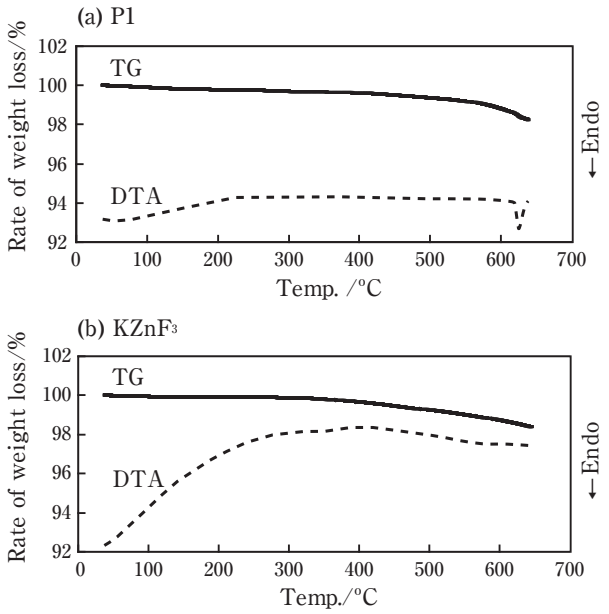



**Fig. 9** Results of TG-DTA for P1 and $KZnF_3$.

were detected. Furthermore, at the maximum temperature of 638°C, $KAlF_4$, $K_3AlF_6$ $Al_2O_3$ and ZnO were detected whereas $KZnF_3$ was not detected. Based on these results, it was considered that $KZnF_3$ reacted with $Al_2O_3$ based on eq. (5) was below 400°C, and it was considered that the reaction of eq. (5) completed at approx. 600°C.

As for the reason why $KAlF_4$ was not detected after heating, it was considered that eq. (8) occurred in parallel with eq. (5) by $KAlF_4$ and ZnO being produced by eq. (5), consequently $KAlF_4$ was consumed. Furthermore, as for the reason why $K_3AlF_6$ was not detected at 388°C and 492°C, it was considered that the amount of $K_3AlF_6$ as the product below 500°C was too low to detect. However, the reason why Zn produced by eq. (8) was not detected is still unclear.

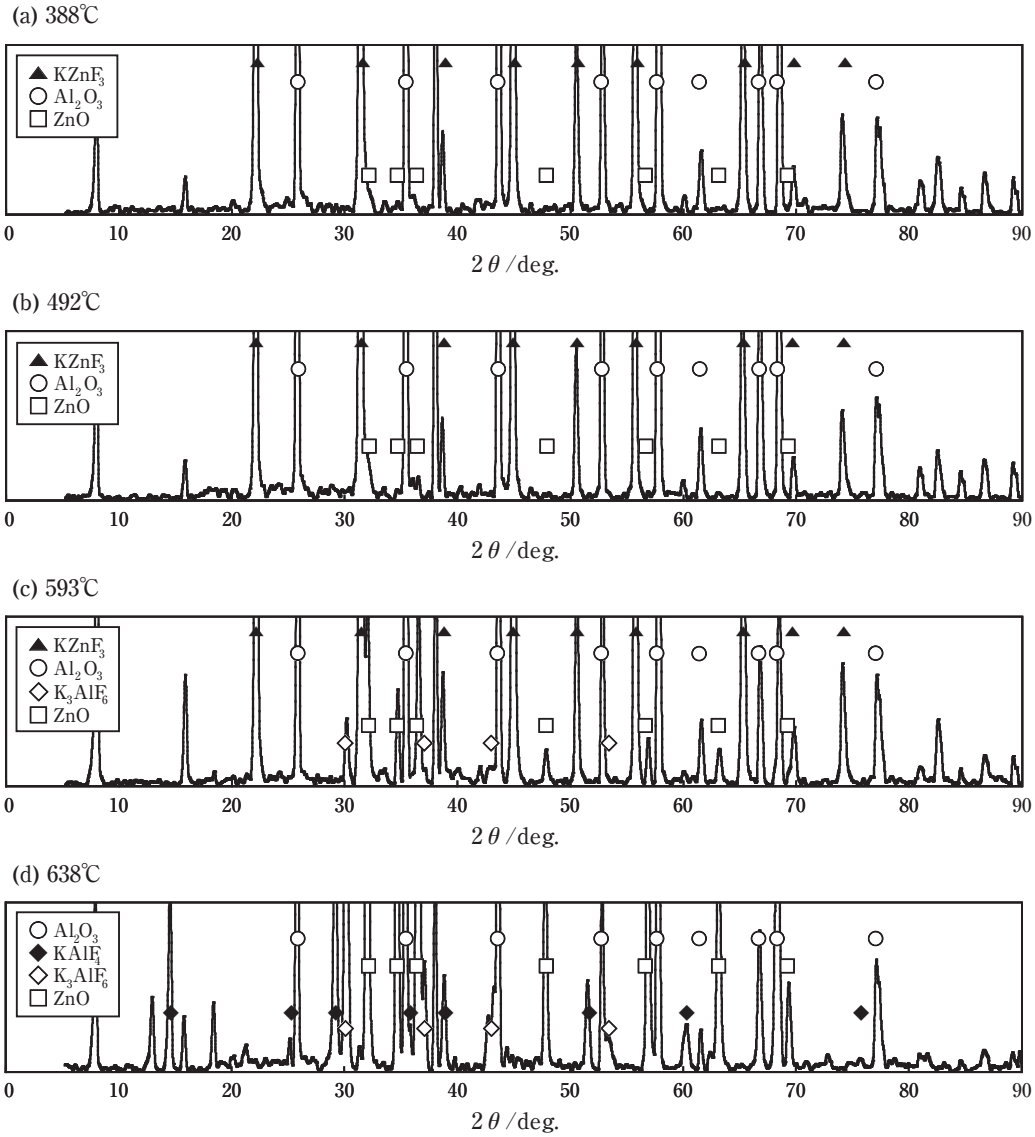



**Fig. 10** XRD patterns of P1 after TG-DTA.

#### 3.2.2 P2 ($KZnF_3$: 100%, Flow gas: Atmospheric air)

**Fig. 11** shows the results of the TG-DTA and **Fig. 12** shows the XRD patterns of P2 after the TG-DTA. For the validation of eqs. (6) and (7), $KZnF_3$ was heated in flowing air at the maximum temperatures of 388°C, 492°C, 593°C and 639°C. A slight exothermic peak was observed at approx. 600°C in the DTA curve, and the weight loss started at approx. 280°C in the TG curve. It was similar to the result of Fig. 9. In the XRD patterns, $KZnF_3$ and ZnO were detected at the maximum temperature of 388°C, 492 °C and 593 °C. $KZnF_3$, K3Zn2F7 and ZnO were detected at the maximum temperature of 639 °C. Therefore, in the case of heating $KZnF_3$ in a high concentration of $O_2$ and $H_2O$, it was considered that the reaction occurred not only by eqs. (6) and (7) but also by eq. (9). Especially, eq. (9) occurred at approx. 600°C.

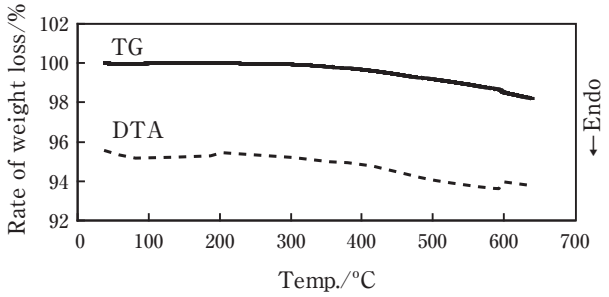



**Fig. 11** Results of TG-DTA for P2.

$$KF + 2KZnF_3 \rightarrow K_3Zn_2F_7 \quad (9)$$

Therefore, eq. (6) and (7) were validated.

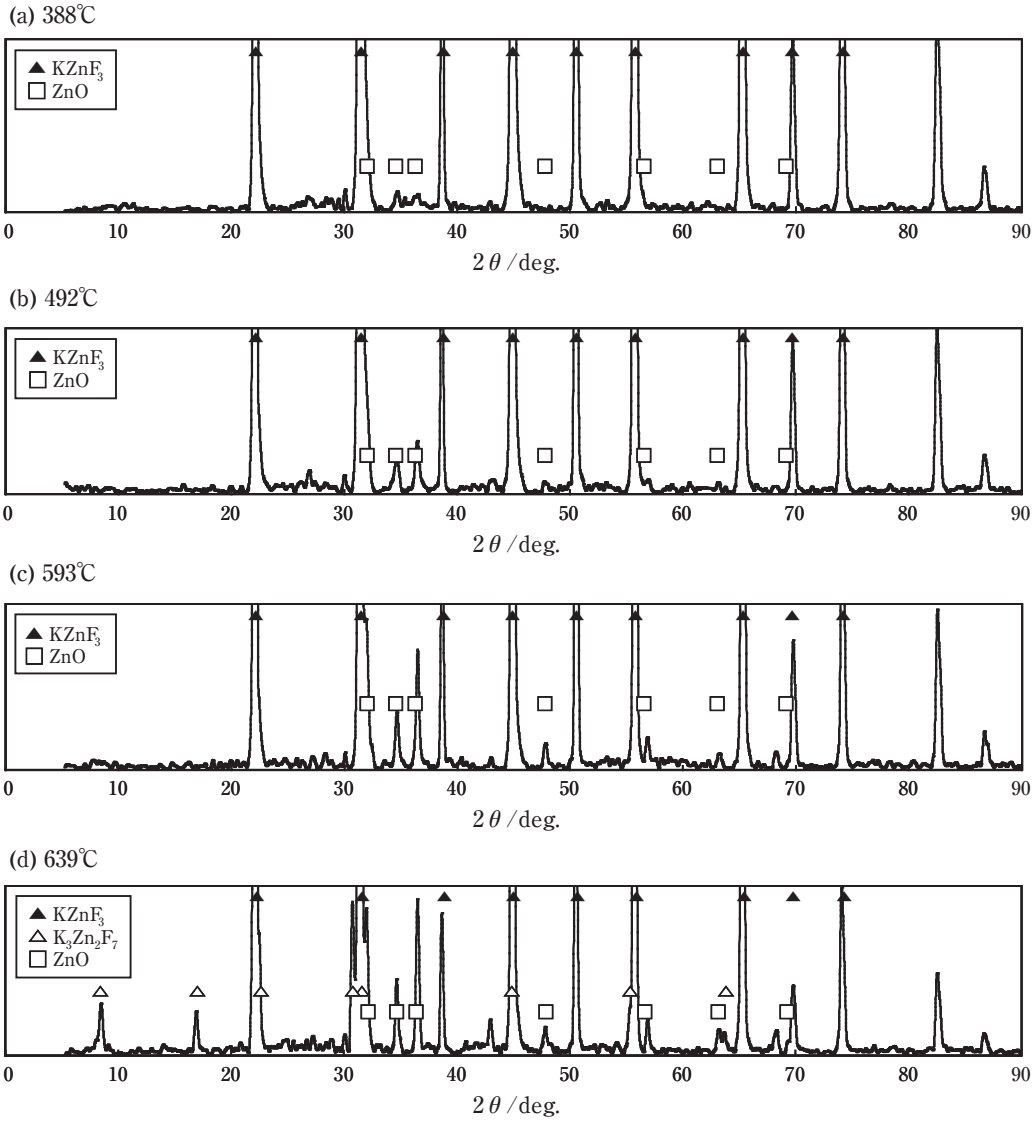



**Fig. 12** XRD patterns of P2 after TG-DTA

### 3.2.3 P3 (NC-flux: 50%, ZnO: 50%, Flow gas: Ar)

**Fig. 13** shows the TG-DTA curves of P3 and the NC-flux and **Fig. 14** shows the XRD patterns of P3 after the TG-DTA. For the validation of eq. (8), the NC-flux and ZnO were mixed and heated in flowing argon gas at the maximum temperatures of 385°C, 489°C, 589°C and 638°C. Clear endothermic peaks were observed at approx. 100°C and approx. 560°C in the DTA curve of both P3 and the NC-flux. A clear weight loss was observed at approx. 100°C and above approx. 380°C and approx. 550°C in the TG curve of both P3 and the NC-flux. As for the reason why the endothermic peak and the weight loss were observed at approx. 100°C, it was considered to be due to the vaporization of the hydrated water in the NC-flux. As for the reason why the endothermic peak and the

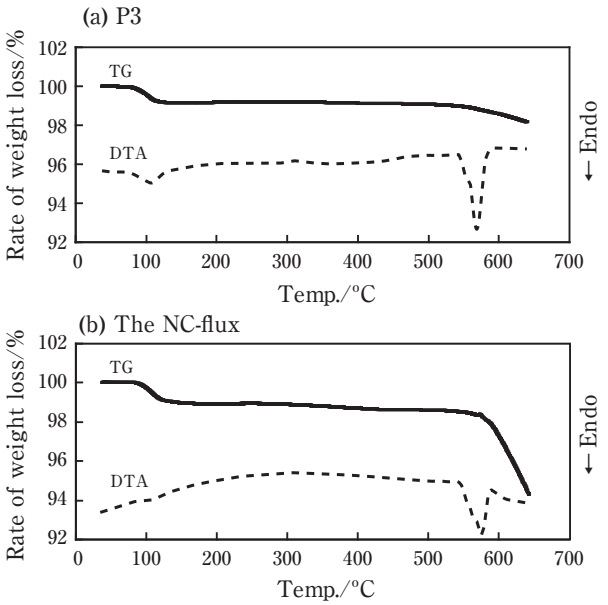



**Fig. 13** Results of TG-DTA for P3 and the NC-flux.

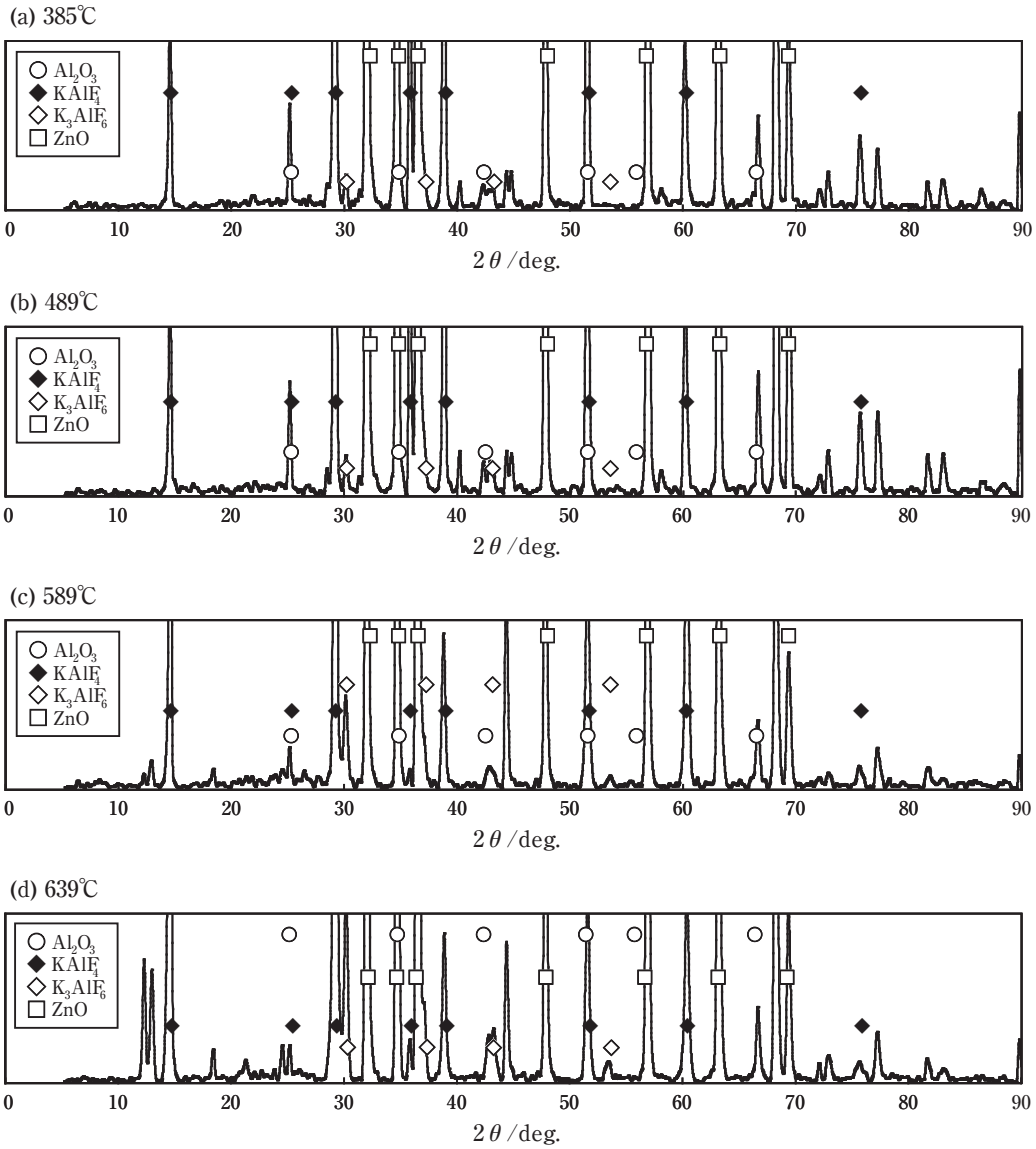



**Fig. 14** XRD patterns of P3 after TG-DTA.

weight loss were observed at approx. 560°C, it was considered to be the melting point of $KAlF_4$. In addition, for the relatively slight weight loss observed above approx. 380°C, it was considered that this weight loss indicated the emission of F gas and the vaporization of $KAlF_4$ [2]. The weight loss due to the vaporization of $KAlF_4$ was especially prominent above approx. 550°C, close to the temperature near the melting point of $KAlF_4$. In the XRD patterns, $KAlF_4$, $K_3AlF_6$, $Al_2O_3$ and ZnO were detected. Therefore, it was considered that eq. (8) occurred at approx. 380°C based on the weight loss at approx. 380°C. However, the reason why Zn produced by eq. (8) was not detected is unclear. For further validation in regard to the formation of Zn, it means the reduction of ZnO, and the additional brazing test shown in the next section.

### 3.3 Additional examination - Further validation for reduction of ZnO

**Fig. 15** shows the appearance of the mixture of the NC-flux and ZnO after brazing and **Fig. 16** shows the XRD patterns of the mixture after brazing. For further validation of eq. (8), the center of the dropped flux on the 3003 alloy sheet (25 mm × 25 mm) after brazing was analyzed by XRD. The black residue was observed on the dropped position of the specimens after brazing. In the XRD patterns, $KAlF_4$, $K_3AlF_6$, Zn and ZnO were detected. It was considered that the black residue was the agglomerated Zn shown in Fig. 7, because $K_3AlF_6$ prevented the Zn from diffusing into the aluminum base material. Therefore, eq. (8) was validated. However, the reason why Zn was not detected on P3 specimens after the TG-DTA whereas Zn was detected after this brazing test is still unclear. This reason was inferred that a produced Zn could not be detected by the XRD because of very slight, or a produced Zn was vaporized. Therefore, the condition of the TG-DTA is needed to rethink.

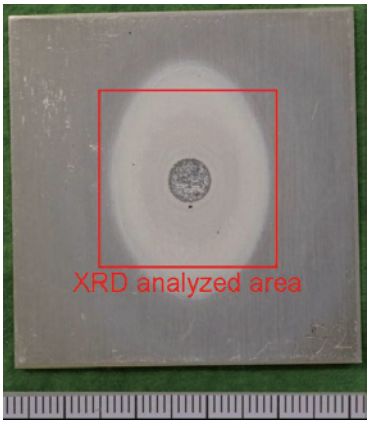



**Fig. 15** Appearance of the NC-flux+ZnO after brazing.

## 4. Conclusion

The reaction behavior of the NC-flux, $KZnF_3$ and their mixture during brazing were investigated.

(1) Regarding the NC-flux, $K_3AlF_6$ increased with the elevating temperature increase during brazing.

(2) Regarding $KZnF_3$, $KZnF_3$ reacted with the oxide film on the aluminum base material and $H_2O$ in the brazing atmosphere, subsequently ZnO was formed below 500°C. Finally, Zn was formed due to the reduction of ZnO by $KAlF_4$.

(3) Regarding the mixture of the NC-flux and $KZnF_3$, $KZnF_3$ reacted with the oxide film on the aluminum base material and $H_2O$ in the brazing atmosphere, then ZnO was formed below 400°C. In the temperature range of 400-500°C, Zn and $Al_2O_3$ were formed from the reductive reaction of ZnO by $KAlF_4$. These reactions occurred not only at the surface of

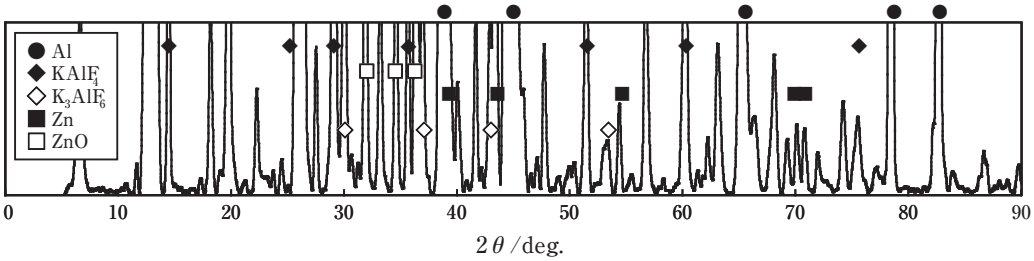



**Fig. 16** XRD patterns of the NC-flux+ZnO after brazing.

the aluminum base material but also all over the specimen. Furthermore, the $Al_2O_3$ formed by this reaction was used as the source of the reaction with $KZnF_3$. Consequently, $KZnF_3$ was completely consumed in the range of 400-500°C. Finally, Zn was formed due to the reduction of ZnO by $KAlF_4$.

## References

1) W. T. Thompson and D. W. G. Goad: Can. J. Chem., **54** (1976), 3342-3349.
2) T. Takemoto, A. Matsunawa and A. Kitagawa: Journal of Materials Science Letters, **15** (1996), 301-303.
3) P.G.Juan, H. W. Swidersky, T. Schwarze and J. Eicher: "Functionalized Inorganic Fluorides: Synthesis, Characterization and Properties of Nanostructured Solides (Ed. A. Tressud), Chapter 7. Inorganic Fluoride Materials from Solvay Fluor and their Industrial Applications", (2010), 210-211, Jhon & Sons, Ltd., Chichester, UK., doi: 10.1002/9780470660768. ch7.

Hidetoshi Kumagai
No. 4 Research Department, Research & Development Division, UACJ Corporation

Naoki Yamashita
No. 4 Research Department, Research & Development Division, UACJ Corporation