



Development of Flux and Filler Metal for Brazing Magnesium Alloy AZ31B

New flux and filler metals were developed to braze more easily and at lower temperatures than materials presently available

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ABSTRACT. This study was carried out to develop new flux and filler metal to braze magnesium Alloy AZ31B more easily at a lower temperature.

A flux was successfully developed consisting of CaCl_2 , LiCl , and NaCl with Ca and Li ions, which made the magnesium alloy surface active at around 450°C .

Additionally, brazing filler metals with a melting temperature below 480°C were successfully developed. Magnesium and indium were the main components, along with 0.2 to 6.4 wt-% zinc to lower the melting temperature.

With a small amount of zinc, the flux and filler metals achieved a joint with a high strength equivalent to the base metal. As the amount of zinc increased, the joint strength decreased.

Introduction

Magnesium and its alloys have been widely used in various fields because they are the lightest of the structural metals, and they possess excellent properties such as high specific strength, low density, good and economical processability with cast technology, and high recycling potential. Recent progress in rolling technology has improved the supply of magnesium plate; however, the development of welding technology for fabricating magnesium products or devices is still insufficient. In particular, there is very little information about brazing technology for joining wide faying surfaces (Refs. 1, 2).

References 1 and 2 have reported a few fluxes and filler metals for brazing magnesium alloys. Unfortunately, most of the fluxes and filler metals have higher melting temperatures than the igniting and

melting temperatures of many magnesium alloys. Therefore, they are not available to braze magnesium Alloy AZ31B, which is used in many applications.

Other previous works have reported on the flux and filler metal to braze magnesium alloys. For example, Markova et al. examined gaseous flux for brazing magnesium alloys and reported that the argon containing boron halides could not create conditions for wetting the filler metal over the magnesium surface, and that the argon containing ammonium chloride could braze the magnesium alloy coated previously with copper, nickel, or silver (Ref. 3). Lehrheuer et al. reported on Mg- or Zn-based filler metals containing Al, Mn, Zr, and Re for brazing magnesium alloys; however, there was no detailed information in the report (Ref. 4).

In this project, new flux and filler metals were developed for brazing magnesium Alloy AZ31B more easily at a lower temperature.

Capabilities of Known Fluxes and Filler Metals

The material used in this study is a rolled magnesium alloy plate AZ31B-H24 0.9 mm thick (hereafter, called the Mg alloy) with a main chemical composition of 2.8 wt-% Al and 0.9 wt-% Zn. The tensile strength is approximately 275 MPa,

the igniting temperature is 532°C , and the solidus is 565°C .

Tables 1 and 2 show the three types of fluxes (Refs. 1, 2) and filler metals (Ref. 2) known for brazing Mg alloys. Both No. 1 and No. 3 fluxes in Table 1 are not available for brazing the Mg alloy because their melting points are higher than the base metal. Furthermore, none of the filler metals shown in Table 2 can be used to braze the Mg alloy because the melting point is higher than the igniting temperature of the base metal.

Therefore, preliminary experiments were conducted to determine whether No. 2 flux in Table 1 could be used to braze the Mg alloy. Based on the preliminary experiments, No. 2 flux would not wet the filler metal developed in this study on the Mg alloy surface. It proved unsatisfactory for brazing the Mg alloy.

Development of Flux for Brazing Mg Alloy

It is well known that the Mg alloy surface is covered with a thick oxide film of MgO (Ref. 5), which is very stable and difficult to reduce. However, the Ellingham diagram (Ref. 6) suggests that active ingredients containing Ca or Li have a great ability to reduce the Mg oxide. In this study, we tried to produce fluxes containing Ca and Li elements based on the CaCl_2 - LiCl - NaCl system phase diagram and CaCl_2 - LiCl - KCl system phase diagram shown in Figs. 1 and 2, respectively (Ref. 7).

Referencing the phase diagrams, eight kinds of flux compositions were selected (Table 3), which were expected to have a melting point of about 450°C . The numbers indicated in the phase diagrams in Figs. 1 and 2 mark the compositions of the selected fluxes. The capability of these fluxes to reduce the oxide was evaluated by the filler metal wetting area on the Mg alloy. The shape of the Mg alloy for the

KEY WORDS

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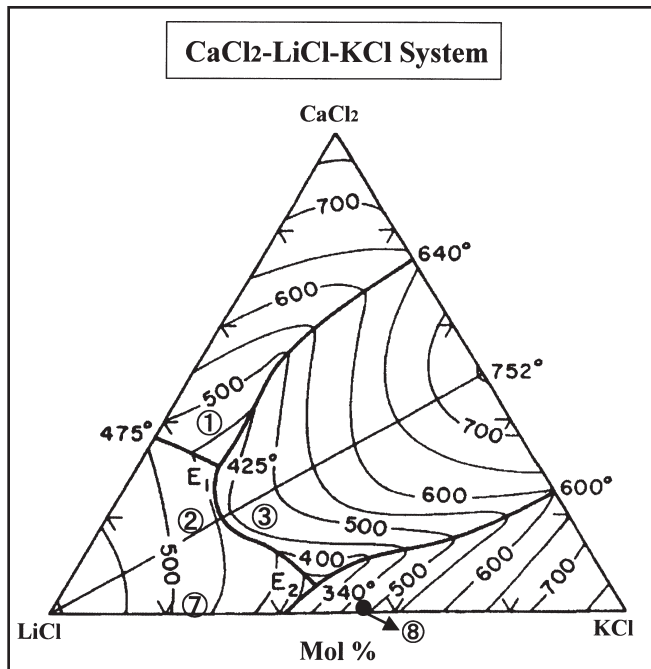


Fig. 1 — Equilibrium phase diagram of $\text{CaCl}_2\text{-LiCl-KCl}$ system. The circled numbers show the flux compositions examined in this study.

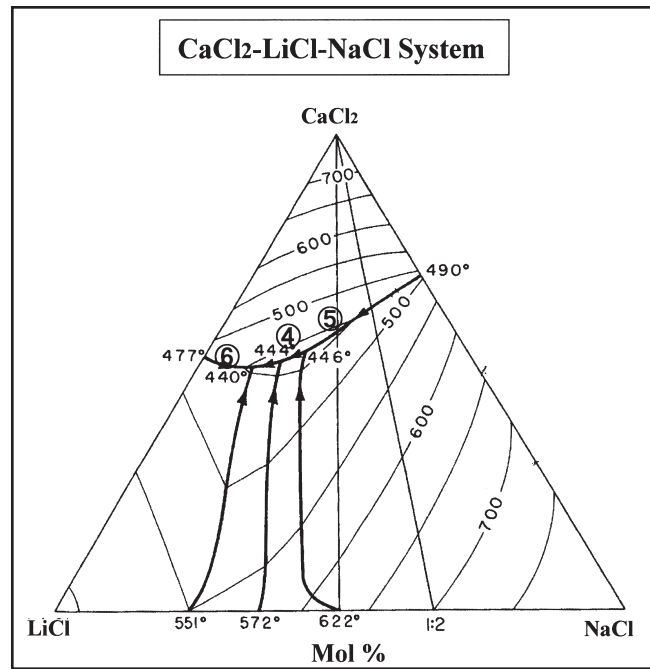


Fig. 2 — Equilibrium phase diagram of $\text{CaCl}_2\text{-LiCl-NaCl}$ system. The circled numbers show the flux compositions examined in this study.

Table 1 — Chemical Composition and Melting Point of Conventional Fluxes for Brazing Magnesium

| | KCl | NaCl | LiCl | NaF | CaCl ₂ | Melting Temp. (°C) |
|-------|-----|------|------|-----|-------------------|--------------------|
| No. 1 | 45 | 25 | 23 | 6 | 0 | 538 |
| No. 2 | 43 | 10 | 37 | 10 | 0 | 388 |
| No. 3 | 54 | 12 | 0 | 4 | 30 | 535 |

Note: mass-%

Table 2 — Chemical Composition, Solidus, and Liquidus of Conventional Filler Metals for Brazing Magnesium

| | Al | Zn | Mn | Be | Solidus (°C) | Liquidus (°C) |
|--------|------|-----|-----|--------|--------------|---------------|
| BMg-1 | 9.0 | 2.0 | 0.1 | 0.0005 | 443 | 599 |
| BMg-2 | 12.0 | 5.0 | — | — | 410 | 566 |
| BMg-2a | 12.0 | 5.0 | — | 0.0005 | 410 | 566 |

Note: mass-%

Table 3 — Chemical Composition of Fluxes Examined in This Study

| | CaCl ₂ | LiCl | KCl | NaCl |
|---|-------------------|------|------|------|
| 1 | 40.0 | 51.5 | 8.5 | — |
| 2 | 20.0 | 64.8 | 15.2 | — |
| 3 | 20.0 | 52.2 | 27.8 | — |
| 4 | 55.5 | 29.8 | — | 14.7 |
| 5 | 59.7 | 18.5 | — | 21.8 |
| 6 | 51.3 | 42.2 | — | 6.5 |
| 7 | — | 74.7 | 25.3 | — |
| 8 | — | 46.5 | 53.5 | — |

Note: mol-%

wetting test was a square 30 mm in length. The surface of the plate was chemically cleaned by immersion into 5 vol-% hydrofluoric acid solution for 5 min after wet polishing using a 400-grit emery paper. Approximately 50 mg of the developed filler metal (4 Zn), shown in Table 4, was set on the Mg alloy plate together with about 50 mg of flux. The heating cycle for the test was as follows: The plate was heated to 460°C at the heating rate of 10°C/s and was held for 30 s, followed by cooling. The wetting area of the filler metal was measured on a photograph taken after the test to evaluate the ability of the flux.

Figure 3 shows the wetting test results for eight kinds of fluxes. Circled numbers 1 to 3 correspond to fluxes of the $\text{CaCl}_2\text{-LiCl-NaCl}$ system, and circled numbers 4 to 6 correspond to fluxes of the $\text{CaCl}_2\text{-LiCl-KCl}$ system. Since the maximum spread area was obtained with the circled number 5 flux, the following experiments for brazing were conducted using flux circled number 5 (59.7% CaCl_2 -18.5% LiCl -21.8% NaCl [mol-%]). The circled numbers 6 and 7 fluxes, which were composed of only LiCl and KCl , were used to examine the effect of CaCl_2 on the wetting. Consequently, it was shown that the fluxes without CaCl_2 also had the ability to wet filler metal.

Development of Filler Metal for Brazing the Mg Alloy

Since the liquidus of the filler metals shown in Table 2 is higher than that of the Mg alloy, a filler metal with a melting point lower than 480°C was attempted. After surveying binary phase diagrams to find alloying elements suitable for brazing the Mg alloy, the elements of Mg, Cd, Pb, and In were nominated as candidates for the filler metal because they make solid solution and intermetallic compounds are difficult to form with Mg. The elements Mg and In were finally selected to produce the filler metal because Cd and Pb are harmful to human beings and the environment.

Figure 4 shows the equilibrium phase diagram for the Mg-In system. The dia-

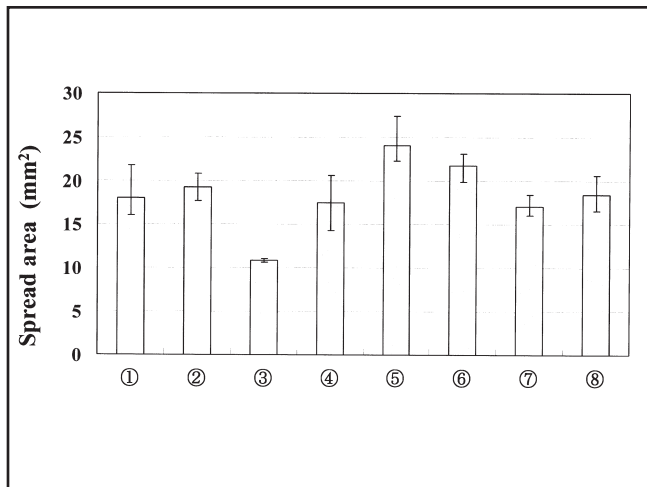


Fig. 3 — Wetting area of the eight fluxes examined in this study.

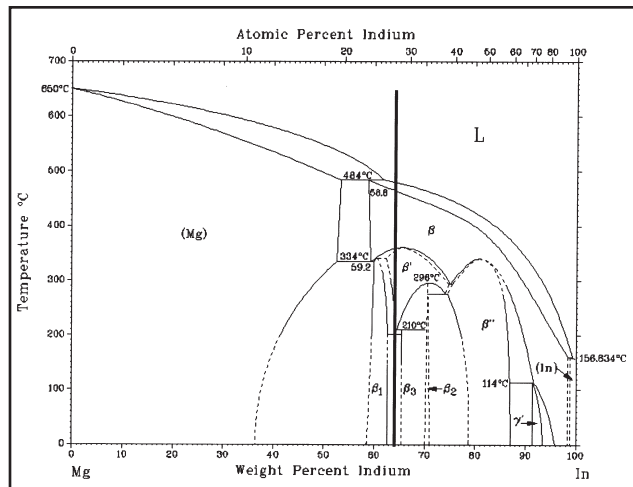


Fig. 4 — Equilibrium phase diagram of Mg-In system.

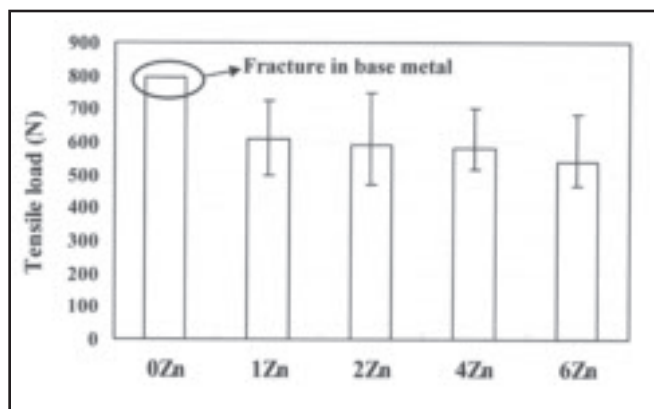


Fig. 5 — Cross tensile load of the joint brazed using filler metals developed in this study.

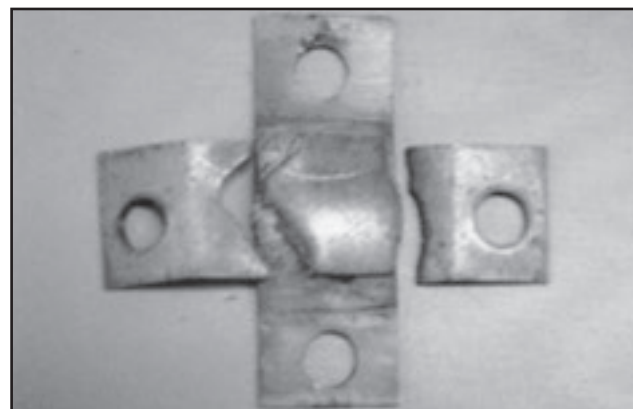


Fig. 6 — Appearance of the joint broken at the base metal after tensile test.

gram shows there is a peritectic point at the concentration of 58 mass-% In, and the peritectic temperature is 484°C. Six kinds of alloys were produced that consisted of 65 mass-% In and Mg, and they contained Zn as a depressant to attain a melting point below 480°C. The experimentally produced filler metals are summarized in Table 4. The table shows the composition, liquidus, Vicker's hardness, and the brazing temperature for the filler metals. The Al in the filler metal is attributed to the Mg alloy AZ31B being used as a raw material to make the filler metal.

Brazing Experiments

Rectangular specimens of 15-mm width, 30-mm length and 0.9-mm thickness were brazed in a lap joint. The brazing surfaces were painted with the circled number 5 flux using about 50 mg. Brazing filler metal was then put on the brazing surface, and the specimens were placed crosswise on a stainless steel stage plate. They were heated by induction heating, and a K-type thermocouple was welded to

the back of the test specimen to track the temperature. No weight was loaded on the specimens during brazing. The heating cycle for brazing was the same as that for the wetting test described previously. Brazing was conducted at a temperature of approximately 10°C higher than the liquidus of each filler metal, as shown in Table 4.

The cross tensile testing was carried out using a jig for cross-shaped joints, and the maximum load obtained in the tensile test was adopted as the cross tensile strength of the joint.

The structure of the brazed layer was characterized with a scanning electron microscope (SEM) and an optical microscope, and was analyzed with EDS.

Strength and Microstructure of a Brazed Joint

Brazed Joint Strength

Figure 5 summarizes the cross tensile load of the joints brazed using the newly developed filler metals of 0 Zn to 6 Zn.

The strength of the joint brazed with 0 Zn filler metal (34.5 mass-% Mg; 64.5 mass-% In), which contained a small amount of Zn, was the greatest. The brazed joint broke in the base metal in the strength test. Figure 6 shows the appearance of the joint broken in the base metal, which was brazed using 0 Zn filler metal. The strength of a brazed joint decreased as the Zn content increased in the filler metal.

Microstructure at the Brazed Layer

Scanning electron microscope photographs and EDS analyses of Zn at the brazed layer with 0 Zn, 2 Zn, 4 Zn, and 6 Zn are shown in Fig. 7. Both upper and lower regions in the photographs correspond to the Mg alloy base metal. In the brazed layer with 0 Zn filler metal, Mg primary crystal (Arrow 1) and the phases having peritectic composition (Arrows 2 and 3) were observed. The EDS mapping analysis of Zn shows there is no segregation of Zn in the brazed layer. However, as the content of Zn in the filler metals 2 Zn to 6 Zn increased, more phases enriched

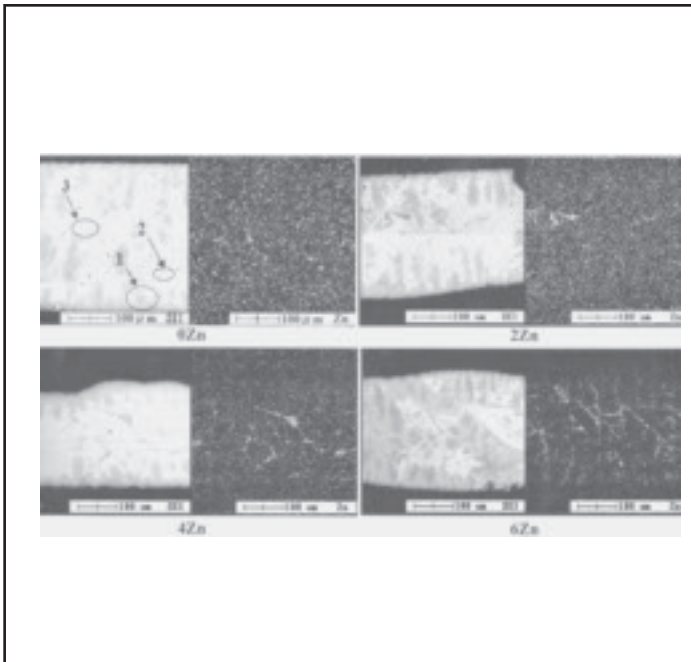


Fig. 7 — Microstructure and EDS mapping analysis of Zn in the brazed layers with 0 Zn, 2 Zn, 4 Zn, and 6 Zn filler metals.

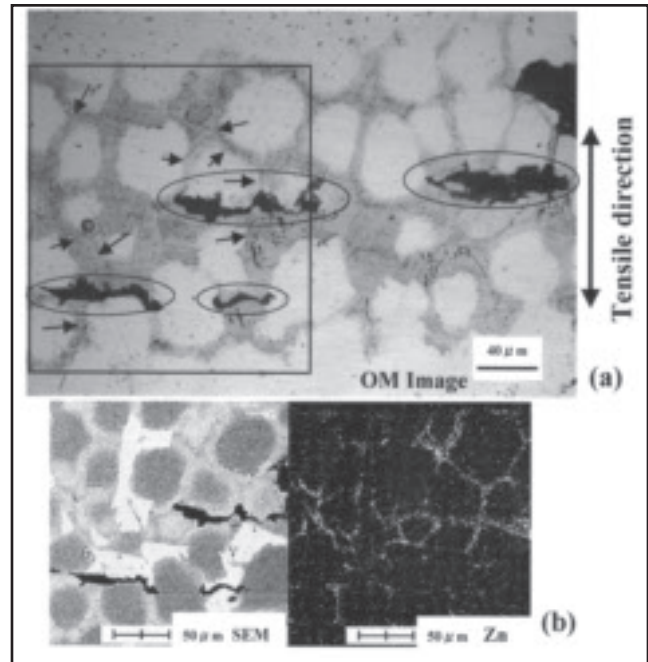


Fig. 8 — Optical and SEM micro images of the crack path that appeared in the brazed layer with 6 Zn filler metal and EDS mapping analysis of Zn.

Table 4 — Chemical Composition, Hardness, Liquidus, and Brazing Temperature of New Filler Metals Developed in This Study

| | Chemical Composition | | | | Hardness HV | Liquidus (°C) | Brazing Temp. (°C) |
|-----|----------------------|------|-----|-----|----------------|------------------|-----------------------|
| | Mg | In | Zn | Al | | | |
| 0Zn | 34.5 | 64.5 | 0.2 | 0.8 | 110 | 476 | 490 |
| 1Zn | 33.4 | 64.6 | 1.2 | 0.8 | 121 | 471 | 480 |
| 2Zn | 32.8 | 64.2 | 2.2 | 0.8 | 132 | 467 | 480 |
| 4Zn | 30.6 | 64.3 | 4.3 | 0.8 | 155 | 451 | 460 |
| 6Zn | 27.8 | 65.1 | 6.4 | 0.7 | 170 | 449 | 460 |

Note: mass-%
Base metal hardness of AZ31B:HV72

with Zn appeared, as shown in the brazed layers with 4 Zn and 6 Zn filler metals. EDS quantitative analysis of the phase in the brazed layer with the 6 Zn filler metal showed the composition of this phase was 59.45% Mg-15.16% Zn-10.98% In-6.14% Al-7.82% O (at-%), and this phase was considerably enriched with Zn.

Figure 5 shows the cross tensile load of the brazed joint decreases with increasing Zn content in the filler metal. Since the above fact seems to relate to the formation of the Zn-enriched phase in the brazed layer, the microstructure of the joint brazed with 6 Zn filler metal was examined after stopping the cross tensile test at the load of 400 N, which corresponds to about 75% of the ultimate cross tensile strength of the joint. Figure 8 shows the optical microstructure of the joint after the cross tensile test was stopped. Many cracks (enclosed by circles) occurred in the brazed layer, as shown in Fig. 8A. Figure 8B shows the SEM photograph and Zn

mapping analysis by EDS in the region surrounded by a rectangular in Fig. 8A. Figure 8 proves that Zn enriches in the narrow band-like phases indicated by arrows, and the cracks occur along these Zn-enriched phases. It seems the decrease in the cross tensile load of the joint as the Zn increased in the filler metal is attributed to the formation of the narrow band-like Zn-enriched phases along which cracks propagate easily.

Conclusions

New flux and filler metals to braze AZ31B magnesium alloy plate at temperatures below 490°C were developed. The main results obtained in this study are as follows:

1) There was success in developing a new flux consisting of CaCl₂, LiCl and NaCl, which enabled magnesium alloy plate to be brazed at temperatures below about 450°C.

2) In order to braze the magnesium alloy, new filler metals with a melting point below 480°C were successfully developed. They consisted of magnesium, indium, and zinc. The joint brazed with the filler metal containing approximately zero Zn showed high cross tensile strength, equivalent to that of the base metal. In addition, the cross tensile load of the brazed joint decreased as the Zn content in the filler metal increased.

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