Liquid phase diffusion bonding of A1070 by using metal formate coated Zn sheet

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Abstract. Aluminium alloy have high strength and easily recycle due to its low melting point. Therefore, aluminium is widely used in the manufacturing of cars and electronic devices. In recent years, the most common way for bonding aluminium alloy is brazing and friction stir welding. However, brazing requires positional accuracy and results in the formation of voids by the flux residue. Moreover, aluminium is an excellent heat radiating and electricity conducting material; therefore, it is difficult to bond together using other bonding methods. Because of these limitations, liquid phase diffusion bonding is considered the suitable method for bonding aluminium at low temperature and low bonding pressure. In this study, the effect of metal formate coating processing of zinc surface on the bond strength of the liquid phase diffusion bonded interface of A1070 has been investigated by SEM observation of the interfacial microstructures and fractured surfaces after tensile test. Liquid phase diffusion bonding was carried out under a nitrogen gas atmosphere at a bonding temperature of 673 K and 713 K and a bonding load of 6 MPa (bonding time: 15 min). As a result of the metal formate coating processing, a joint having the ultimate tensile strength of the base aluminium was provided. It is hypothesized that this is because metallic zinc is generated as a result of thermal decomposition of formate in the bonded interface at lower bonding temperatures.

1. Introduction
In the past, methods such as brazing, friction stir welding and laser welding have been used for bonding aluminium alloy [1, 2]. However, the adverse effect of the flux has on the environment is also something need to be concerned [3]. In addition, these methods have some shortcomings: (1) a high heat input is required to compensate for high heat radiation and (2) micro cracks are developed owing to the softening of the weld zone. Moreover, tools used for friction stir welding have short lifespan and this translates to higher running costs. Hence, in this study, liquid phase diffusion bonding method is considered the most suitable method for bonding of A1070. In liquid phase diffusion bonding, materials are bonded together by applying heat and pressure to promote interdiffusion without significant deformation. Moreover, since liquid phase diffusion bonding involves only low bonding temperature, there is little damage to a component, thus making this technique suitable for bonding precision assemblies. However, a bonding surface has various defects such as surface irregularities, a native oxide film and a processing layer, which act as inhibitors to successful bonding.
In this study, liquid phase diffusion bonding of A1070 with Zn sheet is carried out on Zn sheet surfaces treated for metal salt coating processing using formic acid. The bonded surfaces were then examined to determine the effectiveness of metal salt coating processing.

2. Experimental details
As shown in Figure 1(a), the pure Zn sheet specimen (thickness: 0.1, 0.8 and 2.0 mm, 99.9% purity) with dimensions of 11 × 11 mm were used. As shown in Figure 1(b), the aluminum specimen is a cylindrical bar cut from A1070 (Table 1). The bonding surface is polished by a #1200 emery paper. In addition, the reason why a Zn sheet was chosen as an insert metal is because a liquid phase is generated by a reaction with the base aluminum and it is supposed that the molten metal fills the gap of the bonding interface. Zn sheet surfaces were modified by boiling in formic acid for optimum time for metal salt coating on the bonding surface. Furthermore, grazing-angle incidence reflection-absorption infrared (GIRAS-IR) spectroscopy was employer to obtain IR spectra at a nanometer-scale depth from the modified zinc surface.

Liquid phase diffusion bonding is performed under a nitrogen gas (99.99% purity) atmosphere using the following conditions; 6 MPa for bonding load, 15 min for bonding time and 673 K and 713 K for bonding temperature. In addition, the effect of the thickness and the modification time of the Zn sheet on the tensile strength of joint is investigated.

After liquid phase diffusion bonding, the joint strength is evaluated using a tensile tester. The tensile test is carried out using INSTRON 5567 universal test machine at room temperature at a displacement speed of 10 mm/min.

Further, a specimen showing the vertical cross-section of the bonded interface was also prepared and was observed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) performed at an acceleration voltage of 15 kV.

3. Results and discussion

3.1. Optimization of the Zn sheet thickness and metal formate coating processing time
To examine the effect of the Zn sheet thickness has on the bond strength of joint, tensile test is carried out after liquid phase diffusion bonding is performed using different Zn sheet thickness ranging from 0.1 ~ 2.0 mm. The bonding temperature is fixed at 673 K and 713 K and the relationships between Zn sheet thickness and tensile strength are shown in Figure 2. As shown in Figure 2, the highest bond strength joints were obtained when the Zn sheet thickness was 0.8 mm at both bonding temperatures.

Table 1. Chemical compositions of A1070 aluminium used in this study (UACJ Corporation, Japan).

| Elements | Si | Fe | Cu | Mn | Zn | Ti | V | Al |
|----------|----|----|----|----|----|----|---|----|
| mass%    | 0.05 | 0.13 | 0 | 0 | 0 | 0 | 0.02 | Bal. |

Figure 1. Schematic illustration of to-be-bonded specimen: (a) pure Zn sheet and (b) A1070.

Figure 2. Relationship between bond strength and thickness of Zn sheet.
From this examination results, when the Zn sheet thickness is thin, the roughness of the bonding surface was not filled; and when the thickness is the optimum thickness, Zn-Al eutectic structure (tensile strength is higher than A1070) was remained in the bonded interface. On the other hand, when the Zn sheet thickness is thick, solidification crack occurred at the bonded interface, and the bond strength decreased. From these reasons, it was determined that the optimum Zn sheet thickness to use in this study is 0.8 mm.

Figures 3 and 4 shows the relationship between the modification time and bond strength. The highest bond strength joint were obtained when the metal formate coating processing time was 5 min at both bonding temperature. From these examination results, when the metal formate coating processing time is short, the zinc oxide film is not substituted to a zinc formate; and when the time is long, an excessive quantity of the formate (oxide and gas is generated at the time of thermolysis) is generated. Therefore, it was determined that the optimum modification time to use in this study is 5 min.

3.2. Effect of metal formate coating processing on the bond strength

Figure 5 shows the relationship between the bond strength of the joint and the bonding temperature when the optimum conditions discussed in section 3.1 were applied. In order to illustrate the effect of metal formate coating processing, the corresponding relationship for a non-modified joint are also shown. As shown in Figure 5, the bond strength decreased with bonding temperature irrespective of metal formate coating processing. However, the bond strength of the joint has about 2 times higher the strength than that of non-modified joint and has the ultimate tensile strength of the base A1070 aluminum at the bonding temperature of 713 K. Furthermore, all the joints broken at the bonded interface and necking was observed in all of them.

![Figure 3](image1.png)  ![Figure 4](image2.png)  ![Figure 5](image3.png)
3.3. Observation of fractured surface

Figures 6 and 7 show the fractured joint surface after the tensile test for specimens bonded at 673 K and 713 K. As shown in Figure 6, when the bonding temperature of 673 K, ductile fracture characteristics were observed irrespective of metal formate coating processing. However, when the metal formate coating processing was not applied, brittle fracture characteristics were observed, although it was not observed when the metal formate coating processing was applied. In addition, when the metal formate coating processing was applied, Zn was detected in more areas compared with the case that the coating processing was not applied. It is therefore thought that a high-bond strength joint was obtained at a same bonding temperature with metal formate coating processing because zinc formate in the bond interface underwent a thermal decomposition reaction and eutectic reaction after close contact between zinc and aluminum was achieved to mention it later.

With a rise in bonding temperature of 713 K, the bond strength were decreased irrespective of metal formate coating processing. The reason for this is because molten zinc was exhausted to the circumference of the junction by a zinc sheet reaching a melting point at this bonding temperature. In addition, when the metal formate coating processing was not applied, the bond strength was very low. The reason for this is because an oxide film of the molten zinc surface inhibited a eutectic reaction with an aluminum base metal.

3.4. Observation of bonded interface

To determine the relationship between interfacial microstructure and bond strength, the bonded interface was observed by SEM. Figure 8 shows SEM micrographs of the bonded interface. When the bonding temperature of 673 K, a lamellar structure with a thickness of about 5 µm was observed irrespective of metal formate coating processing. As a result of the EDX analysis, this lamellar structure revealed that it was a eutectic structure containing about 30 mass% Zn. When the metal formate coating processing was not applied, black-colored thin layer with a thickness of about 1 µm were observed between lamellar structure and an aluminum base metal. As a result of the EDX analysis, this black-colored thin layer revealed that it was zinc oxide, namely a zinc oxide film.
With a rise in bonding temperature of 713 K, when the metal formate coating processing was applied, a divided lamellar structure was observed. However, when the metal formate coating processing was not applied, almost none of the lamellar structure was observed. Therefore, it is inferred that the promotion of the eutectic reaction with an aluminum base metal by applying the metal formate coating processing greatly had an influence on the improvement of the bond strength.

3.5. Chemical analysis of metal formate coating surface
Figure 9 shows the FT-IR analysis result of the Zn sheet surface before and after metal formate coating processing. As shown in Figure 9, the absorption bands of about 1637 and 1504 cm \(^{-1}\) correspond to a carboxyl ligand. When the thermal decomposition of Zinc formate were occurred in a bonding process, the compound thermally decomposed in to nano particles of zinc oxide and several kind of gases at temperature of 560 K or more \([4, 5]\). It is therefore thought that a high-bond-strength joint was obtained at a lower bonding temperature with metal formate coating processing because zinc formate underwent a thermal decomposition reaction after close contact between Al1070 and Zn atomic plane was achieved.

4. Conclusions
The conclusions of this study are summarized as follows.
(1) From the FT-IR spectrum, it is revealed that zinc formate, for which the decomposition reaction occurs at a low temperature is formed by metal formate coating processing on the zinc surface.
(2) A higher bond strength can be achieved at the same bonding temperature through the use metal formate coating processing.
(3) The increase surface area of the metallic-Zn promotes the eutectic reaction between Zn sheet and Al1070 base metal contributes to increase of bond strength of joint.

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