TEM Observation of Interfaces between Particles in Al–Mg Alloy Powder Compacts Prepared by Pulse Electric Current Sintering \(^*\)

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Aluminum–Magnesium (Al–Mg) alloy powders with various amounts of Mg addition were sintered using the pulse electric current sintering (PECS) process. The behavior of Mg in the surface oxide film and the effect of Mg amounts on characteristics of the interfaces between Al–Mg alloy powders were investigated using transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The results showed that there were interfaces of direct metal/metal bonding and metal/oxide layer/metal bonding for all Al–Mg alloy powders compacts. In pure Al powder compacts, the oxide layer in the interface was amorphous alumina. And precipitates were observed in the bonding interface for the alloys powders compacts with Mg addition. The amounts of the precipitates increased, and the compositions of the precipitates changed with an increase in Mg amount in the alloys powders: MgAl\(_2\)O\(_4\) for Al–0.3Mg, MgAl\(_2\)O\(_4\) + MgO for Al–1.0Mg, and MgO for Al–2.5, 10Mg alloy powders compacts.

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1. Introduction

The surfaces of aluminum (Al) particles and its alloy powders are covered with an oxide film layer. The oxide layer is tenacious and cannot be broken and/or removed by heat, preventing solid-state sintering. It is difficult to sinter the powders by conventional hot press sintering processes.\(^{1–3}\) In order to achieve effective sintering, the surface oxide layer needs to be removed and/or reduced. The previous investigations have shown some effective methods to remove and/or reduce the surface oxide film, for example, the use of liquid phases in the solid-state sintering,\(^{4}\) mechanical breakdown by friction between surfaces,\(^{5,6}\) ion beam bombardment treatment in a vacuum chamber,\(^{7,8}\) the use of active alloying elements such as magnesium (Mg) and lithium (Li),\(^{9–12}\) and so on.

Recently, much attention has been paid to the pulse electric current sintering (PECS) process, which is regarded as one of the most advanced materials processing. Some researchers call this process plasma-activated sintering (PAS),\(^{13}\) or spark plasma sintering (SPS).\(^{14}\) In the PECS process, pulse electric current flows directly in the sintered materials and mold. A very high heating efficiency is offered. It can easily consolidate a high quality compact that is sintered at a lower sintering temperature and in a shorter time than the conventional processes, even to those materials that are very difficult to be sintered by the other processes. It has been reported that Al metal powders\(^{15,16}\) and its compounds powders\(^{13}\) have been sintered using the PECS process. The PECS process improved densification of Al metal and its compounds powders. The breakdown of a surface oxide film layer was confirmed, and the effects of oxide film behavior between powder particles on tensile properties and electrical resistivity of powder compacts were shown. Recently, we have carried out sintering of Al alloy powders containing Mg as an active alloying element using the PECS process. It caused an obvious improvement on the tensile properties and a decrease of the electrical resistivity of powder compacts by the Mg addition. In order to understand the cause of the properties improvement, the microstructures of the interfaces between powder particles were investigated by means of transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). In the present study, Al–Mg alloy powders with various amounts of Mg addition (0, 0.3, 1.0, 2.5, 10 mass%) were sintered using the PECS process. The behavior of Mg in the surface oxide film and the effect of the amount of Mg on interface characters were investigated.

2. Experimental Methods

Al–Mg alloy powders with different magnesium contents were used in the present study. The particle size distributions of the starting powders are presented in Table 1. The chemical compositions of the alloy powders are shown in Table 2.

The sintering was carried out in a vacuum using a pulse electric current sintering system (SPS-520 model; Izumi Technology Company, Ltd.). The sintering temperature (\(T_s\)) used was about 0.72 times as the solidus temperature of the alloys in this study, namely, 673 K, 673 K, 663 K, 643 K and 573 K for Al–0, 0.3, 1.0, 2.5 and 10Mg alloys, respectively. The heating speed was 50 K/min (room temperature to \(T_s\)-50 K) and 12.5 K/min (\(T_s\)-50 K to \(T_s\)). The holding time at the sintering temperature was 5 min. The pulse frequency was 40 kHz. The loading pressure was 23.5 MPa. The uniaxial pressure model was conducted using the top and bottom graphite punches. The shape of the powder compacts obtained by the PECS process was that of the tensile speci-
Microstructural analyses of the interfaces between powder particles in the compacts were carried out using TEM and EDS. Thin foil specimens were cut from the Al–Mg alloy powder compacts by a diamond saw, ultrasonically cut into 3 mm diameter disks and mechanically thinned followed by dimpling and ion milling to electron transparency for TEM observations. Conventional and high resolution transmission electron microscopy (CTEM and HRTEM) experiments and EDS analyses were performed at room temperature using a JEM-ARM 1000 TEM equipped with an EDS system. The system was operated at 1000 kV for TEM observation and at 400 kV for EDS analysis. The diameter of the electron beam for the EDS analysis was about 100 nm.

### Table 1
Particle size distributions of Al–Mg alloys powders.

<table>
<thead>
<tr>
<th>Powder</th>
<th>10</th>
<th>40</th>
<th>40</th>
<th>10</th>
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</thead>
<tbody>
<tr>
<td>Al</td>
<td>below 16.72 µm</td>
<td>16.72–40.83 µm</td>
<td>40.83–80.41 µm</td>
<td>over 80.41 µm</td>
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<tr>
<td>Al–0.3Mg</td>
<td>below 16.04 µm</td>
<td>16.04–46.87 µm</td>
<td>46.87–145.3 µm</td>
<td>over 145.3 µm</td>
</tr>
<tr>
<td>Al–1.0Mg</td>
<td>below 16.24 µm</td>
<td>16.24–49.93 µm</td>
<td>49.93–130.6 µm</td>
<td>over 130.6 µm</td>
</tr>
<tr>
<td>Al–2.5Mg</td>
<td>below 16.75 µm</td>
<td>16.75–46.96 µm</td>
<td>46.96–120.9 µm</td>
<td>over 120.9 µm</td>
</tr>
<tr>
<td>Al–10Mg</td>
<td>below 16.92 µm</td>
<td>16.92–48.84 µm</td>
<td>48.84–153.3 µm</td>
<td>over 153.3 µm</td>
</tr>
</tbody>
</table>

### Table 2
Chemical compositions of Al–Mg alloys powders.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Composition (mass%)</th>
<th>Al</th>
<th>Mg</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Zn</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>99.81 0.01 0.06 0.12 TR* TR TR TR</td>
<td></td>
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<tr>
<td>Al–0.3Mg</td>
<td>99.68 0.25 0.05 0.02 TR TR TR TR</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Al–1.0Mg</td>
<td>98.68 1.10 0.22 TR TR TR TR TR</td>
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<td></td>
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<tr>
<td>Al–2.5Mg</td>
<td>97.51 2.44 0.05 TR TR TR TR TR</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al–10Mg</td>
<td>91.04 8.92 0.03 0.01 TR TR TR TR</td>
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</table>

*: TR indicates below 0.01 mass%.

3. Results and Discussion

For the pure Al powder compact (Al–0 mass%Mg powder compact) produced by the PECS process, TEM observations and EDS analyses showed that there were two types of interfaces in the powder compacts. One is the direct metal/metal bonding interface. The other is the metal/intermediate layer/metal bonding interface. The intermediate layer is amorphous with a thickness of about 10 nm. An EDS spectrum obtained from the interface region including the intermediate layer demonstrated that there were aluminum and oxygen elements in the region. It is suggested that the intermediate layer results from the oxide film originally covered in the surface of the powder particle. Similar results were shown in details elsewhere.\(^{17}\) For the breakdown of the oxide film at the Al powder surface, it has been suggested that it is mainly caused by plastic deformation of powder particles under loading pressure.\(^{15}\)

For the Al–Mg alloys powders compacts with the additions of 0.3, 1.0, 2.5 and 10Mg, there also existed two kinds of bonding interfaces between powder particles. Except for a direct metal/metal bonding interface, the bonding interfaces with precipitates were observed in all of the Al–Mg alloy powder compacts. Figure 1 shows a TEM observation of an interface between powder particles in the Al–0.3Mg compact produced by the PECS process at a sintering temperature of 673 K. Figure 1(a) shows a bright field image of the interface and precipitates are visible as indicated by arrows. Figure 1(b) is the selected area diffraction (SAD) pattern taken from the corresponding interface region in Fig. 1(a). It is seen that, except for the diffraction spots from the matrix, some weak diffraction rings are observed in the SAD pattern as shown by arrows. These diffraction rings may be indexed from MgAl\(_2\)O\(_4\) crystallites. However, γ-Al\(_2\)O\(_3\) is isostructural with MgAl\(_2\)O\(_4\). They belong to the same space group (Fd\(_3\)m), and the lattice parameters are also very similar: 0.790 nm for γ-Al\(_2\)O\(_3\) and 0.808 nm for MgAl\(_2\)O\(_4\). Therefore, it is not possible to differentiate γ-Al\(_2\)O\(_3\) from MgAl\(_2\)O\(_4\) by the electron diffraction pattern alone. So it is necessary to further investigate by the EDS analyses. Figures 2(a) and (b) show the EDS spectra taken from the interface region and within a matrix in Fig. 1(a), respectively. Comparing with the matrix, the EDS spectrum from the interface showed to be enriched in magnesium and oxygen. The presence of substantial magnesium indicated that the precipitates at the interface were more likely to be MgAl\(_2\)O\(_4\). Figure 3 gives a TEM observation of an interface in the Al–1.0Mg powder compact produced by the PECS process at 663 K. Figure 3(a) shows a bright field image with the interface region, and Fig. 3(b) shows the SAD pattern corresponding to the interface region. Precipitates are visible in the interface, and they are determined to be mainly MgAl\(_2\)O\(_4\) from the SAD pattern and the EDS spectra taken from the interface region and within a matrix. Furthermore, it was also observed that there were particles of MgO in some interface regions.

Figures 4(a) and (b) show a bright field image and the SAD pattern taken from the interface region, respectively, for the Al–2.5Mg powder compact produced by the PECS process at 643 K. It could be seen that there existed precipitates in the bonding interface between powder particles. In the SAD pattern corresponding to the interface region in Fig. 4(a), diffraction rings are observed, as shown by arrows in Fig. 4(b). These diffraction rings can be indexed from MgO crystallites, but they do not fit to MgAl\(_2\)O\(_4\). Figure 5 shows the corresponding EDS spectra. Figure 5(a) is the spectrum taken from the interface region, and Fig. 5(b) is that taken from within a matrix. It is determined that the interface region is enriched in magnesium and oxygen, which is the same as the results.
TEM Observation of Interfaces between Particles in Al–Mg Alloy Powder Compacts Prepared

of Al–0.3Mg powder compacts. But the intensity ratio between magnesium and oxygen was different from those of Al–0.3Mg. The precipitates in the interface for Al–10Mg powder compact produced by the PECS process at 573 K were also determined to be MgO, which were similar to those of the Al–2.5Mg powder compact. Figures 6(a) and (b) show the bright field image with the interface region and the corresponding SAD pattern, respectively, for the Al–10Mg powder compact. Furthermore, it was observed that the amounts of precipitates at the interface between powder particles increased with an increase in Mg amounts (referred to Figs. 1(a), 3(a), 4(a) and 6(a)).

The presence of MgAl$_2$O$_4$ at the interface between powder particles in Al–Mg alloys powder compacts suggests the following possible reaction for the formation of MgAl$_2$O$_4$:

$$3\text{Mg} + 4\text{Al}_2\text{O}_3 \leftrightarrow 3\text{MgAl}_2\text{O}_4 + 2\text{Al}$$

which is a partial reduction reaction. The reaction has been observed at bonding interfaces in metal matrix composites and in studies of the oxidation behavior of Al–Mg alloys. Because of the relative changes in free energy, this reaction is favored at the low magnesium levels. At relative high magnesium levels, MgO presents at the interface between powder particles, and the complete reduction is suggested as follows:

$$3\text{Mg} + \text{Al}_2\text{O}_3 \leftrightarrow 3\text{MgO} + 2\text{Al}.$$ 

4. Conclusions

Al–Mg alloys powders with various amounts of Mg addition were sintered using the PECS process. The behavior of Mg in the surface oxide film and the effect of Mg amounts on character of the interfaces between Al–Mg alloys powders particles were investigated. It was observed that there were the direct metal/metal bonding interface and the metal/oxide layer/metal bonding interface for all Al–Mg alloys powders compacts. In the pure Al powder compacts, the oxide layer in the interface was amorphous alumina. And precipitates were observed in the bonding interface for the alloys powders compacts with Mg addition. The amounts of the pre-
Fig. 4 TEM micrographs of Al–2.5Mg alloy powder compact using PECS by 643 K. (a) bright field TEM image; (b) the SAD pattern corresponding to interface region in (a).

Fig. 5 EDS spectra of Al–2.5Mg alloy powder compact using PECS by 643 K. (a) taken from the interface region corresponding to Fig. 4(a); (b) taken from within the matrix.

cipitates increased, and the compositions of the precipitates changed with an increase in Mg amount in the alloys powders: MgAl$_2$O$_4$ for Al–0.3Mg, MgAl$_2$O$_4$+$\text{MgO}$ for Al–1.0Mg, and MgO for Al–2.5, 10Mg alloys powder compacts.

REFERENCES