Effect of Mg on the Sintering of Al-Mg Alloy Powders by Pulse Electric-Current Sintering Process

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Utilization of deoxidization mechanism of magnesium (Mg) is an effective method to remove the oxide films at aluminum (Al) alloy powder surface in pulse electric-current sintering (PECS) process. The continuous amorphous oxide film at Al alloy surface are broken and removed by deoxidization of Mg. Crystalline particles of MgAl2O4 or MgO, or both of them, are formed, which depend on Mg content in Al alloy powder and sintering temperature. After that the metal/metal contact is caused, and solid state sintering of Al alloy powder is facilitated.

The electrical resistivity and tensile properties of powder compacts are improved by Mg addition. Based on the analyses of electrical resistivity, tensile properties and microstructures of the sintered specimens, optimum amount of Mg addition to improve the sintering properties of Al powder is determined to be 0.3–2.5 mass%.

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1. Introduction

Automotive industry is traditionally the largest consumer of powder metallurgy (PM) parts. Previously, the used PM parts were predominantly made from steel. To improve the fuel efficiency by weight reduction of components, steel usage has decreased substantially in favor of aluminum (Al). It is apparent that the PM part market is increasing. Significant potential therefore exists for the sintered Al. However particle surfaces of Al metal and its alloy powders are covered with oxide films. The oxide layer, which is tenacious and cannot be broken and/or removed by heat, prevents solid-state sintering. It is difficult to form metallurgical bonding between Al powders by the conventional sintering process. In order to achieve effective sintering, the surface oxide layer needs to be broken and/or removed. The previous investigations have shown some effective methods to break and/or remove surface oxide film, for example, use of liquid phases in solid-state sintering, mechanical breakdown by friction between surfaces, ion beam bombardment treatment in a vacuum chamber, use of active alloying elements such as magnesium (Mg) and lithium (Li), and so on.

Recently, pulse electric-current sintering (PECS) process, or call spark plasma sintering (SPS), or plasma-activated sintering (PAS) process by some researchers, has received much attention as one of the most advanced materials processing. In PECS process, pulse electric current flows directly in the sintered materials and mold. A very high heating efficiency is offered. It can easily sinter a high quality specimen at a lower sintering temperature and in a shorter time than conventional sintering processes, even to those materials that are very difficult to be sintered by other processes. We have sintered Al metal powder using PECS process. Breakdown behavior of oxide film layer at Al particle surface in PECS process and its effect on electrical and mechanical properties of the sintered Al specimens were shown. The oxide film at Al powder particle surface was broken by plastic deformation of powder particle under loading pressure. However, the oxide film cannot be completely removed in Al powder compacts. In order to remove the oxide film, deoxidization is considered to be effective. Mg is a typical element to reduce surface oxide films of Al metal and its alloys according to its standard free energy of formation of oxides. However, little is known about the effect of Mg addition on properties of the sintered Al alloy specimens in PECS process.

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 PECS process. Formation products of deoxidization at interface between powder particles of the sintered specimens were evaluated. Deoxidizing effect of Mg and optimum amount of Mg addition were investigated.

2. Experimental Methods

Al-Mg alloy powders with various Mg contents (0, 0.3, 1.0, 2.5, and 10 mass%) were used in the present study. The starting powders were prepared by air atomized method. The chemical compositions of alloy powders are shown in Table 1. The particle sizes and distributions of the starting powders were determined by laser diffraction method. The powders with Mg content of 0, 0.3, 1.0, 2.5, and 10 mass% were sintered using PECS process.

Table 1 Chemical composition of the starting Al-Mg alloy powders.

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

*: TR indicates below 0.01 mass%
powders are presented in Table 2.

An appropriate amount of powder, which was based on 100% of theoretical density at a compact thickness of 5 mm, was put into a graphite die. Then, pressing and heating of powder were simultaneously carried out in vacuum using a PECS system (Model SPS-520, Izumi Technology Company, Ltd., Kawasaki, Japan). A pulse power frequency of 40 kHz was used in the present study. A uniaxial pressuring method was conducted using top and bottom graphite punches. Loading pressure was 23.5 MPa. The heating speed was 50 K/min (from room temperature to $T_s$-50 K) and 12.5 K/min ($T_s$ to $T_s$) ($T_s$: sintering temperature). The holding time at sintering temperature was 5 min. The details of heating and loading pressure control model in PECS process has been described in previous paper.16) The temperature measurement and control were conducted by a sheath thermocouple with K type, which was inserted into the graphite die with a distance of 5 mm from the sintered specimen. The temperature was calibrated with the directly measured center temperature of the sintered specimen. The shape of the sintered specimens obtained by PECS process was tensile specimen, with a length of 20 mm and a width of 5 mm at the gauge part. The detail geometry of the sintered specimen has been shown in previous paper.16)

Density of the sintered specimens was determined by measuring their weight and size. Electrical resistivity was obtained using a conventional four-point probe method. Tensile testing was carried out using an autograph tester (Model AG-250KNG, Shimadu Corporation, Kyoto, Japan) at room temperature at a strain rate of 2 mm/min. Microstructures of the fractured surfaces were observed using a scanning electron microscope (SEM) (Model JSM-6400, JEOL, Tokyo, Japan).

Characteristics of interfaces between powder particles in the sintered specimens were investigated using transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). Thin foil specimens were cut from the sintered specimens by a diamond saw, then punched into 3 mm diameter disks and mechanically thinned followed by dimpling and ion milling to electron transparency. TEM observations 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.

3. Results

3.1 Density, electrical resistivity and tensile properties

Al-Mg alloy specimens with a tensile test plate were fabricated using PECS process at various sintering temperatures. Relative density, electrical resistivity and tensile properties of the sintered specimens were investigated.

Figure 1 shows relationship between relative densities of the sintered specimens and sintering temperatures at various Mg contents with a loading pressure of 23.5 MPa, pulse frequency of 40 kHz, and holding time of 5 min. Figure 2 presents the results of tensile strengths. Increasing in Mg content at the same sintering temperature, or increasing in sintering temperature at the same Mg content, the relative density and tensile strength of Al-Mg alloy specimen increase.

Table 2 Particle sizes and distributions of the starting Al-Mg alloy powders.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Particle size distribution (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Al</td>
<td>below 16.72 μm</td>
</tr>
<tr>
<td>Al-0.3Mg</td>
<td>below 16.04 μm</td>
</tr>
<tr>
<td>Al-1.0Mg</td>
<td>below 16.24 μm</td>
</tr>
<tr>
<td>Al-2.5Mg</td>
<td>below 16.75 μm</td>
</tr>
<tr>
<td>Al-10Mg</td>
<td>below 16.92 μm</td>
</tr>
</tbody>
</table>

Fig. 1 Effects of Mg content and sintering temperature on relative density of Al-Mg alloy specimens prepared by PECS process with 23.5 MPa, 40 kHz, 5 min.

Fig. 2 Effects of Mg content and sintering temperature on tensile strength of Al-Mg alloy specimens prepared by PECS process with 23.5 MPa, 40 kHz, 5 min.
Figure 3 shows the results of the effects of Mg contents and sintering temperatures on electrical resistivity of Al-Mg alloy specimens prepared by PECS process with 23.5 MPa, 40 kHz, 5 min. It is seen that electrical resistivity of the sintered specimens with Mg addition is obviously lower than that of pure Al specimen at the same sintering temperature. Increasing sintering temperature at the same Mg content, electrical resistivity of the sintered specimens decreases.

3.2 Microstructure of the fractured surface
After tensile test, microstructures of the fractured surfaces of Al-Mg alloy specimens prepared by PECS process were observed using SEM. Here, the results at sintering temperature of about 0.94 times as solidus temperature of alloys, namely, 873 K, 870 K, 854 K, 835 K, and 749 K corresponding to Al-0, 0.3, 1.0, 2.5, and 10Mg alloys, respectively, were described (solidus temperature: 934 K, 930 K, 914 K, 893 K and 801 K to Al-0, 0.3, 1.0, 2.5, and 10Mg alloys). Figure 4 shows the micrographs of the fractured surfaces of Al, Al-0.3Mg and Al-10Mg alloy specimens. Figure 4(a) gives the result of pure Al specimen. The dimple at the fractured surface is observed, but only cleavage is shown in some regions. Figure 4(b) presents the result of Al-0.3Mg alloy specimen. It is seen that the fractured surface is ductile and there are the numbers of dimples at the fractured surface. The results of Al-1.0, 2.5Mg specimens are similar to that of Al-0.3Mg, but the amount of the dimples at the fractured surfaces seems to be decreased with an increase of Mg content. Figure 4(c) shows SEM image of the fractured surface for Al-10Mg alloy specimen. The fractured surface is brittle, and little of dimples are observed at the fractured surface.

3.3 Characteristics of interface between powder particles
Characteristics of interfaces between powder particles in Al-Mg alloy specimens prepared by PECS process were investigated by TEM observations and EDS analyses. For Al-Mg alloy specimens with 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 interfaces, bonding interfaces with crystalline particles were observed in all of Al-Mg alloy specimens. TEM observations and EDS analyses demonstrated that the types of interfaces in the sintered specimens. One is the direct metal/metal bonding interfaces. The other is the metal/intermediate layer/metal bonding interfaces. The intermediate layer is amorphous with a thickness of about 10 nm by a high-resolution TEM observation and selected area diffraction (SAD) pattern analysis. 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 oxide film originally covered on the surface of powder particle. Similar results were shown in details elsewhere.18)
Compositions of the crystalline particles depended on the amount of Mg addition in the alloys and sintering temperature, which are determined to be MgAl$_2$O$_4$ or MgO, or both of them. Recently, we have reported the results at a sintering temperature of about 0.72 times as the solidus temperature for Al-Mg alloys$^{19}$ and those of Al-1.0 mass%Mg alloy at various sintering temperature.$^{20}$ Using the same analyses method, we have investigated the compositions of the crystalline particles on each Mg content and various sintering temperatures. The results are shown in Fig. 5. It is seen that the compositions of the crystalline particles change with sintering temperatures and Mg contents in the alloy powders. For Al-0.3Mg alloy specimens, the crystalline particles in the interfaces between powder particles are MgAl$_2$O$_4$, and for Al-10Mg alloy specimens, it is MgO in the present experimental temperature ranges. For Al-1.0Mg and Al-2.5Mg alloys specimens, the compositions of the crystalline particles change from MgO to MgAl$_2$O$_4$ with an increase in sintering temperature. Moreover, TEM observations also demonstrated that the amounts of the crystalline particles in the interfaces and the thickness of the interface layer increased with an increase in the amount of Mg addition in the alloys.

4. Discussion

4.1 Deoxidization mechanism of oxide film by Mg addition

It has been demonstrated that, for pure Al powder, breakdown of oxide film at surface is mainly caused by plastic deformation of Al particles under loading pressure in PECS process. Two kinds of bonding interfaces, namely, the direct metal/metal bonding and the metal/oxide film layer/metal bonding interfaces, were caused in pure Al specimen. Electrical resistivity and mechanical properties of the specimens depended on fraction of the direct metal/metal bonding interfaces in the specimens.$^{15,16}$

Based on the results by TEM observations and EDS analyses, it was clear that there also existed two kinds of bonding interfaces between powder particles in Al-Mg alloy specimens with additions of 0.3, 1.0, 2.5 and 10Mg. Except for the direct metal/metal bonding interfaces, bonding interfaces with crystalline particles were observed in all of Al-Mg alloy specimens prepared by PECS process. With an increase in Mg content in alloy powders, the amount of the crystalline particles in the interfaces and the thickness of the interface layer increased, and the composition changed from MgAl$_2$O$_4$ to MgO. It is not clear whether the increase of the interface layer thickness with Mg content is from the originally surface oxide films difference in the present.

The presence of MgAl$_2$O$_4$ at powder interface in Al-Mg alloy specimens suggests the following possible deoxidization reaction

$$3\text{Mg} + 4\text{Al}_2\text{O}_3 \rightarrow 3\text{MgAl}_2\text{O}_4 + 2\text{Al} \quad (1)$$

which is a partial deoxidization reaction. The reaction has been observed at bonding interfaces in metal matrix composites$^{3,7,21}$ and in studies of the oxidation behavior of Al-Mg alloys.$^{22,23}$ Because of relative changes in free energy, this reaction is thermodynamically favored at low Mg levels. At relative high Mg levels, MgO becomes more stable. MgO presents at interface between powder particles, and a complete deoxidization is suggested as follows$^{3,7,23}$

$$3\text{Mg} + \text{Al}_2\text{O}_3 \rightarrow 3\text{MgO} + 2\text{Al} \quad (2)$$

Based on above results by TEM and EDS (refer to Fig. 5), and discussion, we can draw a schematic diagram of breakdown/remove mechanism of oxide film at interfaces between particles in Al-Mg alloy specimens prepared by PECS process, as shown in Fig. 6. There are two processes to remove oxide film in Al-Mg alloy specimens in PECS process, namely, mechanical breakdown by plastic deformation of powder particles under loading pressure and deoxidization by Mg with oxide film. Based on temperature range of the formation products in the deoxidization, it has been deduced that the temperature at the contact interface between powder particles is higher than the average temperature for Al-Mg alloy specimens during PECS process.$^{20}$ Due to a high interface temperature in PECS process, it facilitates the breakdown and deoxidization of surface oxide films more than that by conventional sintering methods.

4.2 Effect of Mg addition on electrical resistivity and tensile properties

Due to the deoxidization of Mg with the surface oxide...
films, they are broken and removed with a synthesis of the crystalline particles of MgAl$_2$O$_4$ or MgO. Therefore, by Mg addition, tensile strength of Al alloy specimens prepared by PECS process increases (Fig. 2), and electrical resistivity decreases (Fig. 3).

However, with an increase in amount of Mg addition, the relative density of specimens increases (Fig. 1), the amount of the crystalline particles at interfaces between powder particles also increases. In order to evaluate comprehensively the effect of breakdown of oxide film by Mg addition, the relationship between electrical resistivities and the relative densities of Al-Mg alloy specimens was summarized. Figure 7 shows the results of Al-Mg alloy specimens prepared by PECS process. It is seen that, at the similar relative density, electrical resistivities of Al-Mg alloy specimens by 0.3–2.5 mass% Mg additions are lower than that of pure Al specimen. In general, the electrical resistivity of powder compacts mainly consists of those from the particles matrix and the interfaces between powder particles. In fact, the electrical resistivity of the particles matrix of Al-Mg alloy is higher than that of pure Al. Therefore the result indicates that Al-Mg alloy specimens by 0.3–2.5 mass% Mg additions provide more metal/metal bonding interfaces than that of pure Al specimen, even though there are the similar contact areas between powder particles. But for Al-10Mg alloy, electrical resistivity of specimen cannot receive an effective improvement, comparing with that of Al specimen. The alternative explanations to this result are that it creates the excess deoxidization products (MgO) in interfaces between powder particles for a powder compact with a large quantity of Mg addition, prevents the metal/metal contact, or it is from the high particles matrix electrical resistivity of Al-Mg alloy.

According to the results in Fig. 2, increasing in Mg content at the same sintering temperature, tensile strengths of the sintered specimens increase. An alternative explanation is that Mg addition helps in remove of oxide film at powder surfaces by deoxidization of Mg with oxide film, facilitates sintering of alloy powders, and provides a strengthening mechanism. Moreover, it is also possible to increase the strength of the sintered specimens by the ageing strengthening effect of Al-Mg alloys. However, the tensile strength of Al-Mg alloy specimens sintered by PECS process is no change by the ageing test during three months. On the other hand, Mg addition also reduces melting point of materials.24) With changing in melting points of materials, metallurgical and mechanical properties are different. Therefore, as a consideration of Mg addition effect, it should be comprehensively evaluated. In order to minimize the effect of various melting points of materials on tensile properties of Al-Mg alloy specimens, the relationship between specific strength (ratio of tensile strength of the sintered specimens to that of parent materials) and equivalent temperature (ratio of sintering temperature to solidus temperature of each Al-Mg alloy) was summarized. Figure 8 shows the results of Al-Mg alloy specimens prepared by PECS process. It is seen that, as a criterion with Al, the amounts of 0.3–2.5 mass% additions are effective to improve tensile properties of the sintered specimens, but specific strength by 10 mass% Mg addition is less than that of pure Al at the same equivalent temperature. Furthermore, microstructures observation on the fractured surfaces with the similar equivalent temperature (about 0.94 times as solidus temperature of alloys) reveals that the fractured surfaces are ductile for the specimens of Al-0.3, 1.0, and 2.5Mg alloys, whereas it is brittle for Al-10Mg specimen.

From the aforementioned analyses and discussion, it is clear that not only the sinterability of Al powder, but also electrical resistivity and tensile properties of Al alloy specimens are improved by PECS process with deoxidization of Mg with oxide films, when including the optimum content of Mg, e.g., 0.3–2.5 mass%.

5. Conclusions

Al-Mg alloy powders with various amounts of Mg addition were sintered using PECS process. Deoxidization mechanism of Mg with surface oxide films of Al powder was investigated. Formation products in the deoxidation at the interface between powder particles of the sintered specimens.
were evaluated. Deoxidizing effect of Mg on mechanical and electrical properties was discussed. The results showed that continuous amorphous oxide films at Al alloy surface is broken and removed due to the deoxidization by Mg. Crystalline particles of MgAl$_2$O$_4$ or MgO, or both of them, are formed, which depend on Mg content in alloy powder and sintering temperature. The metal/metal contact is caused. Solid state sintering of Al alloy powder is facilitated. Electrical resistivity and tensile properties of the specimens are improved. Optimum amount of Mg to improve sintering properties of Al powder is determined to be 0.3–2.5 mass%.

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**REFERENCES**