Fabrication of Laminated Spark Plasma Sintered Compacts Composed of Alumina-Particle-Dispersed Magnesium and Magnesium

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To reduce the weight of 20 vol% Al₂O₃-particle-dispersed Mg (Al₂O₃/Mg) compacts produced by spark plasma sintering (SPS), which are much harder than practical high strength AZ91 Mg alloys, 20/0/20 vol% laminated SPS compacts sandwiching a lightweight 0 vol% Al₂O₃/Mg (0 vol%) layer between two 20 vol% Al₂O₃/Mg (20 vol%) layers were fabricated by a mechanical milling/SPS process, and their microstructures and mechanical properties were investigated. The density of the 20/0/20 vol% laminated SPS compacts was 1.88 Mg·m⁻³, and they could be lightened to approximately 80% of the weight of equivalent 20 vol% SPS compacts. The 20/0/20 vol% laminated SPS compacts had a slightly higher hardness than the 20 vol% SPS compacts and a much higher hardness than AZ91 alloys. The bending strength of the 20/0/20 vol% laminated SPS compacts was almost the same as that of the 20 vol% SPS compacts, and was higher than the value calculated from those of the 20 and 0 vol% SPS compacts using the rule of mixtures. A new phase appeared at the flat interface between the 20 and 0 vol% layers with excellent adhesion to the adjoining layers, so this phase probably had a strong effect on the bending strength of the 20/0/20 vol% laminated SPS compacts. The new phase generated a monotonically decreasing hardness gradient from the 20 vol% layer to the 0 vol% layer and was formed by diffusion of Al and O from the 20 vol% layer and diffusion of Mg from the 0 vol% layer. The new phase most likely consisted of Mg₆/Al₁₂, and the concentrations of Al in the αMg, MgO, and Mg₁₇Al₁₂ components of this phase were considered to decrease from the 20 vol% layer to the 0 vol% layer.

Keywords: mechanical milling, alumina-particle-dispersed magnesium, laminated spark plasma sintering compact, different phase, hardness, bending strength

1. Introduction

In recent years, advances in automotive weight reduction have led to an increase in the demand for Mg alloys as lightweight substitutes for Al alloys. However, Mg alloys generally have inferior mechanical properties such as hardness, 0.2% proof stress, the tensile strength and bending strength compared to Al alloys. To improve these mechanical properties, composites of pure Mg reinforced by ceramic particles have been fabricated using powder metallurgical processes, and their mechanical properties have been investigated.

In a previous study, we prepared Al₂O₃ particles uniformly dispersed in pure Mg (Al₂O₃/Mg) powders by mechanical milling (MM) powder mixtures of pure Mg powder and 0–30 vol% Al₂O₃ particles, and then investigated the mechanical properties of compacts obtained from these Al₂O₃/Mg powders by spark plasma sintering (SPS). The 20 and 30 vol% Al₂O₃/Mg SPS compacts had a higher hardness (over 200 HV) than practical high-strength AZ91 Mg alloys. Furthermore, the 20 vol% Al₂O₃/Mg (20 vol%) SPS compacts had a higher bending strength than the 0 vol% Al₂O₃/Mg (0 vol%) SPS compacts. However, the light weight of the Al₂O₃/Mg SPS compacts disappears with increasing the Al₂O₃ content because the density of Al₂O₃ (3.9–4.0 Mg·m⁻³) is more than twice that of Mg (1.74 Mg·m⁻³).

In the present study, to reduce the weight of the 20 vol% SPS compacts, 20/0/20 vol% laminated SPS compacts sandwiching a lightweight 0 vol% Al₂O₃/Mg (0 vol%) layer between two 20 vol% Al₂O₃/Mg (20 vol%) layers were fabricated using an MM/SPS process, and their microstructures and mechanical properties were investigated.

2. Experimental Procedure

Pure Mg powder (180-µm particle size; Kojundo Chemical Laboratory Co., Ltd.; purity: 99.5%) and α-Al₂O₃ particles (1-µm particle size; Kojundo Chemical Laboratory Co., Ltd.; purity: 99.9%) were used as starting materials. Powder mixtures of the Mg powder and 20 vol% Al₂O₃ particles were fed into an Al₂O₃ container together with 5-mm-diameter Al₂O₃ balls. An Al₂O₃ agitator arm was rotated at 300 rpm for 180 ks in an Ar atmosphere to mill the mixed powders. 4 mass% stearic acid was added as a lubricant. Mg powder without Al₂O₃ particles was also subjected to the same treatment.

The 20 vol% Al₂O₃-particle-dispersed Mg (20 vol%) powder and the Mg (0 vol%) powder were obtained by the above process. Figure 1 shows cross-sectional SEM images of the 20 vol% powder. The MM treatment decreased the particle size of the initial Mg powders and distributed fine Al₂O₃ particles homogeneously throughout the Mg powder.

Figure 2 shows the procedure for producing laminated SPS compacts with a 20/0/20 vol% layered structure. Given weights of 0 and 20 vol% powders were measured out, and the powders were placed in a graphite die (20-mm inner di-
ameter) in the order of 20, 0, and 20 vol% and compacted at 20 MPa using a hydraulic press.

The laminated green compacts with a three-layered structure of 20/0/20 vol% powders were densified in the graphite die using an SPS apparatus (DR. SINTER LAB™ SPS-515S; Fuji Electronic Industrial Co., Ltd.) at 40 MPa and 848 K for 0.6 ks in an Ar atmosphere. The graphite die was then cooled to below 323 K in the SPS apparatus to obtain laminated SPS compacts with a layered structure of 20/0/20 vol% powders.

The 20/0/20 vol% laminated SPS compacts were finished by adjusting their thickness by emery polishing and buffing both surfaces until the volume ratio of the 20 vol% layers to the 0 vol% layers was 1 to 4. For comparison, 0 and 20 vol% SPS compacts were also fabricated using the process shown in Fig. 2.

Microstructural observations and qualitative analysis of the Al2O3/Mg powders and SPS compacts were performed using optical microscopy, SEM-EDS, and XRD. The surface and cross-sectional hardnesses of the Al2O3/Mg SPS compacts were measured using a Vickers hardness tester at 49 N for 10 s and a micro-Vickers hardness tester at 0.098 N for 10 s, respectively. Bending specimens were given prescribed dimensions by electric discharge machining of the Al2O3/Mg SPS compacts. After buffing both surfaces of the specimens, three-point bending tests were conducted at a crosshead speed of 2.0 mm/min. The bending strengths were calculated from the obtained maximum loads using the general formula.

3. Results and Discussions

3.1 Cross-sectional observation of 20/0/20 vol% laminated SPS compacts

Figure 3 shows a cross-sectional optical micrograph of the 20/0/20 vol% laminated SPS compact. The two ends and the central region were the 20 and 0 vol% layers, respectively, and a new phase appeared at the interface between the 20 and 0 vol% layers. The approximate thickness of the new phase was a nearly constant 40 μm.

3.2 Characteristics of 20/0/20 vol% laminated SPS compacts

Figure 4 shows XRD results from the surfaces of 20/0/20 vol% laminated SPS compacts and from separate 20 and 0 vol% SPS compacts. From these results, the constituent phase of the 0 vol% SPS compact was identified as Mg and MgO5-7).

The surface (20 vol%) layer of the 20/0/20 vol% laminated SPS compact was identified as Mg, Al2O3, MgO, and Mg17Al12, which is identical to that of the 20 vol% SPS compact5-7). During SPS, Mg17Al12 is formed in the 20 vol% layer by solid-phase reaction between Mg and Al2O35-7). If the Al-Mg binary phase diagram10) is applied to the solid-phase reaction of Mg and Al2O3, the following reaction might occur at the interfaces between the Mg and Al2O3 particles in the 20 vol% layer.

$$3\text{Mg} + 7\text{Al}_2\text{O}_3 \rightarrow 15\text{Mg} + 2\text{Al} + \text{Mg}_{17}\text{Al}_{12} + 21\text{MgO}$$ (1)

Here, it was estimated that the solid solubility limit of Al in Mg was 11.5 mol% Al at a reaction temperature of 710 K10). Al and O decompose at the interfaces between the Mg and Al2O3 particles, Al dissolves in Mg, and O produces MgO in response to Mg. Mg17Al12 is produced when the solid solution of Mg and Al (αMg) exceeds the solid solubility limit of Al in Mg5-7).

![Fig. 2 Fabrication process for laminated SPS compacts.](image)

![Fig. 3 Cross-sectional optical macrograph (a) and higher magnification (b) of a 20/0/20 vol% laminated SPS compact. The volume ratio of 20 vol% Al2O3/Mg to 0 vol% Al2O3/Mg was 4 to 1.](image)

![Fig. 4 XRD results from the surfaces of 20/0/20 vol% laminated (a), 20 vol% (b), and 0 vol% (c) SPS compacts.](image)
Though MgAl$_2$O$_4$ (Spinel) is also estimated to product by the solid-phase reaction of MgO and Al$_2$O$_3$ particles, it is difficult to identify Spinel by XRD and TEM-EDS. Therefore, it is considered that there is very little production of Spinel.

Figure 5 shows the densities of 20/0/20 vol% laminated SPS compacts, 20 vol% SPS compacts, and 0 vol% SPS compacts. The density of the laminated SPS compact was 1.88 Mg m$^{-3}$, or approximately 80% of the 20 vol% SPS compacts (2.28 Mg m$^{-3}$). The densities of the laminated SPS compacts were almost the same as the values calculated from those of the 20 and 0 vol% SPS compacts using the rule of mixtures. Here, the calculated values were defined as the range of values that includes the new phase to 0 or 20 vol% layers.

Figure 6 shows Vikers hardness and specific hardness values of 20/0/20 vol% laminated SPS compacts, 20 vol% SPS compacts, and 0 vol% SPS compacts. The laminated SPS compacts had a slightly higher hardness than the 20 vol% SPS compacts, 215 HV, which is much higher than that of AZ91 Mg alloys, as shown in Fig. 6(a).

Some paper about the mechanical properties of ceramics particle strengthened pure Mg matrix composites fabricated using powder metallurgical processes has listed the Vikers hardness values of 65 HV–179 HV.

To express both lightness and high hardness of the laminated SPS compacts, “specific hardness” was defined as the Vikers hardness per density. The laminated SPS compacts had a higher specific strength than the 20 and 0 vol% SPS compacts, as shown in Fig. 7(b).

Figure 8 shows a cross-sectional optical micrograph of a 20/0/20 vol% laminated SPS compact fractured by the bending test. The adhesion between the new phase and both Al$_2$O$_3$/Mg layers was excellent, as no abrasion was observed at their interfaces, as shown in Figs. 8(a)–8(d).

If the bending strength of the 20 and 0 vol% layers is assumed to satisfy the rule of mixtures, then the bending strengths of the 20/0/20 vol% laminated, 20 vol% and 0 vol% SPS compacts can be used to obtain the bending strength of the new phase as follows:

$$\sigma_{20/0/20} = \sigma_{20}V_{20} + \sigma_{0}V_{0} + \sigma_{a.p}V_{a.p},$$

which can be rearranged to

$$\sigma_{a.p} = (\sigma_{20/0/20} - \sigma_{20}V_{20} - \sigma_{0}V_{0})/V_{a.p},$$
where $\sigma_{a.p.}$ is the bending strength of the new phase, $\sigma_{a/20}$, and $\sigma_0$ are the bending strengths of the 20/0/20 vol% laminated compact, 20 vol% SPS compact, and 0 vol% SPS compact, respectively. $V_{a.p.}$ is the volume fraction of the new phase, and $V_{20}$ and $V_0$ are the volume fractions of the 20 vol% and 0 vol% SPS compacts.

Using eq. (3), the bending strength of the new phase $\sigma_{a.p.}$ was calculated to be approximately 600 MPa, which is more than triple those of the 20% vol% SPS compacts. Therefore, the new phase should have a strong effect on the bending strength of the 20/0/20 vol% laminated SPS compacts.

### 3.3 The new phase at the interface between 20/0/20 vol% $\text{Al}_2\text{O}_3$/Mg layers

To investigate the new phase in detail, micro-Vikers hardness tests and SEM-EDS line analysis were conducted over cross-sections of the laminated SPS compacts. Figures 9(a) and 9(b) show an optical macrograph and micro-Vikers hardness distribution of the cross-section of a 20/0/20 vol% laminated SPS compact, respectively. The results showed that the hardness of the new phase decreased monotonically from the 20 vol% layer to the 0 vol% layer. Here, the space of the hardness measurement position is smaller than a rule of JIS (Z2244), but it is thought that there is little effect of the measurement space on the hardness value because the hardness value measured at the space according to the rule did not almost same as the value of Fig. 9(b). Therefore, it may be said that there is little effect of the work-hardening on the hardness values.

Figures 10(a) and 10(b) show a cross-sectional SEM micrograph and SEM-EDS line analysis results for a 20/0/20 vol% laminated SPS compact, respectively. In the new phase, the EDS profile of Mg tended to decrease from the 0 vol% layer to the 20 vol% layer. Moreover, Al and O were detected in the phase. Therefore, the new phase was formed by the diffusion of Al and O from the 20 vol% layer and Mg from the 0 vol% layer.

From the above results, we propose a mechanism for the formation of the new phase in the 20/0/20 vol% laminated compacts. Prior to SPS, the 20 vol% layer in the 20/0/20 vol% laminated green compacts consists of Mg, $\text{Al}_2\text{O}_3$, and MgO.
whereas the 0 vol% layer consists of Mg and MgO according to the XRD results. Then, during SPS, because of the previously mentioned solid-phase reaction between the Mg and Al2O3 particles\textsuperscript{5–7)}, the Al and O atoms that decomposed from the Al2O3 particles at the edge of the 20 vol% layer near the interface between the 20 and 0 vol% layers diffuse into the 0 vol% layer, which contains no Al2O3 particles. Meanwhile, Mg at the edge of the 0 vol% layer near the interface between the 20 and 0 vol% layers diffuses into the 20 vol% layer, in which the Mg concentration is less than that of the 0 vol% layer. Consequently, the new phase formed during the SPS. Finally, after SPS, the newly formed phase likely consists of α\textsubscript{Mg}, MgO, and Mg\textsubscript{17}Al\textsubscript{12}, and the concentrations of Al in α\textsubscript{Mg}, MgO, and Mg\textsubscript{17}Al\textsubscript{12} in the phase is considered to decrease from the 20% layer to the 0% layer.

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REFERENCES