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% Al_2O_3 -particle-dispersed Mg ($\text{Al}_2\text{O}_3/\text{Mg}$) 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% $\text{Al}_2\text{O}_3/\text{Mg}$ (0 vol%) layer between two 20 vol% $\text{Al}_2\text{O}_3/\text{Mg}$ (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 $1.88 \text{ Mg}\cdot\text{m}^{-3}$, 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 αMg , MgO , and $\text{Mg}_{17}\text{Al}_{12}$, and the concentrations of Al in the αMg , MgO , and $\text{Mg}_{17}\text{Al}_{12}$ components of this phase were considered to decrease from the 20 vol% layer to the 0 vol% layer. [doi:10.2320/matertrans.M2016289]

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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^{1–4)}.

In a previous study^{5–7)}, we prepared Al_2O_3 particles uniformly dispersed in pure Mg ($\text{Al}_2\text{O}_3/\text{Mg}$) powders by mechanical milling (MM) powder mixtures of pure Mg powder and 0–30 vol% Al_2O_3 particles, and then investigated the mechanical properties of compacts obtained from these $\text{Al}_2\text{O}_3/\text{Mg}$ powders by spark plasma sintering (SPS). The 20 and 30 vol% $\text{Al}_2\text{O}_3/\text{Mg}$ SPS compacts had a higher hardness (over 200 HV) than practical high-strength AZ91 Mg alloys⁸⁾. Furthermore, the 20 vol% $\text{Al}_2\text{O}_3/\text{Mg}$ (20 vol%) SPS compacts had a higher bending strength than the 0 vol% $\text{Al}_2\text{O}_3/\text{Mg}$ (0 vol%) SPS compacts. However, the light weight of the $\text{Al}_2\text{O}_3/\text{Mg}$ SPS compacts disappears with increasing the Al_2O_3 content because the density of Al_2O_3 ($3.9\text{--}4.0 \text{ Mg}\cdot\text{m}^{-3}$) is more than twice that of Mg ($1.74 \text{ Mg}\cdot\text{m}^{-3}$).

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% $\text{Al}_2\text{O}_3/\text{Mg}$ (0 vol%) layer between two 20 vol% $\text{Al}_2\text{O}_3/\text{Mg}$ (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 $\alpha\text{-Al}_2\text{O}_3$ 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% Al_2O_3 particles were fed into an Al_2O_3 container together with 5-mm-diameter Al_2O_3 balls. An Al_2O_3 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 Al_2O_3 particles was also subjected to the same treatment.

The 20 vol% Al_2O_3 -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 Al_2O_3 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-

Fig. 1 Cross-sectional SEM image (a) and higher magnification (b) of 20 vol% Al_2O_3 -particle-dispersed Mg powder.

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 LABTM 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% Al₂O₃/Mg (20/0/20 vol% laminated SPS compacts).

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 formula⁹.

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 μ m.

Fig. 2 Fabrication process for laminated SPS compacts.

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.

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 (α Mg) exceeds the solid solubility limit of Al in Mg⁵⁻⁷.

Fig. 3 Cross-sectional optical micrograph (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.

Fig. 4 XRD results from the surfaces of 20/0/20 vol% laminated (a), 20 vol% (b), and 0 vol% (c) SPS compacts.

Though MgAl_2O_4 (Spinel) is also estimated to product by the solid-phase reaction of MgO and Al_2O_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 $1.88 \text{ Mg}\cdot\text{m}^{-3}$, or approximately 80% of the 20 vol% SPS compacts ($2.28 \text{ Mg}\cdot\text{m}^{-3}$). 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 Vickers 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 alloys⁸⁾, as shown in Fig. 6(a).

Some paper¹⁻³⁾ about the mechanical properties of ceramics particle strengthened pure Mg matrix composites fabricated using powder metallurgical processes has listed the Vickers 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 Vickers hardness per density. The laminated SPS compacts had a higher “specific hardness” than the 20 vol% SPS compacts, as shown in Fig. 6(b).

Figure 7 shows the bending strength and specific strength of 20/0/20 vol% laminated, 20 vol%, and 0 vol% SPS compacts. The bending strengths of the laminated SPS compacts were almost the same as those of the 20 vol% SPS compacts, and were higher than the expected values calculated from the strengths of the 20 and 0 vol% SPS compacts using the same method used to calculate the density, as shown in Fig. 7(a).

The specific strength was defined as the bending strength

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 an 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 $\text{Al}_2\text{O}_3/\text{Mg}$ 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:

$$\sigma_{20/0/20} = \sigma_{20}V_{20} + \sigma_0V_0 + \sigma_{a.p.}V_{a.p.}, \quad (2)$$

which can be rearranged to

$$\sigma_{a.p.} = (\sigma_{20/0/20} - \sigma_{20}V_{20} - \sigma_0V_0)/V_{a.p.}, \quad (3)$$

Fig. 5 Densities of 20/0/20 vol% laminated, 20 vol%, and 0 vol% SPS compacts.

Fig. 6 Vickers hardness (a) and specific hardness (b) of 20/0/20 vol% laminated, 20 vol%, and 0 vol% SPS compacts.

where $\sigma_{a.p.}$ is the bending strength of the new phase, $\sigma_{20/0/20}$, σ_{20} , and σ_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% $\text{Al}_2\text{O}_3/\text{Mg}$ layers

To investigate the new phase in detail, micro-Vickers 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-Vickers hardness distribution of the cross-section of a 20/0/20 vol% laminated SPS compact, respectively. The results shows 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, Al_2O_3 , and MgO,

Fig. 7 Bending strength (a) and specific strength (b) of 20/0/20 vol% laminated, 20 vol%, and 0 vol% SPS compacts.

Fig. 8 Cross-sectional optical macrograph of 20/0/20 vol% laminated SPS compact fractured by the bending test.

Fig. 9 Optical macrograph (a) and micro-Vickers hardness distribution (b) of the cross-section of a 20/0/20 vol% laminated SPS compact.

Fig. 10 SEM micrograph (a) and SEM-EDS line analysis results (b) for cross-section of a 20/0/20 vol% laminated SPS compact.

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 Al_2O_3 particles^{5–7)}, the Al and O atoms that decomposed from the Al_2O_3 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 Al_2O_3 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 αMg , MgO, and $\text{Mg}_{17}\text{Al}_{12}$, and the concentrations of Al in αMg , MgO, and $\text{Mg}_{17}\text{Al}_{12}$ in the phase is considered to decrease from the 20% layer to the 0% layer. As mentioned previously, it is considered that there is very little production of Spinel.

Because the atomic radii of Mg (0.160 nm) and Al (0.143 nm) are similar¹¹⁾, the effect of the solid-solution strengthening of Mg due to the increase of Al on the hardness distribution of the new phase should be small. However, a strong negative hardness gradient is generated from the 20% layer to the 0% layer in the new phase, as can be seen in Fig. 9.

Therefore, the primary cause of the large hardness gradient along the new phase is probably a decrease in the production of MgO and $\text{Mg}_{17}\text{Al}_{12}$ from the 20% layer to the 0% layer.

4. Conclusion

20 vol% Al_2O_3 -particle-dispersed Mg ($\text{Al}_2\text{O}_3/\text{Mg}$) SPS

compacts have a much higher hardness than the conventional AZ91 high strength Mg alloy, but are also heavier. To reduce their weight, laminated SPS compacts sandwiching a light-weight 0 vol% $\text{Al}_2\text{O}_3/\text{Mg}$ (0 vol%) layer between two high-strength 20% $\text{Al}_2\text{O}_3/\text{Mg}$ (20 vol%) layers (20/0/20 vol% laminated SPS compacts) were fabricated using an MM/SPS process and their microstructures and mechanical properties were investigated. The following results were obtained:

- (1) The density of the 20/0/20 vol% laminated SPS compacts was $1.88 \text{ Mg}\cdot\text{m}^{-3}$ and their weights could be reduced to approximately 80% of the weight of an equivalent 20 vol% SPS compact.
- (2) The laminated SPS compacts had a slightly higher hardness than the 20 vol% SPS compacts and were much harder than AZ91 Mg alloys.
- (3) The bending strength of the laminated SPS compacts was similar to that of the 20 vol% SPS compacts and was higher than the value calculated based on those of the 20 and 0 vol% SPS compacts.
- (4) A new phase was formed at the flat interface between the 20 vol% and 0 vol% layers. The adhesion between the new phase and both layers was excellent, and this phase is thought to have a strong effect on the bending strength of the laminated SPS compacts.
- (5) The new phase most likely consists of αMg , MgO, and $\text{Mg}_{17}\text{Al}_{12}$, and the concentrations of Al in the αMg , MgO, and $\text{Mg}_{17}\text{Al}_{12}$ in the phase is considered to decrease from the 20% layer to the 0% layer.

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