Effect of Microstructure on the Mechanical Properties of Magnesium Composites Containing Dispersed Alumina Particles Prepared Using an MM/SPS Process

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Magnesium composites containing 0–20 vol% Al_2O_3 particles were produced via mechanical milling (MM) followed by spark plasma sintering (SPS), and the effect of the microstructure on their mechanical properties was investigated. Microstructural observation of the MM powders and SPS compacts was achieved using scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM)/energy dispersive X-ray spectroscopy (EDS). The mechanical properties of the MM powders and SPS compacts were evaluated on the basis of the results of the Vickers hardness test. SEM micrographs indicated that Al_2O_3 fine particles were dispersed in the Mg composites with 10 and 20 vol% Al_2O_3 . The hardness values for the MM powder and the SPS compact containing 10 vol% Al_2O_3 were nearly the same owing to their similar microstructures. However, the hardness of the SPS compact was higher than that of the MM powder for the Mg composite with 20 vol% Al_2O_3 . TEM/EDS and XRD analyses revealed that the needle-like $\text{Mg}_{17}\text{Al}_{12}$ and equiaxed nano MgO particles formed in the Mg matrix with 20 vol% Al_2O_3 during the SPS process. The increase in hardness of the SPS compact compared to that of the MM powder is attributed to strengthening resulting from the formation of the $\text{Mg}_{17}\text{Al}_{12}$ and MgO phases. [doi:10.2320/matertrans.Y-M2013845]

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1. Introduction

Magnesium has a lower specific gravity than that of aluminum and the demand for Mg alloys has recently increased compared to that for Al alloys. However, nearly all Mg alloys are inferior to Al alloys with respect to their mechanical properties. Recently, composites of magnesium and ceramic particles have received much attention owing to the improvement in the mechanical properties of these Mg materials.^{1–5)} Particularly in the composite of magnesium and alumina, Hassan and Gupta^{6–9)} reported that Mg composites containing up to 1.1 vol% fine Al_2O_3 particles were produced using a powder metallurgy technique and exhibited superior mechanical properties. However, literature concerning Mg composites containing more than 10 vol% fine Al_2O_3 particles is limited. One of the present authors recently revealed that compacted Mg composites containing 10–30 vol% fine Al_2O_3 particles can be produced via mechanical milling (MM) followed by spark plasma sintering (SPS) or a hot pressing and that the optimal Al_2O_3 composition to enhance the mechanical properties falls between 10 and 20 vol%.^{10–13)} However, the effect of the microstructure on the mechanical properties of Mg composites containing more than 10 vol% Al_2O_3 is not yet clear. The purpose of this paper is to clarify the relation between the microstructure and the mechanical properties of the Mg compacts containing 10 to 20 vol% fine Al_2O_3 particles that are produced using the MM/SPS processes.

2. Experimental Procedure

Commercially pure Mg powder (99.5 mass% purity) and $\alpha\text{-Al}_2\text{O}_3$ powder (99.9 mass% purity) were used in this study. The initial particle sizes of the pure Mg and Al_2O_3 powders were approximately 180 and 1 μm , respectively. Mechanical milling (MM) was applied to these powders using an attritor

ball mill (Mitsui Mining Co., Ltd.) under Ar atmosphere at room temperature. Mixed powders consisting of pure Mg and 0–20 vol% Al_2O_3 were mechanically milled for 180 ks at an agitator arm rotation speed of 300 rpm. Stearic acid (2 mass%) was added as a lubricant. A mixed powder of 200 mL of Mg and 0–20 vol% Al_2O_3 was fed into Al_2O_3 container (capacity 5.5 L) along with 3 L of $\phi 5$ mm Al_2O_3 balls. The composite MM powders containing the pure Mg and Al_2O_3 were then sintered using a spark plasma sintering (SPS) apparatus (SPS-515S; SPS Syntex Co., Ltd.) at 848 K and 40 MPa for 0.6 ks and the composite discs with about $\phi 20$ mm were obtained. The microstructural observation of the MM powders and SPS compacts containing Mg and Al_2O_3 was achieved using scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM)/energy dispersive X-ray spectroscopy (EDS). The samples for SEM and TEM analysis were prepared using an ion-beam polish and focused ion beam system, respectively. A spot size for EDS analysis used 1.0 nm. XRD profiles were measured under the condition of diffraction angle of 20–90 degree, tube voltage of 40 kV and tube current of 40 mA. The mechanical properties of the MM powders and SPS compacts were evaluated using the Vickers hardness test at 0.098 and 9.8 N, respectively, for 15 s.

3. Results and Discussions

3.1 Microstructure and hardness of the MM powders and SPS compacts

Figure 1 shows SEM micrographs of the MM powders containing 0–20 vol% Al_2O_3 particles. The pure Mg powder milled for 180 ks can be seen in Fig. 1(a), and the composite MM powders with 10 and 20 vol% Al_2O_3 particles can be seen in Figs. 1(b) and 1(c), respectively. The MM treatment decreased the size of the initial Mg particles and distributed fine Al_2O_3 particles homogeneously within the Mg powder.

Fig. 1 SEM back scattered images of (a) MM powder without Al_2O_3 , (b) MM powder with 10 vol% Al_2O_3 , and (c) MM powder with 20 vol% Al_2O_3 .

It should be noted that the Al_2O_3 particles in 20 vol% composite were finer than those in the 10 vol% composite (Figs. 1(b) and 1(c), respectively) owing to the greater impingement of each Al_2O_3 particle during the MM treatment at 20 vol%.

The microstructures of the SPS compacts obtained after sintering of the MM powders are shown in Fig. 2. The SEM micrographs in Figs. 2(a), 2(b), and 2(c) correspond to the sintered compacts of the MM powders shown in Figs. 1(a), 1(b), and 1(c), respectively. Average grain sizes of the Mg matrices in Figs. 2(a), 2(b), and 2(c) are approximately 4.9, 5.2 and 3.4 μm , respectively. The size and distribution of the Al_2O_3 particle are nearly the same before and after sintering. However, in the Mg composite with 20 vol% Al_2O_3 , many ultra-fine particles are observed in the Mg matrix. The porosity of Mg compact was estimated using several SEM

Fig. 2 SEM back scattered images of (a) SPS compact of the MM powder without Al_2O_3 , (b) SPS compact of the MM powder with 10 vol% Al_2O_3 , and (c) SPS compact of the MM powder with 20 vol% Al_2O_3 .

micrographs to be 3.9% and the pores are observed in the interior of grains and at grain boundaries (Fig. 2(a)). The porosity of Mg composite with 10 vol% Al_2O_3 was estimated using several SEM micrographs to be 2.5% and the pores are found at the interface between the Mg matrix and the Al_2O_3 particles, as shown in Fig. 2(b). The porosity of Mg composite with 20 vol% Al_2O_3 was estimated using several SEM micrographs to be 2.4% and the pores are observed at the grain boundaries (Fig. 2(c)). Pores at interface between the Mg and Al_2O_3 particles are not observed so much in the 20 vol% Al_2O_3 composite.

The hardness of the MM powders and the SPS compacts presented in Figs. 1 and 2 is shown in Fig. 3. The ordinate and abscissa in Fig. 3 correspond to the Vickers hardness and Al_2O_3 volume fraction, respectively. The hardness of both

Fig. 3 Vickers hardness results for the MM powders and the SPS compacts of the Mg composites with 0 to 20 vol% Al₂O₃.

Fig. 4 XRD results for the SPS compacts of pure Mg and Mg composites with 10 and 20 vol% Al₂O₃.

MM powder and SPS compact without Al₂O₃ is approximately 50 HV, and that of both MM powder and SPS compact with 10 vol% Al₂O₃ is approximately 75 HV. However, the hardness of the MM powder with 20 vol% Al₂O₃ is approximately 140 HV, while that of the SPS compact is approximately 200 HV. It is interesting to note that the hardness of SPS compact drastically raises compared to the MM powder when the Al₂O₃ addition changes from 10 to 20 vol%. This drastic increase of the hardness is caused by not only effect of the Al₂O₃ addition and the grain refinement but also other effect. Therefore, in order to uncover the reason for this increase of the hardness, the microstructure of the Mg composites with 0–20 vol% Al₂O₃ were observed in detail (see below).

3.2 Detailed microstructure of the SPS compacts with 0–20 vol% Al₂O₃

Figure 4 shows XRD profiles of the pure Mg compact and the Mg composites with 10 and 20 vol% Al₂O₃ particles. The

Fig. 5 TEM micrograph of the SPS compact of the pure Mg powder milled for 180 ks.

Fig. 6 TEM micrograph of the SPS compact of the Mg composite with 10 vol% Al₂O₃.

pure Mg compact consists of Mg and MgO, while the Mg composite with 10 vol% Al₂O₃ consists of Mg, Al₂O₃, and MgO, and the Mg composite with 20 vol% Al₂O₃ consists of Mg, Al₂O₃, MgO, and Mg₁₇Al₁₂. The formation of the Mg₁₇Al₁₂ phase is one cause for the increased hardness of the composite with 20 vol% Al₂O₃.

Figure 5 shows a TEM micrograph of the pure Mg compact of the MM powder milled for 180 ks. Some nanoparticles with a dark contrast can be observed as indicated by the arrows. Figure 6 shows a TEM micrograph of the Mg composite with 10 vol% Al₂O₃ particles. The large particles with a dark contrast correspond to Al₂O₃. An enlargement of this TEM micrograph, along with the EDS line analysis results, is shown in Fig. 7. Nanoparticles with a size of approximately 20 nm are observed in Fig. 7(a). The EDS line analysis results for the horizontal line in Fig. 7(a) are shown in Fig. 7(b). The EDS profiles indicate an increase in the oxygen concentration at the position of the nanoparticles. Then, the aluminum was not detected in this area. Thus, the EDS results shown in Fig. 7 and the XRD results shown in Fig. 4 reveal that the nanoparticle in Fig. 7(a) is MgO. Similarly, the nanoparticle shown in Fig. 5 is MgO.

Figure 8 shows a TEM micrograph of the Mg composite with 20 vol% Al₂O₃. The particle with a dark contrast

Fig. 7 TEM micrograph (a) and EDS line analysis results (b) for the SPS compact of Mg composite with 10 vol% Al_2O_3 .

Fig. 8 TEM micrograph of the SPS compact of the Mg composite with 20 vol% Al_2O_3 .

corresponds to Al_2O_3 , and a large number of very fine particles are observed in the Mg matrix, an enlargement of which is shown in Fig. 9. Nanosized equiaxed and needle-like precipitates are widely observed in the Mg matrix in this figure. It cannot be denied that a shape of the needle-like precipitates is actually plate-like. However, these are called needle-like precipitates for convenience in this paper. A TEM micrograph of the needle-like precipitates and equiaxed nanoparticles is shown in Fig. 10, along with the results of the EDS line analysis. Two needle-like precipitates are located in the middle of the micrograph, and an equiaxed nanoparticle lies at the right side of the needle-like precipitates (Fig. 10(a)). The EDS profiles for the horizontal line in Fig. 10(a) are shown in Fig. 10(b) and indicate that the aluminum concentration increased

Fig. 9 High magnification image of the TEM micrograph in Fig. 8 of the Mg composite with 20 vol% Al_2O_3 .

Fig. 10 TEM micrograph (a) and EDS line analysis results (b) for the Mg compact with 20 vol% Al_2O_3 .

and the magnesium concentration decreased, whereas the oxygen concentration remained unchanged at the position of needle-like precipitates. As a result, the needle-like precipitates have roughly same concentration of Mg and Al. At the site of the equiaxed nanoparticle in Fig. 10(b), the oxygen concentration increased and the aluminum concentration remained unchanged. Furthermore, in Fig. 4, the formation of $\text{Mg}_{17}\text{Al}_{12}$ and an increase in the MgO concentration in the Mg composite containing 20 vol% Al_2O_3 was observed. Therefore, it was concluded the needle-like precipitates and the equiaxed nanoparticle shown in Figs. 9 and 10 correspond to $\text{Mg}_{17}\text{Al}_{12}$ and MgO, respectively.

A TEM micrograph in the vicinity of the Al_2O_3 particle in the Mg composite with 20 vol% Al_2O_3 can be seen in

Fig. 11 EDS elemental mapping results for the SPS compact with 20 vol% Al_2O_3 .

Fig. 11(a), and the EDS mapping results for Mg, Al, and O can be seen in Figs. 11(b), 11(c), and 11(d), respectively. Al and O are observed in the Mg matrix in the vicinity of the Al_2O_3 particle as shown in Figs. 11(c) and 11(d). This result suggests that a solid-state reaction occurs in the Mg composite with 20 vol% Al_2O_3 . The solute oxygen and magnesium may immediately produce MgO, because magnesium barely dissolves in oxygen. On the other hand, magnesium can dissolve to a significant extent in aluminum. However, the magnesium that cannot dissolve may bond to aluminum, resulting in the formation of $\text{Mg}_{17}\text{Al}_{12}$. Such a solid-solution reaction would occur as follows:^{11,12)}

The needle-like $\text{Mg}_{17}\text{Al}_{12}$ and a large number of MgO particles are not observed in the Mg composite with 10 vol% Al_2O_3 (Fig. 6). The solid-solution reaction shown in eq. (1) is unlikely to occur because the contact area between the Mg matrix and the Al_2O_3 particles is reduced in correlation with the pores at the interface between the Mg matrix and the Al_2O_3 particles (Figs. 2(b) and 2(c)).

Therefore, a drastic increase in the hardness of the SPS compact, when the Al_2O_3 addition changes from 10 to 20 vol%, is attributed to the formation of $\text{Mg}_{17}\text{Al}_{12}$ and MgO (Fig. 9) in the Mg composite with 20 vol% Al_2O_3 .

4. Conclusion

Magnesium composites containing 0–20 vol% Al_2O_3 were fabricated via mechanical milling (MM) followed by spark plasma sintering (SPS). The microstructures and mechanical properties of the Mg/ Al_2O_3 composites were evaluated using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and the Vickers hardness test. The Mg compact with 10 vol% Al_2O_3 consisted of an Mg matrix, fine Al_2O_3 particles, and nano MgO particles. The Mg compact with 20 vol% Al_2O_3 consisted of an Mg matrix, fine Al_2O_3 particles, equiaxed nano MgO particles, and needle-like $\text{Mg}_{17}\text{Al}_{12}$ phase. The hardness of the MM powder and the SPS compact were nearly the same for the pure Mg and Mg composite with 10 vol% Al_2O_3 . However, the hardness of the SPS compact was higher than that of the MM powder for the Mg composite with 20 vol% Al_2O_3 . The drastic increase in the hardness of the SPS compact, when the Al_2O_3 addition changes from 10 to 20 vol%, is attributed to the formation of the needle-like $\text{Mg}_{17}\text{Al}_{12}$ and equiaxed nano MgO particles.

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