Properties of boride-added powder metallurgy magnesium alloys

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Abstract. Magnesium alloys with metallic borides, magnesium diboride (MgB_2) or aluminum diboride (AlB_2), were investigated regarding their mechanical properties, transverse rupture strength (TRS) and micro Vickers hardness (HV). The alloys were made from pure Mg, Al and B powders by mechanical alloying and hot pressing to have boride content of between 2.0 and 20 vol%. The alloy with AlB_2 exhibited an obvious improvement of HV around a boride content of 6 vol% though the other alloy, with MgB_2, did not. TRS showed moderate maxima around the same boride content region for the both alloys. X-ray diffraction measurements indicated an intermetallic compound, Mg_{17}Al_{12}, formed in the alloy with AlB_2, which was consistent with its higher hardness.

1. Introduction

Magnesium alloys have attracted much interest as structural materials because of their lower density and higher specific strength even than widely used aluminum alloys.[1] These characteristics satisfy the criteria required from structural materials for various vehicles like car, airplane and so on. Their weight saving will reduce the energy consumption as well as carbon dioxide emission.[2] In spite of these advantages, the use of wrought magnesium alloys is very limited because of their insufficient strength and low workability.

Powder metallurgy is expected to overcome these problems. This method is known to strengthen materials by its microstructure, fine particle dispersion, with high workability.[3] Powder metallurgy enables to form complicated and accurate sintered bodies by its forming method. Dispersion of hard boride particle or microcrystals by powder metallurgy is expected to improve the mechanical properties of Mg alloy with high workability. Boride-dispersed Mg alloys, however, have not been adequately studied so far.[4, 5, 6]

In this work, we focus on MgB_2 and AlB_2 as the particle to disperse in Mg alloy. They both have a hexagonal crystal structure, low density (MgB_2: 2.6 g/cm³, AlB_2: 3.2 g/cm³), high melting point and high hardness.[7, 8] We investigated the boride-content dependence of mechanical properties for the Mg alloys and discussed in their microstructure.

2. Experimental procedure

Samples were prepared by powder metallurgy: raw material powders were mixed, mechanically alloyed and then sintered by hot pressing. The Mg alloy with MgB_2 was made from Mg and B
Table 1. Chemical composition of sample alloys (vol%).

|                | Magnesium | 100 | 98 | 96 | 94 | 92 | 85 | 80 |
|----------------|-----------|-----|----|----|----|----|----|----|
| Boride in Alloy-1 | 0.0       | 2.0 | 4.0 | 6.0 | 8.0 | 15 | 20 |
| Boride in Alloy-2 | 0.0       | 2.0 | 4.0 | 6.0 | 8.0 | 15 | 20 |

powders. The other alloy with AlB₂ was from Mg, Al and B powders.

Raw material powders were pure Mg (99.9 mass%, 180 µm, Kojundo Chemical Laboratory Co., Ltd.), Al (99.9 mass%, 10 µm, Kojundo Chemical Laboratory Co., Ltd.) and B (96.8 mass%, 0.8 µm, H. C. Starck Co., Ltd.). All the powders were used without further purification.

Table 1 shows the boride content for both Alloy-1 (Mg-B alloy) and Alloy-2 (Mg-Al-B) that was controlled between 2 vol% and 20 vol%. Here all the added boron is assumed to form MgB₂ in Alloy-1 and AlB₂ in Alloy-2. We mixed the raw material powders with 3 mass% of zinc stearate as lubricant agent, then put the mixture into a stainless steel milling pot with stainless steel balls of 8-mm diameter. The volume ratio between the powder and balls was 1/20. The mixed powder was mechanically alloyed by a planetary ball mill (Itou Seisakujo Co., Ltd.) that rotated the pot in argon atmosphere at 200 rpm for 20 hours. The alloyed powder was then investigated by X-ray diffraction.

Each mechanically alloyed powder was hot-pressed under a pressure of 98 MPa, in Ar atmosphere, at 600 °C for 30 minutes. Then the sintered bodies were machined to 5.0 x 10 x 30 mm blocks for X-ray diffraction (XRD) measurement and mechanical properties investigation.

Transverse rupture strength (TRS) and micro Vickers hardness (HV₁₀₀) were measured on the sintered bodies. The former was performed with the three-point bending method, and the latter was carried out with a diamond indenter of square-based pyramid form loading 0.98 N for 10 seconds. HV₁₀₀ for each alloy was obtained by averaging 30 measured values on three specimens, 10 points for each. Microstructure and composition analyses were performed on the alloys after the hot pressing by a scanning electron microscope (S-4100, Hitachi Co. Ltd.) and an X-ray diffractometer (RAD-rR, Rigaku Co. Ltd.).

3. Results and discussion

XRD patterns of the alloys with 6 vol% boride, as representative samples, before and after the mechanical alloying and of sintered bodies are shown in figure 1. The mechanically alloyed powders exhibited broadened diffraction peaks of raw materials and newly reacted borides. The peaks were sharpened after the sintering, indicating further alloying and reduction of strain caused by mechanical alloying. An intermetallic compound, Mg₁₇Al₁₂, was formed in the Alloy-2.

Figure 2 shows transverse rupture strength (TRS) of Alloy-1 and Alloy-2. The datum for pure Mg made by same process is shown in comparison. Both Alloy-1 and Alloy-2 generally have high TRS compared to the pure Mg. As shown in the figure, boride improves TRS more for the Alloy-1 than for the other. The boride content dependence of TRS exhibits a moderate maximum around the content of 6 vol%.

Figure 3 shows the micro Vickers hardness (HV₁₀₀) of Alloy-1 and Alloy-2. The two alloys exhibited a quite different behavior compared to the TRS results. Though the hardness of Alloy-1 was totally independent on the boride content, that of Alloy-2 was clearly improved as the boride content increased. The boride addition obviously increased the hardness of Alloy-2 in high boride content region over 6 vol%, which finally reached 250 HV that was quite high for
Figure 1. XRD patterns of (a) Alloy-1 and (b) Alloy-2 with 6% of boride: before and after mechanical alloying and after sintering.

Figure 2. Boride content dependence of TRS for Alloy-1, Alloy-2 and pure Mg.
Figure 3. Boride content dependence of micro Vickers hardness for Alloy-1, Alloy-2 and pure Mg.

Figure 4. SEM micrograph of (a) Alloy-1 and (b) Alloy-2, both containing 6 % boride.

A Mg alloy.

Figure 4 shows SEM micrographs of (a) Alloy-1 and (b) Alloy-2 containing 6 vol% boride. Alloy-1 consisted of two phases: a light gray phase and a dark one. Energy-dispersive X-ray spectroscopy (EDX) revealed that the light gray phase consisted of Mg, and the dark phase of both Mg and B that was indicated to be boride by XRD in figure 1. This figure also shows that the boride was formed mostly around magnesium grain boundary, which could have a role of the grain growth inhibition by its pinning effect.

Alloy-2 in figure 4(b) exhibited finer microstructure than Alloy-1. Here light gray Mg phase was separated into smaller grains than in Alloy-1 by dark gray grain boundary. The grain boundary consisted of Mg, B and Al according to the EDX result. Since Al was indicated to form Mg$_{17}$Al$_{12}$ by XRD, the particles in the boundary were borides and the intermetallic compound that is a very hard material which can improve hardness.[9] The hard but brittle Mg$_{17}$Al$_{12}$ was supposedly formed and finely milled during the mechanical alloying process; it then brought out the pinning effect in shorter range than in Alloy-1.

The results showed that the boride addition improves TRS and HV of the magnesium alloys. The remarkable improvement in the hardness of the Alloy-2 is mainly attributed to the formation of Mg$_{17}$Al$_{12}$ observed in figure 4. XRD peaks corresponding to the Mg$_{17}$Al$_{12}$ become obvious
in high boride content region as shown in figure 5. Aluminum did not fully react with boron but with magnesium to form the intermetallic, which resulted in TRS reduction and hardness improvement in high boride content region. The maxima of TRS for both alloys and steep improvement of hardness of Alloy-2 occur around the boride content of 6 vol%. There can be some interaction between the microstructure and the intermetallic compound formation which directly defines the mechanical properties, which is to be studied in future work.

4. Conclusion
Magnesium alloys with dispersed MgB$_2$ (Alloy-1) and MgB$_2$ and AlB$_2$ (Alloy-2) dispersed were investigated for their hardness (HV$_{100}$) and TRS. The alloys were prepared by powder metallurgical technique: mechanical alloying and hot pressing.

The boride addition surely improved both TRS and HV$_{100}$ of the alloys. The alloys with 6 vol% exhibited the highest TRS. Though HV$_{100}$ of Alloy-1 was almost independent of the boride content for more than 2 vol% boride, the hardness of Alloy-2 increased for boride content over 6 vol%. The formation of hard Mg$_{17}$Al$_{12}$ and the finer microstructure is supposed to improve the hardness of Alloy-2. Formation of Mg$_{17}$Al$_{12}$ lowers TRS of Alloy-2 compared to Alloy-1.

The mechanism of the coincidence of TRS maximization on both alloys and steep hardness improvement of Alloy-2 is still unclear. Further analysis about microstructure and particle dispersion is expected to clarify this mechanical property improvement.

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