Preparation of Ultra Fine-Grained Magnesium Alloy by Mechanical Alloaying of AZ31 Chip-Aluminum Powder Mixture*

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To produce magnesium alloy with ultra fine-grain size, powder mixtures, which aluminum powder was added with various contents to turning chips of AZ31 alloy, were mechanically alloyed for various milling times. Micro-structural changes of the mechanically alloyed powder with milling were investigated. Super-saturated solid solutions of the magnesium phase with crystalline size of nanometer scale are formed in the Mg-12 mol%Al and 30 mol%Al powder mixtures mechanically alloyed for long milling time and, especially, it forms the eutectic structure together with Mg17Al12 in the Mg-30 mol%Al powder. In the case of the Mg-40 mol%Al and 61.5 mol%Al powders, formation of the intermetallic compounds yields by the mechanical alloying for shorter milling time, and these crystals become to amorphous phase after the prolonged milling time. The harnesses of particles in the powder mechanically alloyed increase with forming of the super saturated solid solution or the intermetallic compound and their refining.

* Key Words: Mechanical Alloaying, Magnesium Alloy, Structural Refinement, Intermetallic Compound, Solid Reaction, Reclamation

1. Introduction

It is understood that magnesium alloys have excellent mechanical strength together with a direct weight reduction these require material properties in airframe, automobile and portable instruments. It has been however manufactured by the die casting, injection molding and thixo-molding techniques, its mechanical properties of the products determine the microstructure and the defects as shrinkage voids and pores, which were formed during the solidification. Especially, the cast structure, which may be coarse grained through slow cooling rate, affects the mechanical strength of the alloy. A way of achieving structural refinement in the magnesium alloys is the minor additions of inoculants as calcium and zirconium. Mechanical alloying is essentially based on solid-state reaction during the milling process, which heavy working of powder particles results in intimate alloying by repeated welding and fracturing. This process has the same attributes as extension of solubility limits, production of intermetallic compound alloy and nanocrystal or amorphous alloy. Mixture of elemental powders was mechanically alloyed to fabricate intermetallic Mg2Si alloy and Mg3Si particle dispersed aluminum composites. Recently, it has been reported that microstructure of Mg-4 mass%Al alloy die-cast, which containing 1.4 mass%Ce of rare earth elements and AlFe particles prepared by the mechanical alloying, forms the distribution of elements in the solid solution. One of the characteristics in the magnesium alloy is it possible to the reclamation of the metal materials. The aim of this study is focused on the reclamation of Mg-Al alloy (AZ31), we investigated the alloying process in the mechanical alloying of powder mixture, which aluminum powder with various contents was added to AZ31 alloy turning chips.
2. Experimental Procedure

Atomized aluminum powder (99.7\% Al, mean particle size; 122 \(\mu\)m) and AZ31 alloy (Al; 3.12 mass\%, Zn; 1.11 mass\%, Mg; Bar.) turning chips were used as starting materials. These powders were mixed for various compositions as shown by 7 arrows in Al-Mg equilibrium diagram\(^{10}\) of Fig. 1. The mechanical alloying was carried out using the oscillatory ball mill (SpeX Mixer/Mill 8000). 3.6 g of the mixed powder was charged together with 72 g of stainless steel balls (diameter; \(\Phi4.67\) mm) in the vial (capacity; 500 ml) and then the inside of vial argon filled to avoid oxidation, milled for up to 500 ks. The obtained alloy powder for each milling time, the formed crystal phases were confirmed by X-ray diffraction (XRD), and it was also performed to search the thermal stability of those phases by differential scanning calorimeter (DSC). Microstructure of cross-sectioned particles was observed by scanning electron microscopy (SEM) and Vickers hardness (indenting load; 25 g) was measured.

3. Results and Discussion

3.1 On the Mg-12 to 30 mol\% Al powder mixture

The solubility limit of aluminum in the \(\alpha\)-Mg phase in binary Mg-Al is 11.8 mol\% at 710 K, as shown in Fig. 1. We might expect from this fact that Mg-alloy of the super-saturated solid solution forms when the Mg-12 mol\% Al powder mixture alloy was mechanically alloyed. Figure 2 shows XRD patterns of Mg-12 mol\% Al powder mixture mechanically alloyed for various milling times. The spectra of magnesium and aluminum become smaller and the intensities of these peaks decrease with milling time. The aluminum peaks disappeared in the powder milled for 10.8 ks. The peak positions of the magnesium shift slightly to lower diffraction angles with milling time.

The XRD pattern in Mg-30 mol\% Al powder mixture mechanically alloyed for various milling times shows in Fig. 3. The spectra of magnesium and aluminum become smaller and broader than, as same as Mg-12 mol\% Al, with the milling time. When the mechanical alloying was carried out for 10.8 ks, the spectra of Mg\(_{17}\)Al\(_{11}\), which is consisting of bcc structure (cI58), are appeared, and those intensities are increased. The Mg-30 mol\% Al is eutectic composition in Mg-Al system. Therefore, the mechanically alloyed Mg-30 mol\% Al powder becomes eutectic structure consisting of \(\alpha\)-Mg and Mg\(_{17}\)Al\(_{12}\) after milling time for 18 ks.

We calculated the lattice parameter of the magnesium phase from the spectra in the XRD patterns, namely axial ratio \(c/a\), of powder milled for various times. The values for the two kinds of mechanically alloyed powders as a function of milling time are shown in Fig. 4. The \(c/a\) value of magnesium in the starting AZ31 alloy was 1.6238 before milling. The \(c/a\) value of Mg-12 mol\% Al powder increases remarkably with the milling time and reaches 1.6258 after 18 ks, remaining at a constant value for still longer milling. The axial ratio in magnesium phase increases by

![Fig. 1 Phase diagram of Mg-Al system and compositions (arrows) investigated in this work](image1)

![Fig. 2 XRD patterns of Mg-12 mol\% Al powder mechanically alloyed for various milling times](image2)

![Fig. 3 XRD patterns of Mg-30 mol\% Al powder mechanically alloyed for various milling times](image3)
Fig. 4 Change of axial ratio c/a of α-Mg phase with milling time in the Mg-12 mol% Al and Mg-30 mol% Al powders

0.00018/mol% Al with increasing aluminum concentration⁶, therefore, the content of about 9 mol% Al in the magnesium phase for the alloy powder was increased by the mechanical alloying for over 18 ks. We conclude from this result, the solid solution of the magnesium phase, which contains nearly all aluminum added in the starting state, is formed, when the Mg-12 mol% Al powder mixture was mechanically alloyed for long milling time. The c/a value in Mg-30 mol% Al powder linearly decreases with the milling time. It is attributable to the formation of Mg₁₂Al₁₅ phase, which have high aluminum content, by consumption of aluminum from the AZ31 (Mg-2.89 mol% Al) powder with milling time.

Secondary electron image (SEM) of cross-sectioned particle of Mg-Al powder mechanically alloyed for various milling times was observed and distribution of magnesium and aluminum, which are main elements, concentration at same position was measured by EPMA. Figures 5 (a) ~ (c) show the SEM and MgKα- and AlKα- X-ray images on the same position of the Mg-12 mol% Al alloy particle mechanically alloyed for 36 ks. The magnesium and aluminum are uniformly dispersed in the location corresponded to the granular-like particle. It seems to suggest that the added aluminum is every solved in the magnesium phase and it became to the super solid-solution, as mentioned from the result of XRD in Fig. 2.

3.2 On the Mg-40 to 61.5 mol% Al powder mixture

Mg-40 and 61.5 mol% Al powder mixtures, which corresponds to the compositions of intermetallic compound Mg₁₁Al₁₅ and Mg₅₂Al₃, respectively, were mechanically alloyed for various milling times. Results of the XRD for the each powder show in Figs. 6 and 7. In the Mg-40mol% Al powder, the intensities of peak of the magnesium and aluminum spectra decrease with milling time and spectrum of Mg₁₁Al₁₅ as new crystal phase appears. After mechanically alloyed over 18 ks, spectra of magnesium and aluminum disappear and the spectrum of Mg₁₁Al₁₅ becomes broader and its intensity decreases with milling time. In the case of the Mg-61.5 mol% Al powder, formation of the intermetallic compounds as MgAl, MgAl₂ and Mg₅₂Al₃ yields by the mechanical alloying for shorter milling time, such as 7.2 ks, and these crystals become
to amorphous phase after the milling time for 54 ks.

Crystalline sizes of $\alpha$-Mg phase in the Mg-12 mol%Al and Mg-30 mol%Al powders, which were calculated from XRD patterns by Sherrer's formula, as function of milling time are shown in Fig.8, compared with the sizes of the intermetallic compound formed in the Mg-40 mol%Al and Mg-61.5 mol%Al powders mechanically alloyed. The crystalline sizes of $\alpha$-Mg phase and intermetallic compounds in all examined powders decrease very rapidly during the initial milling stage. When the milling time is prolonged, the sizes of $\alpha$-Mg phase reach to 20 nm in the Mg-12 mol%Al powder and to 30 nm in the Mg-30 mol%Al powder. In the case of Mg-40 mol%Al powder, the crystalline size of intermetallic compound is under 10 nm after 18 ks, and this phase becomes the amorphous. The tendencies to a refinement of the structure become pronounced with increasing aluminum content.

3.3 Vickers hardness and thermal stability of mechanically alloyed powder

The hardness measurements of the powder particles are affected by a quite significant scatter ranging from $H_v=50$ to 100 in all examined samples, thus a clear dependence of the formed crystal phases in the particle on the milling time was observed. Figure 9 shows the Vickers hardness data obtained on the particles of Mg-12 and 30 mol% Al powder mechanically alloyed for various milling times. The hardness of both powder particles increases very rapidly during the initial milling stage I. In general, the mechanical strength of the alloy is remarkably depended by the crystalline size. As mentioned in the term of 3.1 on both Mg-12 mol%Al and -30 mol%Al powders, aluminum content in the $\alpha$-Mg increases and its crystalline size decreases with increasing of the milling time in the initial stage. The increase of the hardness may correspond to the features given here. The hardness of both powders mechanically alloyed for 18 - 36 ks (stage II) are a constant. In this stage, aluminum content in $\alpha$-Mg and the crystalline size are not change. The hardness of powder mechanically alloyed for over 36ks (stage III) increases by the formation of intermetallic compound as Mg$_{17}$Al$_{12}$ phase, though no change the crystalline size of $\alpha$-Mg phase.

Figure 10 shows on the change of Vickers hardness with the milling time in the Mg-40 mol%Al and 61.5 mol%Al powders. In the first stage 1 by the mechanical alloying, the formation of the intermetallic compounds had been cleared by the results of XRD for both milled powders in the team of 3.2. Consequently, the hardness in the particles increases drastically in this stage. We confirm that the hardness in the powders would reach a saturation value after milling times much longer than 18 ks (stage II). In the case of Mg-40 mol%Al powder, the hardness is about $H_v=200$, whereas, the hardness in the Mg-61.5 mol%Al powder become to about $H_v=250$. In both powders mechanically alloyed for over 36 ks (stage III), the hardness is again increased because of the powder become to amorphous alloy.

We carried out DSC measurement for the each
powder mechanically alloyed for 36 ks, in order to confirm the thermal stability of the structure formed in the powder by the mechanical alloying. These results are shown in Fig. 11. In the Mg-12 mol%Al, 30 mol%Al and 40 mol%Al powders, endothermic reactions occur at 705, 720 and 735 K, respectively, quantity of heat in the reaction increases with the increasing of the aluminum content. Since those endothermic reactions are attributable to the dissolution of the crystal phase, the endothermic temperatures in the powder are equal or over than the eutectic temperature. We could be confirmed that nearly all contents of aluminum added in AZ31 chips were alloyed and become to equilibrium by the mechanical alloying for 36 ks. On the other hand, exothermic reaction occurs at 530 and 650 K in the Mg-61.5 mol%Al powder. It is presumed that R (often designates, rhombohedral structure, hR53) phase precipitates from metastable phases, as MgAl and MgAl2, at 530 K, and then become to equilibrium phase of Mg2Al3 at 650 K.

4. Conclusions

Powder mixtures, which aluminum powder was added to AZ31 chips with various contents, were mechanically alloyed for various milling times. The changes in microstructure of the mechanically alloyed powder were investigated. The super saturated solid solutions of the magnesium phase with crystalline size of nanometer scale are formed in the Mg-12 mol%Al and 30 mol%Al powder mixtures mechanically alloyed for long milling time. Mg-30 mol%Al powder becomes to the eutectic structure. In the case of the Mg-40 mol%Al and 61.5 mol%Al powders, formation of the intermetallic compounds yields by the mechanical alloying for shorter milling time, such as 7.2 ks, and these crystals become to amorphous phase after the prolonged milling time. The hardnesses of particles in the powder mechanically alloyed increase with forming of the super saturated solid solution or the intermetallic compound and their refining. It can expects that improve the wear — or corrosion-resistance in the magnesium alloy, if these mechanical alloyed powder is covered on surface of magnesium alloy.

Acknowledgments

We are indebted to the staff of the Instrumental Analysis Center in Musashi Institute of Technology, Dr. Akira Yoshida and Ms. Emi Shinoh for their help through this study. We are also grateful to Dr. Yoshinari Oki and Mr. Tsutomu Murai in SANKYO Aluminum Industry Co. Ltd. for supply the AZ31 turning chips.

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