研 究

Thermal Behavior of AZ31 and Si in Solid State Synthesis of Mg_2Si Ritsuko Tsuzuki^{☆1}, Masaya Ishihara^{☆2}, Katsuyoshi Kondoh^{☆1} and Eiji Yuasa^{☆3}^{☆1}Research Center for Advanced Science and Technology, The University of Tokyo 4-6-1 Komaba Meguro-ku, Tokyo 153-8904.^{☆2}Graduate school of Musashi Institute of Technology, 1-28-1 Tamazutsumi Setagaya-ku, Tokyo 158-8557.^{☆3}Musashi Institute of Technology, 1-28-1 Tamazutsumi Setagaya-ku, Tokyo 158-8557.

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SYNOPSIS

Mg_2Si/Mg composite which shows high mechanical properties was expected to be produced via solid-state synthesis using AZ31 powder and Si powder as initial material. For the first step of this research, thermal behavior of AZ31 and Si was investigated in this paper.

AZ31/Si compacts with various compositions were examined by differential scanning calorimeter and analyzed by X-ray diffraction to confirm reactivity between them.

The detailed result indicated that Si could completely react with AZ31 and synthesize Mg_2Si when heated at 753 K, which is almost the same temperature as in the case of using purity Mg. The starting temperature of synthesis became lower and exothermic heat increased as Si content increased. Repeated plastic working (RPW) was also effective to decrease their synthesizing temperature. That is because the reaction between Mg and Si occurred easily due to the mechanisms of RPW process such as (1) breakage of oxide film on the surface of Mg particles and (2) refinement of both of the Mg and Si particles. In addition, it was observed as the result of optical microstructure that Mg_2Si particles were dispersed into matrix and they existed at the interface of Mg grain.

KEY WORDS

 Mg_2Si , AZ31, solid-state synthesis, repeated plastic working, Mg composite

1 Introduction

Mg has the lowest density among the commercially available structural materials and has the excellent specific strength and elastic modulus¹⁾. From the view point of the environment problem, therefore, it is effective to use Mg or Mg alloys for reduction of energy consumption and air pollutions during industrial manufacture process owing to its effect of weight reduction. The demands of Mg and/or Mg alloys are also increasing for use in the automobile and aerospace industry, the field of information technology and so forth. However, they have some weak points, such as poor mechanical and tribological properties. To cover those defects, Mg_2Si , which is known as the intermetallic compound having excellent mechanical properties, is studied to product Mg composite¹⁾. Usually Mg alloys are fabricated by casting process such as die-casting²⁾. However, it causes some problems such as large Mg grains that reduce the strength and ductility of the composite. Therefore, instead of die-casting, in-situ solid-state synthesis of Mg_2Si has been developed recently^{1,3,4)}, and the process of in-situ solid state synthesis of Mg_2Si was established^{6,7)}. In particular, the effect of the raw powder

characteristic on the synthesis was investigated^{7,8)}.

While AZ31 Mg-Al-Zn system alloy is widely used for structural materials such as sheet, bar and tube, and its weld ability, mechanical properties and manufacture process were investigated⁹⁻¹²⁾.

Then it is expected to product Mg/ Mg_2Si composite which has high mechanical properties via in-situ solid-state synthesis using AZ31 and Si.

In this report, the thermal behavior of AZ31 against Si is investigated to confirm reactivity between AZ31 and Si, and the temperature of solid-state synthesis of Mg. In addition, the effects of Si contents and plastic working process on the thermal behavior were discussed. On every evaluation, the results were also compared with the result in the case of using purity Mg powder.

2 Experimental procedures

AZ31 powder (nominal composition: Mg-3Al-1Zn/mass%, mean particle size: 89 μm), industrial purity of Mg powder (purity: 99.9%, mean particle size: 112.0 μm) and Si powder (purity: 99.99%, mean particle size: 22.3 μm) were prepared for raw materials. AZ31 or Mg powders were

weighted and mixed to Si powder at various compositions. Those powder mixtures were consolidated to product green compact for evaluation with two methods, cold compress and repeated plastic working (RPW)¹¹⁾. Cold press was performed with conventional compaction method at 620 MPa for 5 seconds. RPW method is explained as shown in Fig. 1. Powder mixtures were filled in the die shielded with Ar gas, and pressed by upper and lower punches. This RPW process includes compaction twice and extrusion once in 1 cycle. The input powders were homogeneously dispersed and strongly fractured by two punches after some cycles of operations.

The green compacts after RPW were analyzed by Differential Scanning Calorimeter (DSC) with heating rate of 0.167 K/s under N_2 gas atmosphere to evaluate their thermal behaviors. X-ray diffraction (XRD) with $\text{CuK}\alpha$ ($\lambda = 0.15405 \text{ nm}$) radiation was also operated at 40 kV and 200 mA to estimate the structures. Microstructure of sample was examined using optical microscope.

3 Results and discussion

3.1 The survey of thermal behavior of AZ31/Mg-Si to solid-state synthesis of Mg_2Si

Mg_2Si is synthesized from Mg and Si elements according to the reaction as the following equation:

In order to obtain the $\text{Mg}_2\text{Si}/\text{Mg}$ composite via solid-state synthesis, it is necessary to confirm the Mg_2Si formation temperature range which is equivalent to the reactive heat quantity, Q , in Eq. 1. To search the formation temperature

Fig.1 Schematic illustration of punch motion during repeated plastic working process.

range, DSC was carried out on AZ31-5wt%Si cold compact as shown in Fig. 2. As a result, exothermic reaction was detected around 750 K. In order to investigate whether this reaction is due to the formation of Mg_2Si , XRD was further carried out for the composites, which were heated at 573 K and 753 K. These were the temperatures before exothermic reaction and after beginning reaction, respectively. Fig. 3 shows the XRD patterns for the composites without heating and after heating at each temperature. On these patterns, Si peak was detected in the non-heating compact and it decreased in the compact heated at 573 K, and finally it disappeared in the compact heated at 753 K. On the other hand, Mg_2Si peak intensity became higher with increase of heating temperature. They suggested the additional Si was completely consumed to react with Mg. Therefore, it was proved that the all exothermic peaks are ascribed to solid-state synthesis of Mg_2Si .

Fig.2 Temperature of heating test on AZ31-5wt%Si cold compact.

Fig.3 XRD patterns of AZ31-5 wt%Si cold compact and ones heated at 573 K and 753 K.

After heating, optical microstructure of compact as shown in Fig. 4 was observed. Mg_2Si particles were dispersed into matrix along grain boundaries. Those dispersoids were inhomogeneous in size and shape.

3.2 Effect of silicon content on thermal behavior of AZ31/Mg-Si

AZ31-2.5, 5, 7.5, 10 wt% Si compacts and Mg-5, 10, 15 wt% Si compacts by cold pressing were analyzed by DSC to search thermal behavior. Fig. 5 shows the DSC curves of the AZ31/Mg-5, 10 wt% Si compacts. On every curve, exothermic peaks due to the formation of Mg_2Si were found. In both of AZ-base and Mg-base compacts, the starting temperatures of exothermic peaks (Ts) shifted to the lower temperature side as Si content increased. It indicated that increase of surface area of Si particles due to increase of its contents leads to react between Mg and Si easily. This tendency was much obvious in Mg-base compact compared

Fig. 4 Optical microstructure of AZ31-5 wt% Si cold compact heated at 753 K.

Fig. 5 DSC curves of AZ31-5, 10 wt% Si and Mg-5, 10 wt% Si cold compacts.

with in the case of using AZ31-base compact. Ts of Mg-base compact were lower than those of AZ-base one, which may be owing to the Al and Zn elements which were contained in AZ31 powder. That is proved by the result of XRD as shown in Fig. 6. Mg peaks of AZ31-base compacts were detected at higher degree than Mg-base compacts, while Si peaks were detected at almost same position on both materials. It explains those two elements, Al and Zn, were still solid stated in Mg after cold press. Also those peaks of AZ31-base were broader than others. From that analysis, it was expected that Al and Zn elements effected reactivity of Mg, and suppressed the reaction between Mg and Si more or less.

Further exothermic heat was also increased with increase of Si content as shown in Fig. 7. This proportional relationship

Fig. 6 XRD patterns of AZ31-2.5, 5 wt% Si and Mg-5, 10 wt% Si cold compacts.

Fig. 7 Dependences of exothermic heat of AZ31-x wt% Si and Mg-x wt% Si in Si contents.

between exothermic heat and Si content on both materials indicated that all (or fixed ratio) of Si powder was used to react with Mg for this temperature range.

As the result of DSC and XRD, it was confirmed AZ31 could react with Si as in the almost same condition as raw Mg powder.

3.3 Effect of repeated plastic working on thermal behavior of AZ31/Mg-Si

It was expected that the particles of each powder (matrix and additive) were refined and uniformly dispersed via RPW process, and next the influence of RPW with thermal behavior of materials were studied.

Fig. 8 shows DSC curves of AZ31/Mg-5 wt% Si after RPW at 100 and 200 cycles. On these curves, small exothermic peaks were found, and they shifted to lower temperature with increase of RPW cycle. It signified the synthesis of Mg_2Si was accelerated by RPW. Powder mixtures were taken severe shear strain by RPW, and the particle sizes were decreased owing to their brittleness. It led to increase total surface area of Si particles. In addition, the oxide films of Mg particles were broken during RPW process and the activated surfaces of Mg particles were exposed. Owing to these two effects, the reaction between Mg and Si became more easily, and progressed as RPW cycle increased. Further, value of strain introduced into particles increased with increase of RPW cycle, then those strains became driving force and accelerated reaction, as well.

While, exothermic heat of each material decreased with increase of RPW cycle as shown in Fig. 9. It was thought that the synthesis of Mg_2Si partly started via RPW process, and non-reacted Si remainder decreased after RPW, then

the value of Mg-Si synthesis decreases with increase of RPW cycle.

RPWed AZ/Mg-Si compacts were analyzed by XRD as shown in Fig. 10. Mg_2Si peaks were detected in every RPWed compacts, and it agreed with the result of DSC. In the case of Mg-base compacts, Mg_2Si peaks increased with increase of RPW cycle, however, in the case of AZ31-base compacts, intensity of Mg_2Si peak didn't depend on the RPW cycles. At the same time, detected peaks of AZ31-base compacts were broader and appeared at higher degree than those Mg-base compacts. Further, Si peak appeared at high cycle. It is thought that Si particles mixed to AZ31

Fig.9 Dependences of exothermic heat of AZ31-xwt%Si and Mg-x wt%Si in RPW cycles.

Fig.8 DSC curves of AZ31-5,10wt%Si and Mg-5,10wt%Si compacts at various RPW cycles.

Fig.10 XRD patterns of AZ31-2.5,5wt%Si and Mg-5,10wt%Si compacts at various RPW cycles.

were refined and solid-state into AZ31 matrix (α -Mg) same as Al and Zn on the initial state of RPW, then started to synthesize Mg_2Si which has very fine crystalline structure close to amorphous, and partial non-reacted Si appeared on XRD patterns as RPW progressed. In other words, in the case of AZ31-base composite, refinement of Si particles took precedence than synthesis of Mg_2Si . Therefore, Ts of AZ31-base compacts became higher than Mg-base ones.

4 Conclusions

- (1) Si was completely reacted with Mg and Mg_2Si was synthesized when heating at 753K. The thermal behaviors of that were almost same in the both case of using AZ31 and purity Mg with Si.
- (2) The starting temperature of synthesis became lower and the exothermic heat increased as Si content increased.
- (3) RPW process effects to decrease their synthesizing temperature.
- (4) Mg_2Si particles were dispersed into matrix and existed on the interface of grain.

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