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Solid-state Synthesis of Mg_2X (X=Si, Ge, Sn and Pb) via Bulk Mechanical Alloying

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Abstract

Solid-state processing via the bulk mechanical alloying enables us to directly fabricate Mg_2X semi-conductive material performs. Precise control of chemical composition leads to investigation on the dilution and enrichment of X in Mg_2X. Two types of solid-state reactivity are introduced: e.g. synthesis of Mg_2Si from elemental mixture Mg – Si is nucleation-controlled process while synthesis of Mg_2Sn from Mg – Sn, diffusion-controlled process. Thermoelectricity of these Mg_2X is evaluated for discussion on the validity and effectiveness of this new PM route as a reliable tool for fabrication of thermoelectric compounds.

Keywords: Solid-state synthesis, Bulk mechanical alloying, Mg_2X, Semi-conductivity, Thermoelectricity

1. Introduction

In early fifties to sixties, many fundamental studies [1] have bee reported about the intrinsic semi-conductivity of Mg_2X (X=Si, Ge and Sn). These three compounds are semi-conducting and Mg_2Pb is a metallic compound. Their band gap decreases monotonically from Si to Pb for X in Mg_2X. Irrespective of much difference in melting points among Mg, Si, Ge, Sn and Pb, the phase diagram for Mg-X systems at the vicinity of 66.67 at% for Mg is nearly the same; the free energy profile in this content range must be common to Mg-X systems. The conventional casting or powder metallurgy processes are difficult to synthesize Mg_2X because of various barriers: significant difference of melting points between Mg and X, high vaporizing pressure of Mg, mechanical adhesion of Mg, Sn or Pb and chemical reactivity of Si and Ge [2]. Bulk mechanical alloying (BMA) [3] is used to make solid-state synthesis of these compounds. In the present study, the solid-state reactivity to form Mg_2X is revisited with consideration on the effect of refinement process in BMA on the reaction. When starting form the elemental powder mixture of Mg and X, material system must be heated up above the meting point of Mg to sustain the exothermic reaction process until full reactivity is attained in the whole materials. This liquid-phase reactivity is expected to change to solid-state reactivity via BMA with refinement of constituent particle sizes for Mg and X. Mg-Si and Mg-Sn systems are employed to describe their solid state reaction processes and to discuss the effect of refinement process on their reactivity. Thermoelectric properties are measured for hot-pressed Mg_2Si and Mg_2Sn samples to demonstrate the effectiveness of this processing.

2. Experimental Procedure

The elemental powders were prepared as a starting material. Their purity and average particle size (D_p) were listed in Table 1. The present experimental procedure is applicable even when starting from elemental granules or platelets in the order of mm. For solid-state synthesis, the bulk mechanical alloying (BMA) was utilized to synthesize Mg_2X from elemental power mixture with the stoichiometric molar ratio of 66.67 at% for Mg and 33.33 at% for X. Each elemental powder mixture was blended homogeneously and then subjected to BMA in a flowing argon atmosphere to prevent the powder compact from oxidation. As-BMA perform with the relative denity of 80% T.D. is hot-pressed to form dense pellets for measurement of thermoelectric properties. Specimens for thermoelectric measurement were cut out from the sintered pellets: a rectangular bar with the size of 2x2x8 mm^3 for measurement of the electrical conductivity. The thermoelectric properties were evaluated form room temperature to about 700 K. The electrical conductivity (σ) was measured by the four-probe dc method in helium atmosphere, using the computer-controlled equipment. X-ray diffraction (XRD) analysis with the monochromatic Cu k_α radiation was used to describe the solid-state reaction via BMA. The differential thermal analysis (DTA) was carried out to explore the onset-temperature of solid-state reaction during BMA process with the heating rate of 20 K/min up to 1073 K in an argon atmosphere. Field emission type scanning electron microscopy (FE-SEM) was utilized to measure the refined constituent size during BMA.

Table 1. Purity and D_p for Mg, Si, Ge, Sn and Pb particles

Element	Mg	Si	Ge	Sn	Pb
Purity (%)	99.9	99.9	99.999	99.9	99.9
D_p (μm)	100	20	100	10	10

3. Experimental Results

Solid-state reactivity to form Mg_2X has two types: ductile – brittle system for Mg-C and Mg-Si and ductile – ductile system for Mg-Ge, Mg-Sn and Mg-Pb. Mg-Si and Mg-Sn systems are employed to describe the fundamental features of these two processes. In particular, solid-state reactivity is compared between Mg-Si and Mg-Sn systems.

After Ref. [3], the solid state reactivity (χ) is experimentally described by the ratio of formation enthalpy to synthesize Mg_2X for BMA samples (ΔH_f) at the time of t to that at t = 0 (ΔH_f^0) in the DTA diagram: i.e. $\chi = \Delta H_f / \Delta H_f^0$. This solid state reactivity as well as refinement of constituents via BMA is thought to be a relaxation process with the well-defined relaxation time (t_R) after the phase change of steels and the relaxation of glasses: e.g. $\chi = \exp(-(t/t_R)^\beta)$. Materials constants and relaxation time can be experimentally determined by measurement of constituent particle size and χ in the function of process time of BMA. Then, variation of χ from un-reacted state (χ = 1.0) to full-reacted one (χ = 0.0) is described by refining process in BMA.

Interparticle distance (D) between two nearest neighboring tin particles describes the refinement process in Mg-Sn system. As shown in Fig. 1, χ reduces monotonically with D/D_0 for the initial particle distance, D_0; χ goes to zero, or, full reactivity is attained as $D/D_0 \rightarrow 0$. This might be common to micro-forging effect often observed in the milling type mechanical alloying. Both constituents deform, finely distribute and fold enough to activate the diffusion and reaction even at the room temperature. In case of Mg-Si system, reduction of Si particle size R drives the refinement process in BMA. Figure 2 depicts the variation of χ with R/R_0 for the initial particle size, R_0. At the critical Si particle size $R_{critical}$, χ becomes nearly zero; since no peaks of Mg_2Si are seen in XRD profiles for $R > R_{critical}$, reactivity ignites itself at $R = R_{critical}$ by nucleation of Mg_2Si embryos on the refined interface between Mg and Si.

Bandgap (E_g), Seebekc coefficient at 323 K (α_{373}), Seebeck coefficient at 609 K (α_{609}), electrical conductivity at 609 K (σ_{609}) and thermal conductivity at 609 K (κ_{609}) are listed for Mg_2Si and Mg_2Sn, respectively in Table 2.

4. Summary

Magnesium binary compounds, Mg_2X are successfully synthesized in solid by bulk mechanical alloying. This solid state synthesis has two types in reaction: 1) nucleation

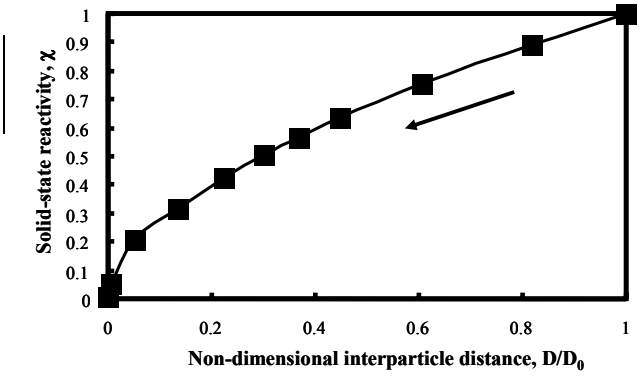

Fig. 1. Variation of χ with D/D_0 in Mg-Sn system.

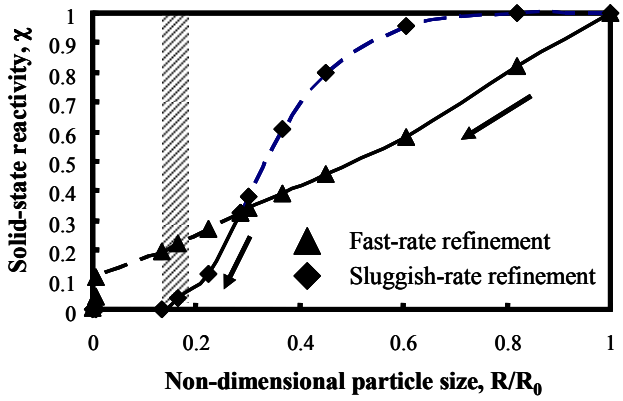

Fig. 2. Variation of χ with R/R_0 in Mg-Si system.

Table 2. Variation of χ with R/R_0 in Mg-Si system

	Eg (eV)	α_{373} (μVK^{-1})	α_{609} (μVK^{-1})	σ_{609} ($\Omega^{-1}m^{-1}$)	κ_{609} ($Wm^{-1}K^{-1}$)
Mg_2Sn	0.31	+ 60	+15	6.4×10^4	2.3
Mg_2Si	0.71	- 750	- 300	2.9×10^3	2.4

controlled process, driven by enlargement of interface area between refined phases of Mg and X (=Si), and, 2) diffusion controlled process, driven by refinement of interparticle distance between refined phases of Mg and X (=Ge, Sn, Pb). Mg_2Si is an n-type thermoelectric semi-conducting material with high Seebeck coefficient while Mg_2Sn is a p-type material with high electrical conductivity.

5. References

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