First-Year Achievement Report

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1. Introduction

The solid-state synthesis has been investigated as a new route to fabricate various alloys and compounds from the elemental particle mixture [1]. In particular, since magnesium is a chemically active material, its alloys and compounds are not so easy, sometimes very difficult or nearly impossible to yield by using the traditional processing like the melting and solidification and the powder metallurgy [2-3]. Through the preliminary works, binary and ternary magnesium based compounds were successfully fabricated by the present processing. The first-year project started on the basis of the fundamental knowledge obtained and summarized in Ref. [4]. Our contribution to MURI-project is divided into three: 1)Thermoelectric (TE) material search to have higher figure-of-merit, 2) Supply of candidate TE-materials to TE-group, especially Prof. Taya TE-group, and 3) Invention of mass-productive processing with less constrains on the processing route.

In this report, the outline of this first-year achievement from August in 2007 to July in 2008 is first summarized with key notes on its important features. Then, three items of them are described in detail by showing the main results in each. These achievements are summarized in the conclusion. In final, important items toward next-year project are pointed out, aiming at the goal of MURI-program.

2. Outline of the first-year achievement

Being related to the contribution 1) to MURI-project, our developing solid-state synthesis is found to have two free design parameters in Mg-Si-Ge-Sn system. Completely different from the conventional processings [5-6], the germanium content (x) as well as the tin content (y) are freely varied to control the Seebeck coefficient, thermal conductivity and electrical conductivity of magnesium based TE-compounds of $Mg_2Si_{1-x-y}Ge_xSn_y$. Selection of Mg and Si system is effective to obtain high Seebeck coefficient to yield Mg_2Si as a negative TE-leg material. Without reduction of this high Seebeck coefficient, x is varied to control the sign of the Seebeck

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14. ABSTRACT

In the first-year of projects related to MURI-program, Mg-Si-Ge-Sn system is found to be a suitable TE-material target for improvement of specific figure-of-merit to be used as the candidate energy harvesting material. The solid-state synthesis is an only approach to utilize two material parameters of germanium and tin contents in order to optimize TE-material property. The germanium content (x) in Mg2Si1-x-yGexSny plays a role to control the Seebeck coefficient; while the tin content (y) in Mg2Si1-x-yGexSny can be optimized to improve the electrical conductivity. Since finer microstructure of Mg2Si1-x-yGexSny is obtained by the present processing, low thermal Conductivity is commonly attained irrespective of x and y. New processing route of this solid-state synthesis is invented to yield dense TE-leg materials. In this approach, the premixed state mixture with fine embryos of TE-compounds is obtained by using the bulk mechanical alloying. Then, these finely premixed state materials are further annealed and consolidated at relatively low holding Temperature to yield targeting TE-leg materials. Forming of these fine pre-mixture before annealing and consolidation, results in formation of variously shaped TE-leg Materials. Extension of this solid-state synthesis approach to mass production is possible by using the larger die-set. This approach has a capability to yield hundred-gram TE-materials in one batch operation.

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coefficient from negative to positive; e.g. the Seebeck coefficient is negative for $x < 0.3$ while it turns to be positive for $x > 0.4$. On the other hand, y is controlled to improve the electrical conductivity.

New solid-state synthesis route is also developed to yield larger volume of magnesium based TE alloys and compounds. This processing is applied in the first year to fabricate higher density bulk billet of Mg_2Si and to deliver it to Prof. Taya group. The crushed particles of Mg_2Si were sent in three times to Prof. Taya group in the first year.

The scaled-up die-set is newly built up with partial aid of the present budget to yield a model billet by using the developing bulk mechanical alloying apparatus. A bulk billet of 150 g can be fabricated in one-batch operation to have fine microstructure even for composites.

3. Materials Design for Mg-Based TE-Compounds

In the present solid-state synthesis, the elemental particles are blended to have the targeting molar ratio to the alloy or compound to be synthesized. Different from the conventional ball-milling type mechanical alloying, larger magnesium particles are utilized as a starting material. Typical powder size and shape is listed in Fig. 1. Since using the larger size particles, initial contaminants are limited to the trace level.

This elemental particle mixture is poured into a die cavity in the developed bulk mechanical alloying apparatus, as shown in Fig. 2. In the present approach, the die-set is scaled-up for mass-production even when using the same BMA-apparatus. The detail is discussed later. The poured elemental particle mixture is subjected to the cyclic loading; Figure 3 depicts the typical pass schedule for this cyclic loading. In this program, one forward extrusion mode is included together with two compression modes. As theoretically and experimentally proven in Ref. [4], intense shear strain is applied in this former process to densified particle mixture, resulting in elongation and fragmentation. During this process, each elemental particle is folded and refined in solid. In the latter compression, the refined mixture is further densified to a billet. Figure 4 depicts a typical change in the particle morphology with increasing the number of cyclic loading in Mg-Si-Ge system. Refinement first advances in this mixture before commencement of solid-state reaction.

X-ray diffraction method (XRD) and differential thermal analysis (DTA) are both utilized to describe the solid-state reaction behavior with increasing N. In case of Mg-Si-Ge system, each characteristic peak intensity to magnesium, silicon and germanium, decreases and broadens with N in Fig. 4. This is a direct proof that the particle size should be reduced by application of cyclic loading to elemental powder mixture. When N > 300, a new peak, is noticed to be corresponding to solid-solution ternary compound of $Mg_2Si_{1-x}Ge_x$. In final, when X > 600, only this peak is recognized in XRD profile; a sing phase TE-compound of $Mg_2Si_{1-x}Ge_x$ is synthesized. This refinement and solid-state reaction behavior is also traced in the variation of DTA diagram with increasing N. As shown in Fig. 5, the exothermic peak shifts to lower temperature side with increasing N; this proves that solid-state reaction ignites in lower temperature since the initial particle mixture is refined to commence the solid reaction by lower heat supply. When N > 300, this exothermic peak intensity also decreases with N; it becomes none when N > 600. This is a proof that every mixture is fully reacted so that the measured diagram is only corresponding to the variation of specific heat for a single phase $Mg_2Si_{1-x}Ge_x$ compound with temperature.

In the case of Mg-Si-Ge system, the germanium content (x) can be controlled to be $0 < x < 1$ by using this processing. As had been denoted in Ref. (5, 6), many difficulties in materials processing hindered the composition design in this compound. Figure 6 depicts the variation of the measured Seebeck coefficient with x. When $x < 0.2$, the Seebeck coefficient becomes still negative: i.e. this $Mg_2Si_{1-x}Ge_x$ provides n-type TE-leg material. At the vicinity of $x = 0.35$, the sign of Seebeck coefficient changes itself from negative to positive abruptly. This pn-transition is true to Mg-Si-Ge and Mg-Si-Sn systems. When $x > 0.4$, $Mg_2Si_{1-x}Ge_x$ becomes p-type TE-leg material, having the same absolute value of Seebeck coefficient. Then, non-stoichiometric value (x) becomes a parameter to yield both n- and p-type TE-leg materials without loss of high Seebeck coefficient. Low thermal conductivity is attained by refined microstructure of solid-state synthesized $Mg_2Si_{1-x}Ge_x$ compound.

The present method provides us the other free parameter or the tin content (y) in the solid-state synthesized $Mg_2Si_{1-y}Sn_y$. Figure 7 depicts the effect of tin content on the temperature dependence of electrical conductivity. Mg_2Sn has much higher electrical conductivity among other magnesium-based compounds. Hence, addition of Mg_2Sn into ternary compounds by $y < 0.2$, improves the electrical conductivity ten times than pure Mg_2Si.

4. New Solid-State Synthesis Route

In the present solid-state synthesis, the final binary and ternary TE-compound materials are fabricated as fully-reacted particles. Hence, densification via SPS or hot-pressing is needed to fabricate both n- and p-type TE-leg materials from theses particles. As shown in Fig. 5, the solid-state reaction is activated to commence at the lower temperature by using the present method. This finding stimulates us to invent a new processing route to fabricate TE-leg materials. In this new route, bulk mechanical alloying is stopped at the intermediate step where the exothermic peak definitely shifts to lower temperature size by formation of fine mixture state of elemental particles.

Mg-Si system is employed to demonstrate this new processing route. In the first stage, let us investigate the relationship between the microstructure change and the change in solid-state reactivity. Figure 8 shows the variation of DTA diagram with increasing the number of cycles in the bulk mechanical alloying; the same pass schedule as depicted in Fig. 2 was used in this experiment. Even in the early stage of cyclic loading, the exothermic peak shift to lower temperature side is seen at N = 150. Figure 9 compares the microstructure of magnesium and silicon particle mixture between at N = 50 and N = 150. In the case when little peak shift is observed, the average particle size of silicon is still large and mixing state in Mg-Si system is rough. However, with increasing the number of cycles to N = 150, the average silicon particle becomes much finer and is homogeneously mixed in the magnesium matrix. Hence, refinement in microstructure results in significant peak shift in DTA. This activation of solid-state reaction is explained by formation of Mg_2Si-embryo. As shown in Fig. 9, Mg_2Si phase is synthesized in the inside of Mg-Si fine mixture.

In order to profoundly understand this peak shift of DTA diagram, annealing experiments were made at the different holding temperature (T_H). As depicted in Fig. 10, Mg-Si system is still a mixture when $T_H <$ peak temperature (T_P); while Mg-Si system is reacted to be homogeneously Mg_2Si when $T_H > T_P$. That is, Mg_2Si TE-leg materials can be synthesized and further consolidated by hot-pressing or SPS when starting this fine mixture state and holding the temperature above T_P.

A role of pre-mixing via the bulk mechanical alloying is only limited to reduction of reaction temperature? Figure 11 compares the microstructure after annealing at the different holding temperature between N = 0 and N = 150. When starting the initial particle mixture at N = 0, residual unreacted silicon is left in system and the average grain size is much coarser. On the other hand, when starting from a sample at N = 150, no silicon residuals are left in system and the average crystalline size of Mg_2Si is much finer.

Starting the magnesium and silicon particle mixture with Mg 66.67 at% and Si 33.33 at%, the premixing via the bulk mechanical alloying is stopped at N = 300 to yield a fine-mixed precursor. This precursor is further annealed at 623 K for 7.2 ks to fabricate fully-reacted Mg_2Si billet. Figure 12 depicts the measured electrical conductivity and Seebeck coefficient. As reported in Ref. [4], an intrinsic semi-conductive property of Mg_2Si is obtained by the present processing. These synthesized Mg_2Si billet was crushed to particles with larger size and delivered to Prof. Taya TE-group in three times.

5. Massive Production via Solid-State Synthesis

Toward mass prediction of magnesium based TE materials in hundreds of grams, a new die-set was built-up to be working in the present bulk mechanical alloying apparatus. Figure 13 depicts an outline of this new die-set loaded to the bulk mechanical alloying. At the present status, there is still no cooling channel in a die and no argon-flow equipments.

In order to demonstrate this capability of processing, the epoxy-resin-base polymer particles with the molecular weight of $M = 6000$, the silica particles with the average diameter of $D = 100\ \mu m$ and the TiO_2-particles were blended, poured into a die cavity and subjected to cycling loading in this new apparatus. Figure 14 depicts a synthesized billet at $N = 400$ with the relative density of 80 % and the weight of 175 g. Success to fabricate a dense billet proves that the direct extension of solid-state synthesis by using a larger die-set should be a solution to requirement for mass production of TE-materials.

Figure 15 compares the microstructure between the thermally melting of the above mixture with use of finer silica particles and the present processing. Nearly the same microstructure is obtained by the present approach without heating and without use of finer silica particles. This finding also demonstrates that fine mixture of starting element particles should be fabricated in the class of hundred-grams by using this new apparatus system.

6. Conclusion

In the first-year of projects related to MURI-program, Mg-Si-Ge-Sn system is found to be a suitable TE-material target for improvement of specific figure-of-merit to be used as the candidate energy harvesting material. The solid-state synthesis is an only approach to utilize two material parameters of germanium and tin contents in order to optimize TE-material property. The germanium content (x) in $Mg_2Si_{1-x-y}Ge_xSn_y$ plays a role to control the Seebeck coefficient; while the tin content (y) in $Mg_2Si_{1-x-y}Ge_xSn_y$ can be optimized to improve the electrical conductivity. Since finer microstructure of $Mg_2Si_{1-x-y}Ge_xSn_y$ is obtained by the present processing, low thermal conductivity is commonly attained irrespective of x and y.

New processing route of this solid-state synthesis is invented to yield dense

TE-leg materials. In this approach, the premixed state mixture with fine embryos of TE-compounds is obtained by using the bulk mechanical alloying. Then, these finely premixed state materials are further annealed and consolidated at relatively low holding temperature to yield targeting TE-leg materials. Forming of these fine pre-mixture before annealing and consolidation, results in formation of variously shaped TE-leg materials.

Extension of this solid-state synthesis approach to mass production is possible by using the larger die-set. This approach has a capability to yield hundred-gram TE-materials in one batch operation.

7. Toward the Second-Year Project

In the second-year project, large-scale fabrication of Mg-base quaternary TE-leg materials via new solid-state processing is planned to perform in Mg-Si-Ge-Sn systems. Mg-Si/Ge-Sn particle mixture is subjected to BMA for $N < 300$-400 to yield Mg-Si/Ge-Sn preform-powders including an embryo of $Mg_2Si_{1-x-y}Ge_xSn_y$. In the latter half, $Mg_2Si_{1-x-y}Ge_xSn_y$ preform-powders are delivered to UW-team for production of TE-legs for module fabrication via low-temperature SPS.

Next, TE-composite material search via solid-state processing is planned to do for further improvement of TE-properties by nano-composite. First, Micro/nano-particles are homogeneously distributed in the perform to distribution of refined nano-particles in perform. In second, nano-oxide particles are in-situ synthesized and distributed in magnesium based TE-compound matrix: e.g. $SiO_2 + 4Mg \rightarrow Mg2Si + 2MgO$ together with $2Mg + Si \rightarrow Mg_2Si$ as an embryo.

[References]

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[5] Y. Noda, et al.: J. Applied Physics, 53 (1989) 487-491.

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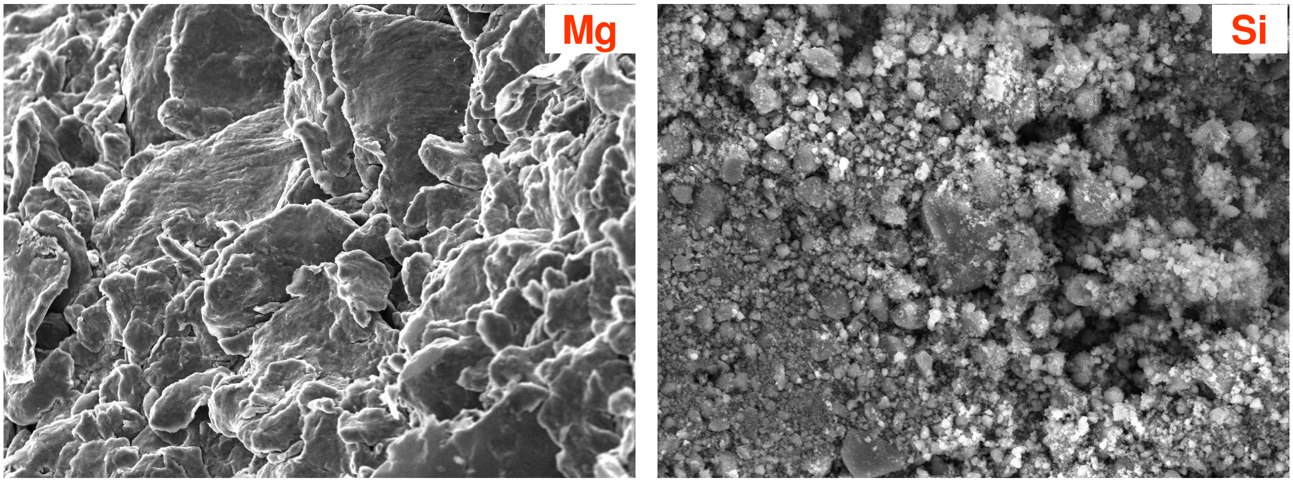
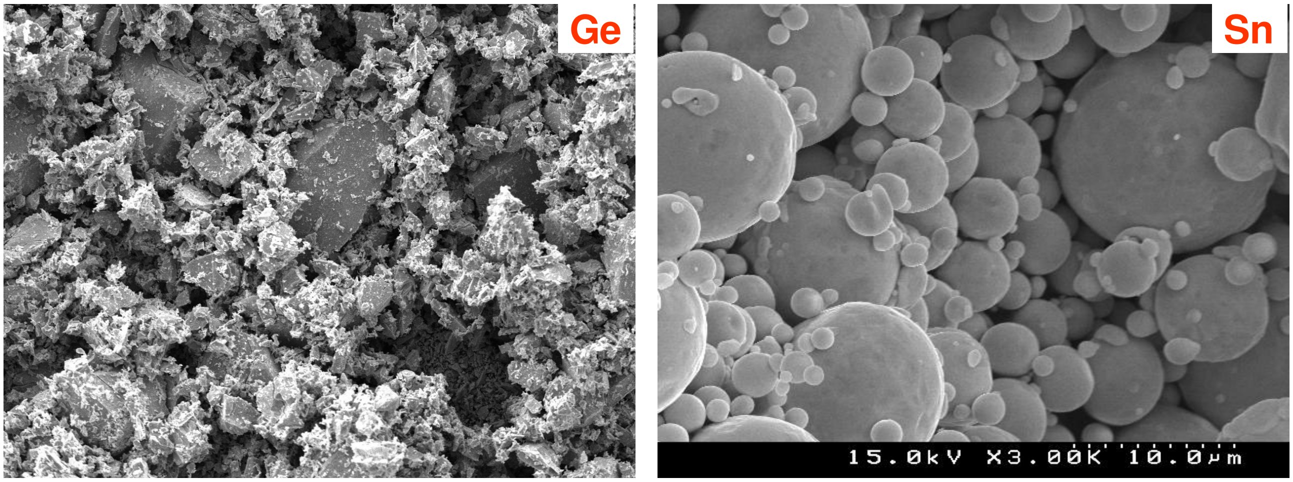


Mg (99.9%, 100 μm) **Si (99.99%, 20 μm)**



Ge (99.999%, 100 μm) **Sn (99.9%, 10 μm)**

Fig. 1: Initial elemental powder particles with their purity and average size.

Fig. 2: Developing bulk mechanical alloying apparatus.

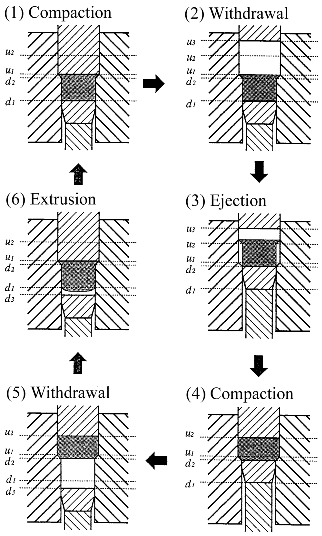


Fig. 3: Typical pass schedule for cyclic loading via the bulk mechanical alloying.

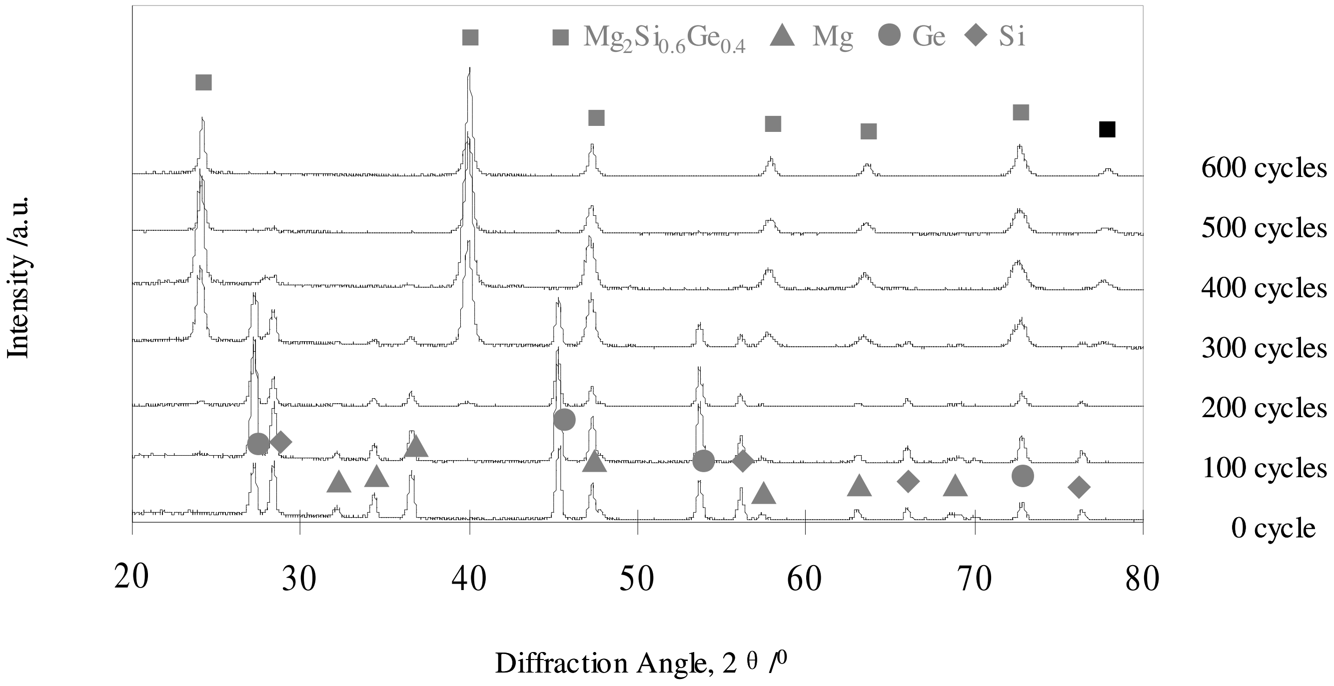


Fig. 4: Variation of XRD profiles with increasing the number of cycles.

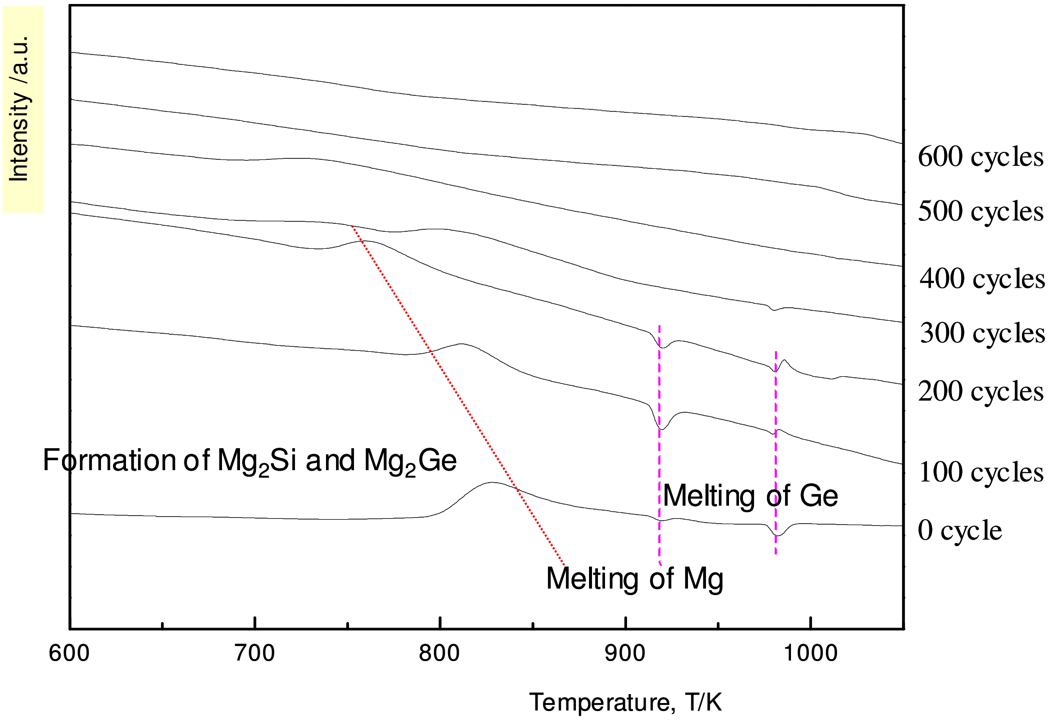


Fig. 5: Variation of DTA diagrams with increasing the number of cycles.

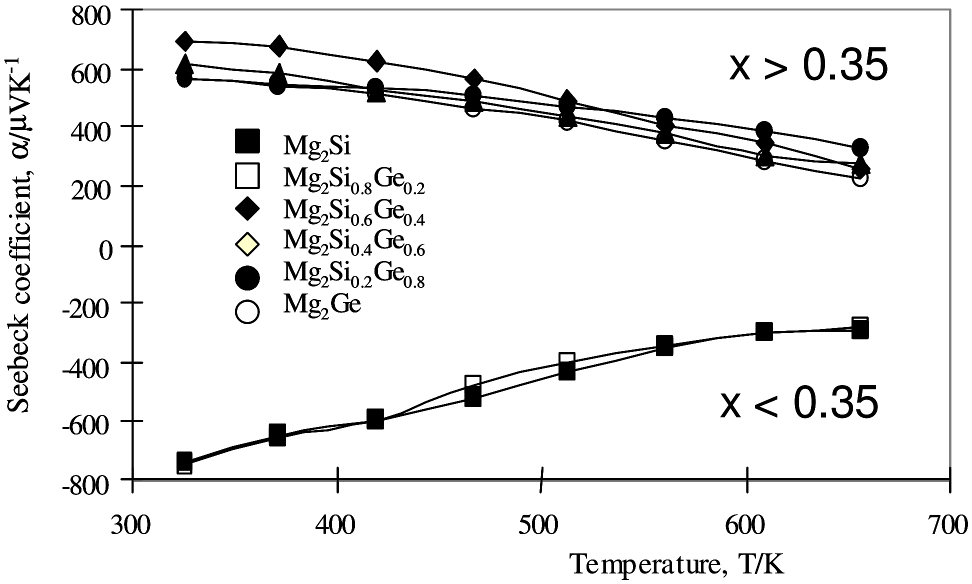


Fig. 6: Variation of Seebeck coefficient with temperature for various germanium contents.

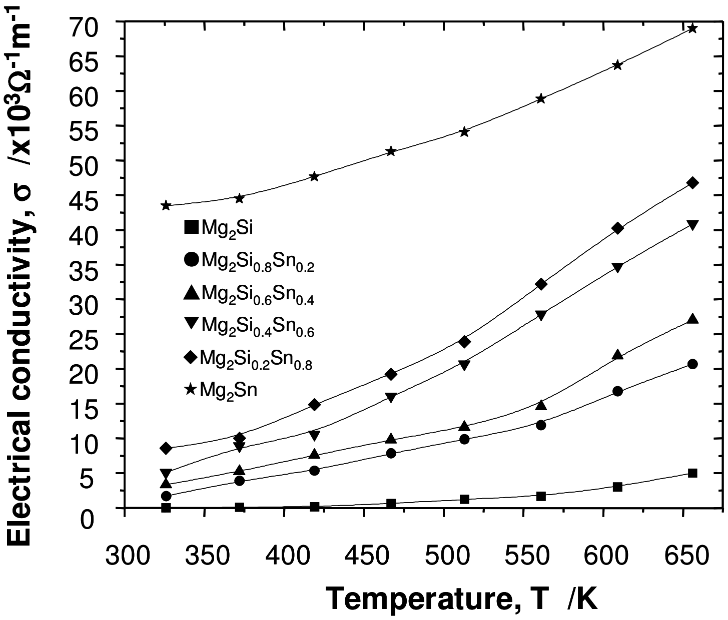


Fig. 7: Variation of electrical conductivity with temperature for various tin contents.

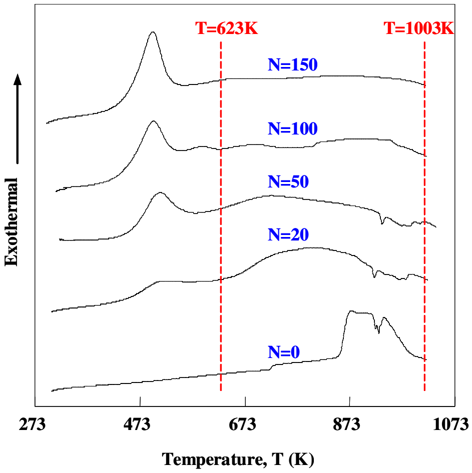


Fig. 8: Variation of DTA diagram with increasing the number of cycles.

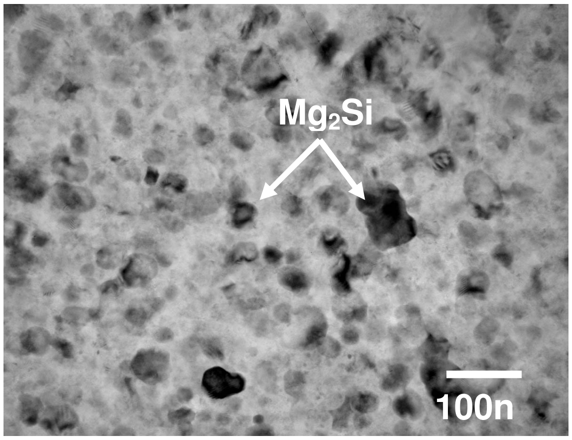
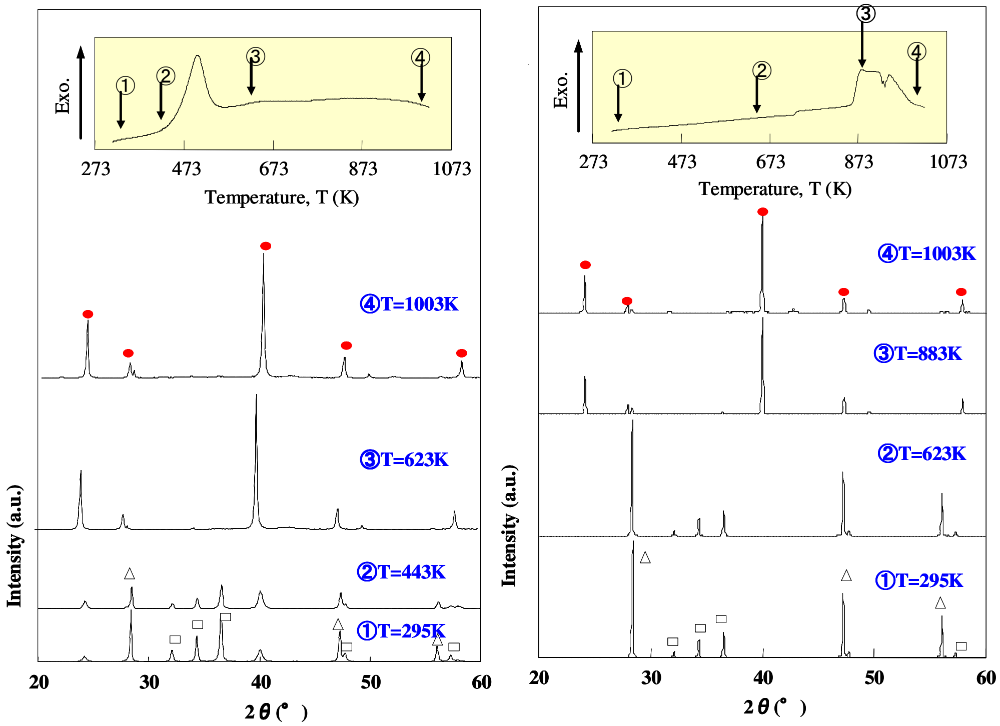


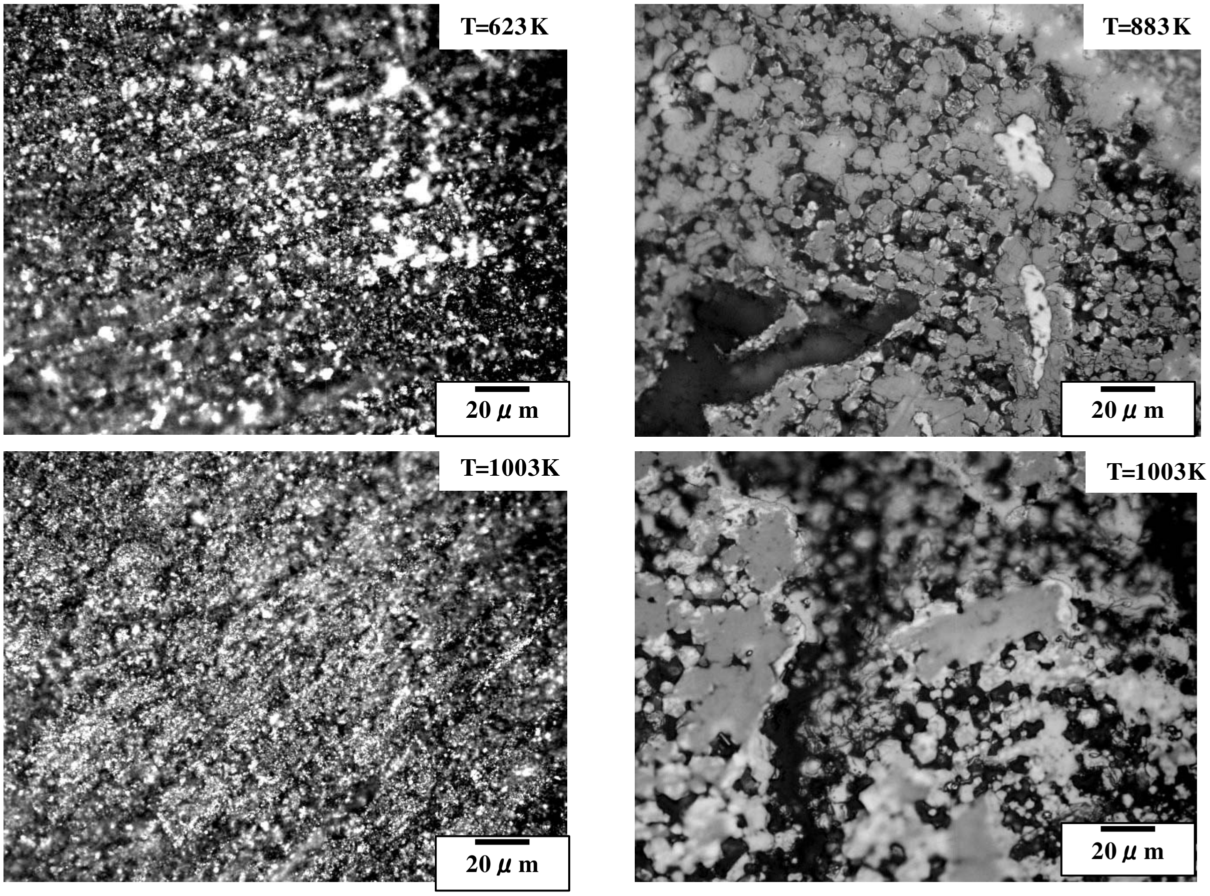
Fig. 9: Formation of Mg$_2$Si-embryo in the inside of Mg-Si mixture.



Starting from sample at N =150

Starting from sample at N = 0

Fig. 10: Comparison of XRD profile change with increasing the annealing temperature between samples at N = 0 and N = 150.



Starting from the sample at N = 150 Starting from the sample at N = 0

Fig. 11: Comparison of annealed samples between samples at N = 0 and N = 150.

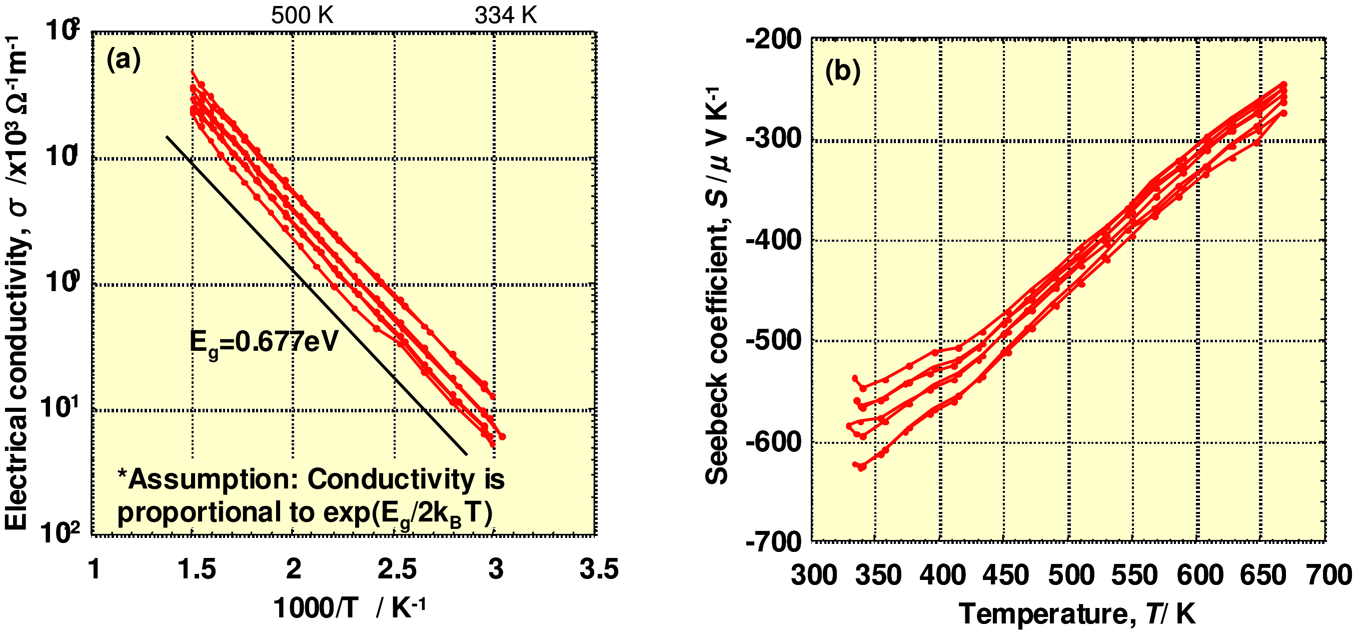
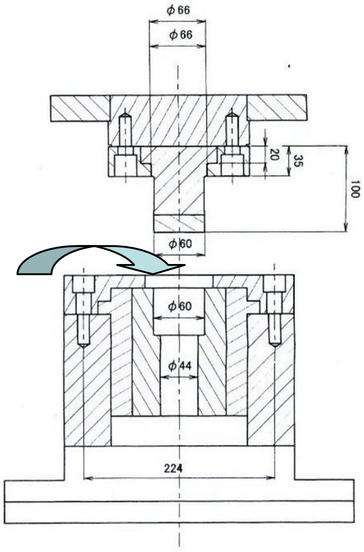


Fig. 12: Measured electrical conductivity and Seebeck coefficient of synthesized Mg_2Si.



Mg/Si
Ge/Sn
particles

Fig. 13: Outline of newly developed large-scaled die-set.

Fig. 14: A densified model sample after bulk mechanical alloying for N = 400 at RT.

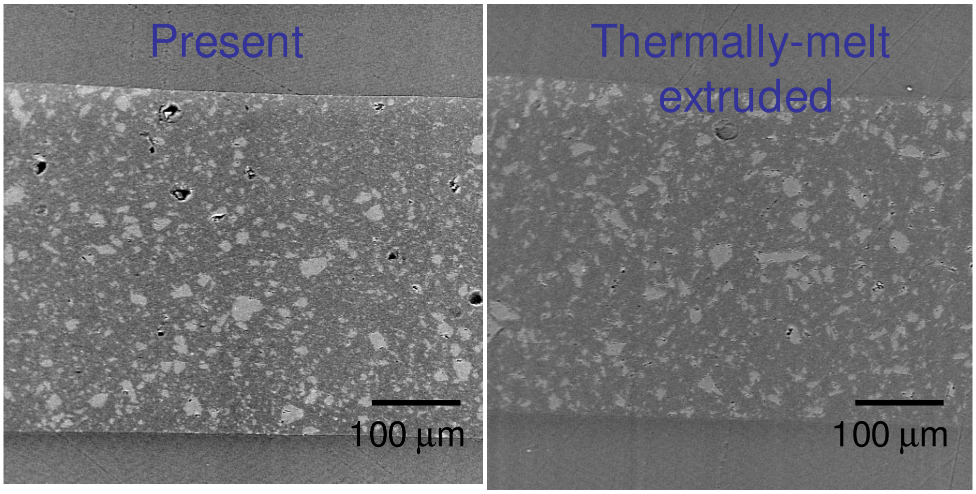


Fig. 15: Comparison of microstructure between thermally melt – extruded samples and the present sample.