Thermoelectric Properties of Nearly Single-Phase $\beta$-FeSi$_2$ Alloys Fabricated by Gas-Atomized Powder Sintering

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Thermoelectric alloys having nearly $\beta$-FeSi$_2$ single-phase microstructure were fabricated by sintering gas-atomized powders using the hot pressing. Since the $\beta$-FeSi$_2$ phase is formed by the peritectoid reaction between $\varepsilon$-FeSi and $\alpha$-Fe$_2$Si$_5$ phases, the reaction rate for the completion of $\beta$-FeSi$_2$ phase transition strongly depends on the diffusion path length which is governed by the morphology and size of solidified microstructure consisting of $\varepsilon$ and $\alpha$ phases. It has been indicated by the wedge drop cast using arc melting that producing fine and fully eutectic microstructure by rapid solidification is quite effective for the completion of $\beta$-FeSi$_2$ phase transition. An argon gas atomization process was chosen as a rapid solidification technique to produce fine and homogeneous alloy powder having fully $\varepsilon$ and $\alpha$ eutectic microstructure, which was turned out to be beneficial for the formation of $\beta$-FeSi$_2$ single-phase microstructure by a short time annealing even within 30 minutes at 1073 K for the gas-atomized powders with the averaged particles size of 20 $\mu$m and under in diameter. Thermoelectric properties were evaluated for these nearly single-phase $\beta$-FeSi$_2$ sintered alloys with the addition of doping elements, n-type Co and p-type Mn, 1.67 at% respectively. The absolute value of Seebeck coefficient and electrical conductivity are higher in a p-type Mn alloy than an n-type Co alloy.

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1. Introduction

Thermoelectric power generation is increasing its importance from the viewpoint to preserve the global environment together with realizing a smart and sustainable society. When we pay attention on the conversion of waste heat into clean electrical power, it is required to develop thermoelectric materials applicable at high temperatures beyond the well-known Bi–Te systems which can be used at temperatures up to around 600 K. Transition metal silicides are attractive candidate materials for high temperature thermoelectric applications. The $\beta$-FeSi$_2$ is one of eco-friendly thermoelectric materials which can be used at relatively high temperatures at around 1073 K. Compared with other excellent thermoelectric materials such as Bi–Te systems, $\beta$-FeSi$_2$ may not have high potentials. However, from the viewpoint of environmental concerns, the $\beta$-FeSi$_2$ is a favorable thermoelectric material composed of elements which are nontoxic, abundant in supply, and low cost. Not only excellent properties and high performance but also reliability and durability are required for practical applications of thermoelectric materials. Therefore, a lot of researches have been conducted and reported,[1–45] focusing on the formation of $\beta$ phase,[1–3,6] the $\beta$ phase transition enhancement by Cu addition,[7–10] unidirectional solidification,[11–15] rapid solidification including atomization powder,[16–17] effects of doping elements on thermoelectric properties,[18–30] powder sintering process,[31–34] oxide particles dispersion to reduce thermal conductivity,[35–42] Si dispersion by eutectoid decomposition,[33–45] and so forth for many other different aspects.

![Fig. 1 The Fe–Si binary phase diagram for the Si-rich side.](image)

We have focused on the development of fabrication process for $\beta$-FeSi$_2$ based thermoelectric alloys. The Fe–Si binary phase diagram[46] is shown in Fig. 1 for the Si-rich side. Note that $\alpha$-Fe$_2$Si$_5$ is denoted as $\alpha$-FeSi$_2$ in the phase diagram books, though the notation of $\alpha$-Fe$_2$Si$_5$ is used in this paper. Since the $\beta$-FeSi$_2$ is not a congruent compound, it is very hard to prepare $\beta$-FeSi$_2$ single-phase alloy simply by a solidification process from the melt. The $\beta$-FeSi$_2$ phase is formed by two different routes. One is the peritectoid reaction in which $\beta$-FeSi$_2$ is synthesized by solid phase reaction between $\alpha$-FeSi$_2$ and $\varepsilon$-FeSi, and the other is the eutectoid reaction. The other route is the eutectoid reaction of $\alpha$-FeSi$_2$ decomposing into $\beta$-FeSi$_2$ and Si, which should be followed by the solid phase reaction between pro-eutectic $\varepsilon$ phase and eutectoid Si phase to form the $\beta$-FeSi$_2$ phase. Figure 2...
represents typical microstructure change observed in the Fe–66.7Si (at%) alloy, having the \( \beta \)-FeSi\(_2\) phase stoichiometric composition, which was fabricated in the present work using the arc melting. Since the stoichiometric composition of \( \beta \) phase is situated at slightly Fe-rich side of the eutectic composition, i.e. hypo-eutectic composition, pro-eutectic \( \alpha \) phase primary crystals develop as coarse dendrites, and rod-type eutectic microstructure of \( \alpha \) and \( \beta \) two-phase forms as the final solidification part, which is shown in Fig. 2(a). Here, \( \varepsilon \) phase is observed with white contrast, and \( \alpha \) phase with black contrast. Typical microstructure after the heat treatment at 1013 K for 24 h followed by water quenching is shown in Fig. 2(b) for the eutectic microstructure region. It is clearly observed that \( \beta \) phase with gray contrast is surrounding eutectic \( \varepsilon \) phase rods since it forms at the interface between \( \varepsilon \) and \( \alpha \) phase by the peritectoid reaction. The \( \beta \) phase also forms enveloping pro-eutectic \( \varepsilon \) phase dendrites as observed in Fig. 2(c) for which the heat treatment was conducted at 1013 K for 24 h and followed by water quenching. The lamellar microstructure consisting of \( \beta \) and Si phases, which is formed by the eutectoid decomposition of \( \alpha \) phase, can be observed locally in the \( \alpha \) phase matrix regions as seen in Fig. 2(c). The peritectoid reaction usually requires long term heat treatment depending on morphology of as-solidified microstructure. It is because that the atomic diffusion rate is not high enough in solid phase reactions. Therefore, the development of fabrication processes has always been inevitable issues which must be somehow overcome. We focused on the refinement of solidification microstructure by means of rapid solidification methods so that the diffusion path for the phase transition from \( \varepsilon \) and \( \alpha \) two-phase to \( \beta \) single-phase via two routes mentioned above becomes as short as possible.

Objectives of the present work are twofold; one is to fabricate \( \beta \)-FeSi\(_2\) single-phase alloys by the hot press sintering using alloy powders prepared using the gas-atomization as an effective rapid solidification technique, and the other is to evaluate thermoelectric properties of those alloys. It may be noteworthy that the gas-atomization process to prepare high quality alloy powders becomes quite important because of the recent drastic progress in the additive manufacturing using 3D printing. Though it is not the case of the present work, at least the effectiveness of the gas-atomization powder preparation is suggested. Since \( \beta \)-FeSi\(_2\) is an intrinsic semiconductor, doping elements of the n-type Co and p-type Mn are selected to control the conduction types for the alloys.

2. Experimental Procedure

2.1 Ingot alloys preparation

Nominal compositions of three alloys prepared in the present work are listed in Table 1. A binary Fe–66.7Si alloy (in at%), corresponding to the stoichiometric composition of \( \beta \)-FeSi\(_2\), was used to observe the effects of rapid solidification rate on microstructure development. Several alloys with compositions of Fe–66.5Si, Fe–66.6Si and Fe–66.8Si were examined for the composition dependence of microstructure in the preliminary investigation (results are omitted here). As the doping elements for the tuning of the conduction type, Co and Mn were selected for n-type and p-type, respectively. Ternary doped alloys of Fe–1.67Co–66.7Si and Fe–1.67Mn–66.7Si, hereafter denoted as Co-doped alloy and Mn-doped alloy, respectively, were prepared for the gas-atomization process to fabricate fine and homogeneous alloy powders. These ternary doped alloys were also used to observe the

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<th>Alloy</th>
<th>Fe</th>
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effects of rapid solidification rate on microstructure development as well. It should be noted that both Co and Mn are known to substitute for the Fe-site in the $\beta$-$\text{FeSi}_2$ phase,\textsuperscript{1} and that 1.67 at% Co and 1.67 at% Mn are soluble in the $\beta$-$\text{FeSi}_2$ phase as checked in the present work and as reported in the literatures.\textsuperscript{20,21}

All the alloys were prepared as button ingots by the arc melting under the slightly positive pressure of an argon gas atmosphere to prevent from the oxidation. High purity raw materials of Fe (4N), Si (5N), Co (3N5), and Mn (3N5) were used. To ensure the compositional homogeneity of alloys, arc melting was repeated four times after flipping (turning) over a button ingot each time. Additionally, the arc-melt drop wedge cast was conducted to observe the effects of cooling rate on the development of solidification microstructure for a Fe–66.7Si alloy, and ternary Co-doped alloy and Mn-doped alloy. Molten alloy was dropped and cast into a wedge shaped mold during arc melting. The conditions of arc melting were the same as mentioned above, and a schematic of wedge shaped ingot is shown in Fig. 3 later. The drop cast hearth system was rapidly driven by the argon gas pressure.

Microstructure observation for the alloys was conducted by the scanning electron microscopy using backscattered electron image compositional mode (SEM-BEI). Constituent phases of each alloy were identified by the electron probe micro analysis (EPMA) using the wave-length dispersive X-ray spectrometry, which was operated with the accelerating voltage of 25 kV.

### 2.2 Alloy powder fabrication

Alloy powders of Fe–1.67Co–66.7Si and Fe–1.67Mn–66.7Si were fabricated using the gas-atomization method [for example Ref. 47–49]. Button ingots of these alloys used for the gas-atomization process were prepared by arc melting.

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**Fig. 3** (a) The inside dimensions of a three-piece split mold for the drop wedge cast used in the present work. (b) A schematic showing the relationship between super cooling and coupled zone of the eutectoid reaction, $\alpha$ phase decomposing into $\beta$ and Si phases, for hypoeutectic composition Fe–66.7Si (at%). Typical microstructure of a drop wedge cast Fe–66.7Si binary alloy; as-cast microstructure of (c) a region solidified at lower rate being located in the thicker edge, and (d) a region solidified at higher rate being situated in the thinner edge close to the tip of a wedge. In the region solidified at higher rate, almost $\beta$ single-phase microstructure, as shown in (e), can be achieved after conducting the heat treatment at 1073 K only for 10 minutes.
As mentioned above, mother ingots prepared by arc melting, about 500 g in total, were melt by the induction heating in an Al₂O₃ tundish, simply a crucible, and then the molten alloy was held at 1543 K for 5 minutes prior to the gas-atomization. As the gas-atomization process, molten alloy was ejected through the orifice placed on the bottom of Al₂O₃ crucible, and sprayed instantaneously by the argon gas jet-flow injecting from 24-fold multiple nozzles which were arranged concentrically surrounding the orifice. Here, the pressure of argon gas to push the molten alloy was 0.4 kgf and that injected from nozzles for jet-flow was 0.95 kgf, respectively. The optimum orifice diameter was set as φ1.5 mm of the diameter for the present work. We can expect to have finer powder particles as an orifice diameter becomes smaller, however, the trial of narrower φ1.2 mm orifice had resulted in the failure of molten alloy stuck in the orifice due to partial solidification during the process. The gas atomization furnace used in this work was equipped with two-stepped cyclones in which sprayed powder particles were inhaled through the ducting system. Powder particles were collected in two containers placed in different distances from the inlet of the duct; coarse (i.e., heavy weight) powder particles were collected in the first container in a short distance, and relatively fine (i.e., light weight) powder particles were collected in the second container. Fine powder particles were mainly used for the experiments after the classification of particle size by sieving, 75 μm and under, 45 μm and under, and 20 μm and under. Although the distribution of atomized powder particle grain size was not measured, as the only available information, the fraction of 45 μm and under powder particles in weight was about 50% according to the roughly estimation for used gas-atomization facility.⁴⁷

Heat treatments were conducted on the gas-atomized powder to understand the dependency of holding time on the β-FeSi₂ phase formation. The conditions of heat treatments were holding at 1123 K for various duration of time, 10, 30, 60, and 120 minutes, under an argon gas atmosphere. Microstructure of the cross section of as-gas-atomized and heat treated powder particles was observed by SEM-BEI. Powder particles embedded in resin were mechanically polished with mirror surface finish using 1 μm diamond particles paste.

2.3 Measurements of thermoelectric properties for sintered bulk alloys

To evaluate the thermoelectric properties of the n-type 66.7Si alloy and the p-type Mn-doped alloy, bulk specimens were sintered using gas-atomized powder by hot-pressing at 1123 K for 90 min under the applied stress of 50 MPa in a vacuum of about 10⁻⁶ Pa after several times of argon gas flushing. Note that the specimens were subjected to pre-annealing which was corresponding to the duration of 120 minutes for heating specimens from room temperature to 1123 K. Microstructure of sintered bulk alloys was observed by SEM-BEI and constituent phases of the alloys were examined using EPMA and the X-ray diffractometry (XRD).

Thermoelectric properties were evaluated in the temperature range from room temperature to 1073 K. The Seebeck coefficient and electrical resistivity were measured simultaneously in a helium gas atmosphere. The Seebeck coefficient was measured using steady state method. A temperature difference ΔT was applied over a 6 mm distance between two R-type thermocouple probes for the measurement. Three sets of ΔT = 5, 10, and 20 K for each test temperature were applied for the extrapolation. The DC four-probe method was used for the electrical resistivity measurement. The thermal conductivity of the alloys was evaluated on the basis of the density, measured by the Archimedes method, and thermal diffusivity and heat capacity, measured by the laser-flash method. Note that the heat capacity measurement using the laser-flash may include about 10% scattering in the accuracy.

3. Results and Discussion

3.1 Effects of cooling rate on solidification microstructure development

A molten alloy was drop into a wedge shaped mold by means of the arc melting, in order to evaluate the effects of cooling rate on solidification microstructure development. The shape of wedge cast sample is schematically depicted in Fig. 3(a), and typical microstructure of drop wedge cast alloy is shown in Figs. 3(c) and 3(d) for a binary Fe–66.7Si alloy. The solidification rate becomes higher at a position getting closer to the tip of a wedge, and contrarily lower at the opposite thicker end. Thus, coarse dendrites of proeutectic ε phase firstly form and rod-type ε and α two-phase eutectic microstructure are formed consecutively at the thicker end as observed in Fig. 3(c), on the other hand, very fine and rather homogeneous ε and α eutectic microstructure is observed to be formed at the tip as represented in Fig. 3(d). It can be described using a schematic illustration in Fig. 3(b) that the formation of fully eutectic microstructure can be achieved at the slightly hypoeutectic composition of Fe–66.7Si. The primary ε phase formation can be suppressed due to sufficiently high cooling rate, and the eutectic reaction takes place within the coupled zone which is defined between extrapolation of two liquidus lines (L + ε and L + α) under the non-equilibrium supercooling, ΔT, condition. Note that Fe–66.7Si was selected as the most suitable alloy composition from the results of preliminary examination conducted in a compositional range between Fe–66.5Si and Fe–66.9Si. Fully fine eutectic microstructure can be easily transformed into β single-phase microstructure by a heat treatment at 1073 K for only 10 minutes as represented in Fig. 3(e). It can be confirmed not only by the change in microstructure but also by the change in measured electrical resistivity from a metallic value of 7.24 × 10⁻⁶ Ω m (3(c)) to a semiconductor value of 1.37 × 10⁻² Ω m (3(e)). Note that cracks penetrating through the sample as shown in Figs. 3(d) and 3(e) are supposed to be generated due to the thermal stress during having subjected to rapid cooling upon drop casting, and that electrical resistivity was measured carefully not being affected by cracks. Consequently, it is beneficial to fabricate fine and homogeneous eutectic microstructure consisting of ε and α phases for the completion of the β phase transition during a short time heat treatment.

Drop wedge as-cast microstructure is shown in Fig. 4 for the ternary Co-doped alloy and Mn-doped alloy. Over all
The detailed morphology becomes different in ternary alloys since the phase equilibrium changes and the degrees of freedom change from 0 (invariant) to 1 (monovariant) for a three-phase equilibrium including $\varepsilon$, $\alpha$, and liquid phases. Therefore, the distinctive feature of coupled growth for eutectic microstructure development may become less prominent in ternary alloys, and it seems to be particularly in Mn-doped alloy. It is indicated that the completion of the $\beta$ phase transition is more difficult in ternary alloys than in binary alloys since a significant amount of pro-eutectic $\varepsilon$ phase remains unreacted at the same heat treatment temperature by which the $\beta$ phase transition can be completed within 10 minutes in a binary Fe–66.7Si alloy as shown in Fig. 3(c).

3.2 Microstructure of gas-atomized powder

It has been proven by the wedge drop cast experiments as mentioned in the section 3.1 that the refinement of $\alpha$ and $\varepsilon$ two-phase microstructure is very effective to drastically promote $\beta$ single phase microstructure formation during the post annealing. The gas-atomization was selected for the present work as a rapid solidification method, for which ultra-high cooling rate is generally estimated about $10^3$ to $10^6$ K/s of orders or higher depending on alloy systems and the atomizing conditions such as holding temperature, orifice diameter, and the rate of gas jet-flow. Typical as-atomized microstructure observed at the cross-sections of powder particles are shown in Fig. 5, (a) through (c) for Co-doped alloys and (d) through (f) for Mn-doped alloys. Gas-atomized powder particles were sieved in three categories by the size of averaged diameter; (a, d) 20 µm and under, (b, e) 45 µm and under, and (c, f) 75 µm and under. Overall shape of powder particles is observed as almost sphere, which is governed by a balance between the surface tension of a molten alloy and the solidification rate. Relatively coarse particles, around 75 µm, tend to contain a large void which has been caused by the shrinkage during rapid solidification (e.g. in (c)), and some particles have distorted sphere shape (e.g. in (f)). Microstructure of powder particles is basically composed of $\varepsilon$ and $\alpha$ two-phase, which is dominated by relatively small pro-eutectic $\varepsilon$ phase grains and the rest of eutectic microstructure regions, as shown in the figure. Here, $\alpha$ phase is observed in dark gray contrast and $\varepsilon$ phase, bright contrast, respectively. It is noteworthy that volume fractions of pro-eutectic $\varepsilon$ phase grains tend to be larger as the particle grain size becomes larger, meaning that the solidification rate becomes lower. Overall microstructure becomes finer as the averaged grain size is smaller. It was anticipated that the surface of powder particles may have been covered with SiO$_2$ or iron oxides, no oxide films are observed at the surface (edge at the cross section) nor no diffraction peaks of oxides were detected by XRD. Many cracks are easily generated in powder particles due to the thermal stress during the rapid solidification, or due to the applied stress during the mechanical grinding for the preparation of microstructure observation, since all the intermetallic phases, $\alpha$, $\beta$, and $\varepsilon$, are very brittle.

Typical heat-treated microstructure observed at the cross-sections of atomized powder particles are shown in Fig. 6, (a) through (c) for the Co-doped alloys and (d) through (f) for the Mn-doped alloys. The applied heat treatment condition was holding at 1123 K for 30 minutes in an argon gas atmosphere. The $\beta$ phase transition seems to be completed in smaller powder particles than about 20 µm during the heat treatment for 30 minutes and longer, and nearly $\beta$ single-phase microstructure can be observed. On the other hand, considerable amount of pro-eutectic primary $\varepsilon$ phase grains with or without eutectoid microstructure regions being composed of $\beta$ and Si two-phase remain in larger powder particles than about 45 µm. Almost the same tendency of microstructure change is observed for the longer heat treatment duration up to 120 minutes, which indicates the difficulty of the completion of $\beta$ phase transition from $\varepsilon$ and $\alpha$ two-phase as-solidified microstructure particularly in ternary alloys.

3.3 Thermoelectric properties of nearly $\beta$-FeSi$_2$ single-phase alloys sintered using gas-atomized powder

Fully dense alloys having nearly $\beta$-FeSi$_2$ single-phase
microstructure were fabricated using the gas-atomized alloy powder with the averaged diameter of 20 µm and under. Typical microstructure observed for the sintered Co-doped alloy powder particles and (d), (e), and (f) are Mn-doped alloy powder particles. Atomized powder particles were sieved in three classes by their averaged diameter; (a, d) 20 µm and under, (b, e) 45 µm and under, and (c, f) 75 µm and under.

Fig. 5 Backscattered electron images showing the cross-sections of as-atomized powder particles; (a), (b), and (c) are Co-doped alloy powder particles and (d), (e), and (f) are Mn-doped alloy powder particles. Atomized powder particles were sieved in three classes by their averaged diameter; (a, d) 20 µm and under, (b, e) 45 µm and under, and (c, f) 75 µm and under.

Fig. 6 Backscattered electron images showing the cross-sections of annealed atomized powder particles; (a), (b), and (c) are Co-doped alloy powder particles and (d), (e), and (f) are Mn-doped alloy powder particles. The annealing condition was 1123 K for 30 minutes. Atomized powder particles were sieved in three classes by their averaged diameter; (a, d) 20 µm and under, (b, e) 45 µm and under, and (c, f) 75 µm and under.

Thermoelectric Properties of Nearly Single-Phase $\beta$-FeSi$_2$ Alloys Fabricated by Gas-Atomized Powder Sintering
Chemical compositions of nearly $\beta$-FeSi$_2$ single-phase matrix measured using EPMA are shown in Table 2 for 1.67Co and 1.67Mn sintered alloys, where the nominal concentration of doping element as solute is fixed at 1.67 at% for both Co and Mn. Through the partitioning behavior of each element in the solidification and phase transformation during the gas-atomization and hot-press sintering processes, Co is concentrated to 1.9 at%, and Mn is diluted to 1.5 at%, respectively, in the $\beta$ phase matrix under the accuracy of EPMA. Based on these measured concentration, $\beta$-FeSi$_2$ phase can be denoted using chemical formula as (Fe$_{0.944}$,Co$_{0.056}$)$_2$Si$_2$ for the Co-doped alloy and (Fe$_{0.955}$,Mn$_{0.045}$)$_2$Si$_2$ for the Mn-doped alloy. Thus the doping concentration is slightly higher in Co-doped alloy than in Mn-doped alloy nevertheless nominal composition is the same. It is indicated that the mass balance should be kept in the whole system including constituent phases and impurities throughout the processes of gas-atomization and powder sintering, except for the changes due to oxidation and vaporization. Difference of solute concentration, i.e. doping concentration, should affect the thermoelectric properties, however, the optimization of solute concentration for the best thermoelectric performance was not conducted in the present work.

Thermoelectric properties were measured for the 1.67Co and 1.67Mn sintered alloys having nearly $\beta$-FeSi$_2$ single-phase microstructure. The temperature dependence of the Seebeck coefficient $S$ and the electrical conductivity $\sigma$ (converted from the electrical resistivity, $\rho$) is represented in Fig. 8 and Fig. 9, respectively. The n-type Co-doped alloy shows negative values and the p-type Mn-doped alloy, positive values of the Seebeck coefficient as shown in the figure. Compared in the absolute value, the Seebeck coefficient of the p-type Mn-doped alloy is higher than that of the n-type Co-doped alloy, while the electrical conductivity of an n-type Co-doped alloy is higher than that of the p-type Mn-doped alloy. It suggests that the carrier
concentration would be higher in the n-type Co-doped alloy, in which the major carrier is electrons, than in the p-type Mn-doped alloy, in which the major carrier is holes. These two alloys exhibit different temperature dependence of transport properties. The absolute value of Seebeck coefficient of n-type Co-doped alloy stays almost constant, slightly increasing and then decreasing, in a range within −200 to −250 μV/K as the temperature increases. A gradual and small decrease at high temperatures should be attributed to the enhanced excitation of major carrier electrons. This temperature dependence of increasing electrical conductivity with temperatures is basically a propensity of semiconductor, however, relatively high values in a low temperature range are affected by mixed contribution of metallic dependency.

On the other hand, the Seebeck coefficient of the p-type Mn-doped alloy decreases as the temperature increases from 450 μV/K at around 420 K down to about 200 μV/K at 1000 K. Correspondingly, the electrical resistivity increases with temperature as a typical tendency of temperature dependence of semiconductor. It is indicated that numbers of excited minor carrier electrons becomes larger as the temperature increases.

As a consequence of electrical properties evaluation, the temperature dependence of the electrical power factor, $S^2/\sigma$, is calculated and represented in Fig. 10. The power factor of n-type Co-doped alloy is superior to that of p-type Mn-doped alloy. Absolute values of the Seebeck coefficient are larger in Mn-doped alloy than in Mn-doped alloy, however, values of electrical conductivity are much larger in Co-doped alloy than in Mn-doped alloy. It should be emphasized that excellent values higher than 1.0 mW m$^{-1}$K$^{-2}$ can be achieved at high temperatures around 700 K to 950 K in the n-type Co-doped alloy. The p-type Mn-doped alloy exhibits fairly good values almost reaching to 0.8 mW m$^{-1}$K$^{-2}$ in a temperature range around 750 K to 850 K.

The temperature dependence of the thermal conductivity is shown in Fig. 11 for the sintered n-type Co-doped alloy and p-type Mn-doped alloy. Generally, the thermal conductivity, $\kappa$, is given as a sum of the carrier contribution, $\kappa_{\text{car}}$, and lattice contribution, $\kappa_{\text{lat}}$, according to the Wiedemann–Franz relationship: $\kappa_{\text{total}} = \kappa_{\text{car}} + \kappa_{\text{lat}}$, where $\kappa_{\text{car}} = \sigma L T$. Here, $\sigma$ is the electrical conductivity and $L$ is the Lorentz number, $2.44 \times 10^{-8}$ V$^2$K$^{-2}$. In Fig. 11, $\kappa_{\text{car}}$ was calculated from the measured electrical conductivity and $\kappa_{\text{lat}}$ was figured out by subtracting $\kappa_{\text{car}}$ from $\kappa$. Deducing from a comparison of electrical conductivity, the carrier contribution should be higher in n-type Co-doped alloy than in p-type Mn-doped alloy. Nevertheless, thermal conductivity of Co-doped alloy is lower than that of Mn-doped alloy. This is because the thermal conduction is dominated by the lattice contribution in both Co-doped alloy and Mn-doped alloy. The carrier contribution slightly increases with temperature depending on the enhancement of carrier excitation. On the other hand, the lattice contribution gradually decreases as temperature increases.

Finally, the temperature dependence of the dimensionless figure of merit, $ZT$, is evaluated and represented in Fig. 12 for the sintered n-type Co-doped alloy and p-type Mn-doped alloy. The maximum $ZT$ value is exceeding 0.22 in Co-doped alloy and reaching almost 0.1 in Mn-doped alloy at around 900 K. The reason why Co-doped alloy is twice as large as Mn-doped alloy is that the power factor is higher and the
thermal conductivity is lower in Co-doped alloy than in Mn-doped alloy. Kido et al.\textsuperscript{20,21} precisely reported the doping element concentration dependence (Co\textsuperscript{29} and Mn\textsuperscript{21}) and the temperature dependence of the thermoelectric properties for $\beta$-FeSi\textsubscript{2} alloys fabricated by spark plasma sintering method and post annealing process using mechanically pulverized powders. Thermoelectric properties evaluated for the present alloys are almost comparable to those of their previous results, which indicates the validity of the present fabrication process. We can expect the further improvement of thermoelectric properties based on the present alloy fabrication process for $\beta$-FeSi\textsubscript{2} alloys through the optimization of doping concentrations and process conditions.

### 4. Conclusions

Effects of the solidification rate on microstructure development were observed for a binary Fe–66.7Si alloy as well as Fe–66.7Si–1.67Co and Fe–66.7Si–1.67Mn ternary alloys using the wedge drop cast with arc melting. Based on these results, nearly $\beta$-FeSi\textsubscript{2} single-phase alloys, Co-doped alloy and Mn-doped alloy, were fabricated by sintering gas-atomized powder using hot-pressing, and thermoelectric properties were evaluated for those sintered alloys. The following conclusions are drawn in the present work.

1) It was demonstrated using the drop wedge cast of arc melting that the rapid solidification is effective to fabricate fully fine $\varepsilon$ and $\alpha$ eutectic microstructure avoiding the formation of pro-eutectic $\varepsilon$ phase at the $\beta$ stoichiometric composition, Fe–66.7Si (at%), and starting from this microstructure the $\beta$ phase transition can be completed by annealing at 1073 K for only 10 minutes.

2) Fine and homogeneous spherical powder particles can be fabricated for the alloys having nominal compositions of Fe–66.7Si–1.67Co and Fe–66.7Si–1.67Mn (at%), using the argon gas atomization process. Each powder particle consists of $\varepsilon$ and $\alpha$ two-phase microstructure.

3) The phase transition of $\beta$ from fine and fully eutectic microstructure of $\varepsilon$ and $\alpha$ two-phase can be completed by the heat treatment at 1123 K for 30 minutes in powder particles having averaged diameters of 20 $\mu$m and under. There remain pro-eutectic $\varepsilon$ phase grains, and the eutectoid microstructure composed of $\beta$ and Si two-phase forms in larger powder particles than about 45 $\mu$m.

4) Nearly $\beta$-FeSi\textsubscript{2} single-phase Co-doped and Mn-doped alloys can be fabricated by hot-press sintering using gas-atomized powder particles which have averaged diameters of 20 $\mu$m and under.

5) Thermoelectric properties of mentioned above nearly $\beta$-FeSi\textsubscript{2} single-phase sintered alloys were evaluated. At the given condition of this work, the absolute values of Seebeck coefficient is larger in Mn-doped alloy than in Co-doped alloy, while electrical conductivity is higher and thermal conductivity is lower in Co-doped alloy than in Mn-doped alloy. Consequently, Co-doped alloy is superior to Mn-doped alloy in power factor and the figure of merit $ZT$.

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