

Article

Production of (Fe,Co)Si₂ and (Fe,Mn)Si₂ Thermoelectric Materials by Spark Plasma Sintering

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Abstract: In this study, FeSi₂ bulk specimens were prepared by mechanical alloying, spark plasma sintering, and subsequent annealing. The annealed FeSi₂ bulk specimens consisted of the β -FeSi₂ phase and exhibited high Seebeck coefficient values. The maximum Seebeck coefficient of 356 μVK^{-1} was achieved in the FeSi₂ bulk specimen annealed at 1173 K for 6 h. However, the power factor of the FeSi₂ bulk specimen was quite small due to its high electrical resistivity, and a drastic improvement is required. Therefore, Mn- and Co-substituted specimens, Fe_{1-x}Mn_xSi₂ ($x = 0.2\text{--}0.8$) and Fe_{1-x}Co_xSi₂ ($x = 0.2\text{--}0.8$), were produced, and their thermoelectric properties were evaluated. The Mn- and Co-substituted specimens exhibited lower electrical resistivity and a higher power factor than the FeSi₂ bulk specimen. The Fe_{1-x}Mn_xSi₂ ($x = 0.2\text{--}0.8$) bulk specimens were p-type thermoelectric materials, and a Seebeck coefficient of 262 μVK^{-1} and a power factor of 339 $\mu\text{Wm}^{-1}\text{K}^{-2}$ were achieved in the Fe_{0.94}Mn_{0.06}Si₂ bulk specimen. On the other hand, the Fe_{1-x}Co_xSi₂ ($x = 0.2\text{--}0.8$) bulk specimens were n-type thermoelectric materials, and a Seebeck coefficient of $-180 \mu\text{VK}^{-1}$ and a power factor of 667 $\mu\text{Wm}^{-1}\text{K}^{-2}$ were achieved in the Fe_{0.96}Co_{0.04}Si₂ bulk specimen.

Keywords: thermoelectric materials; iron silicide; mechanical alloying; spark plasma sintering



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1. Introduction

Humanity is facing the critical issue of preventing or at least slowing the progress of global warming, which is known to be caused by greenhouse gases, particularly those emitted by burning fossil fuels such as coal and oil. Although burning such fossil fuels is still necessary to secure energy supplies, more than 60% of the energy generated is lost as waste heat [1]. Thus, research on waste heat recovery is currently a focus of attention [2–4]. Various studies on technologies for waste heat recovery have been reported [5,6]. One of the techniques to recover waste heat is thermoelectric generation, which can convert waste heat to electricity by means of thermoelectric materials.

Until now, only the bismuth telluride (Bi₂Te₃) compound has been used in thermoelectric modules such as those for the electric cooling of computer devices [7–12]. However, Bi₂Te₃ cannot be used for thermoelectric generation because it consists of scarce and toxic elements. The iron silicide (β -FeSi₂) compound, another thermoelectric material, consists of nontoxic and abundant elements. The thermoelectric properties of the β -FeSi₂ compound have been studied, and numerous efforts have been made to produce it [13–19]. Unfortunately, the β -FeSi₂ compound is found to be a peritectoid phase, which is difficult to produce from the melt. It exhibits an unfavorably high electric resistance for a thermoelectric material.

From the viewpoint of achieving the Sustainable Development Goals (SDGs) formulated by the United Nations, the use of nontoxic β -FeSi₂ compound as a thermoelectric material to realize thermoelectric generation for waste heat recovery is attracting renewed interest. It has been found that sintering is a suitable method for obtaining the β -FeSi₂

compound [20,21] and that the thermoelectric properties of the β -FeSi₂ compound are improved by the addition of Co or Mn [22,23]. However, the amount of the Co or Mn added to the β -FeSi₂ compound needs to be optimized to improve its thermoelectric properties [24]. Therefore, further studies are necessary to improve these compounds.

The thermoelectric properties of the β -FeSi₂ compounds are deeply dependent on the processing conditions. β -FeSi₂ compounds have been produced by sintering of elemental powder mixtures or Fe-Si alloy powder with the composition of FeSi₂ [18,25], but it was found that β -FeSi₂ compounds produced by mechanical alloying and subsequent spark plasma sintering exhibited better thermoelectric properties [19,26]. Therefore, we produced β -FeSi₂ compounds and those Co-doped and Mn-doped specimens by mechanical alloying and spark plasma sintering. The thermoelectric properties of the resultant β -FeSi₂ compounds were systematically investigated.

2. Materials and Methods

2.1. Mechanical Alloying (MA)

Elemental Fe (99.9%) and Si (99.9%) were weighed and then mixed with a mortar and pestle in an argon-filled glove box (argon purity: 99.99%). The nominal composition of the powder mixture was Fe-66.7at%Si (FeSi₂). The mixed powder of 40 g in weight was poured into a cylindrical steel container together with steel balls (10 mm in diameter) having a total weight of 400 g and then sealed in an argon-filled glove box. Mechanical alloying of the mixed powders was performed for 20 h with a ball-to-powder ration of 10:1 using a planetary ball mill at a rotation speed of 250 rpm (FRITSCH: Planetary Mono Mill PULVERISETTE 6, Idar-Oberstein, Germany). The planetary ball mill is known as a high-energy ball mill. Details of the planetary ball mill are described elsewhere [27]. After the mechanical alloying, the powder was removed from the container in the argon-filled glove box. The same procedure was used to prepare powder mixtures of Fe_{1-x}Mn_xSi₂ ($x = 0.2-0.8$) and Fe_{1-x}Co_xSi₂ ($x = 0.2-0.8$).

2.2. Spark Plasma Sintering

Samples of the mechanically alloyed FeSi₂ powder of 1 g in weight were put into a carbon die and consolidated into bulk materials by the spark plasma sintering method. The consolidation was performed in a vacuum at 1073 K for 300 s under a pressure of 100 MPa. Bulk specimens were prepared under vacuum by the SPS method using a spark plasma sintering apparatus (Plasman, S. S. Alloy, Hiroshima, Japan). The temperature of the specimen was increased from room temperature to the consolidating temperature of 973 K over a period of 300 s and then held at the consolidating temperature for 300 s, in accordance with the SPS method. After the specimens were cooled to room temperature, they were taken from the carbon die and subsequently annealed at 1073–1173 K for 6–20 h in an argon atmosphere. The bulk materials of Fe_{1-x}Mn_xSi₂ ($x = 0.2-0.8$) and Fe_{1-x}Co_xSi₂ ($x = 0.2-0.8$) were annealed at 1173 K for 6 h in an argon atmosphere.

2.3. Characterization

The mechanically alloyed powders and bulk materials were characterized by X-ray diffraction (XRD) using Cu K α radiation (MiniFlex600, Rigaku, Tokyo, Japan), and the morphology of the specimens was investigated using a scanning electron microscope (JSM-IT300LA, JEOL, Tokyo, Japan). The thermal properties of the specimens were measured in an argon atmosphere at a heating rate of 0.16 K/s using a differential thermal analysis (STA7300, Hitachi-hightech, Tokyo, Japan). Samples measuring 1 × 1 × 8 mm were cut out from the bulk materials using a low-speed diamond saw, and the Seebeck coefficient and electrical resistivity of the specimens were measured by the standard DC four-probe technique in a helium atmosphere using a ZEM-3 Seebeck Coefficient/Electric Resistance Measurement System (Advance Riko, Inc., Kanagawa, Japan). The power factor of the specimens was obtained from the Seebeck coefficient and electrical resistivity values.

3. Results and Discussion

3.1. FeSi₂ Compound

The mechanically alloyed FeSi₂ powder was consolidated at 1073 K into a bulk specimen. Figure 1 shows the XRD patterns of the mechanically alloyed powder, the bulk specimen, and the annealed bulk specimen. The binary phase diagram of the Fe-Si system alloys is shown in Figure 2 [28]. The XRD pattern of the mechanically alloyed powder prepared from the powder mixture with the nominal composition of FeSi₂ showed diffraction peaks of the α -Fe phase together with small and broad diffraction peaks of the Si phase. There have been several reports on the formation of the β -FeSi₂ phase by mechanical alloying [29,30], but the mechanically alloyed powder in the present study did not contain the β -FeSi₂ phase. On the other hand, diffraction peaks of ϵ -FeSi and α -Fe₂Si₅ phases were found in the XRD pattern of the bulk specimen consolidated at 1073 K. According to the Fe-Si phase diagram, the equilibrium phase in this specimen is the β -FeSi₂ phase at 1073 K. However, the bulk specimen consisted of ϵ -FeSi and α -Fe₂Si₅ phases. The β -FeSi₂ phase is a peritectoid phase that is formed by a peritectoid reaction from ϵ -FeSi and α -Fe₂Si₅ phases. Thus, a bulk specimen consisting of the β -FeSi₂ phase could be obtained by annealing the bulk specimen containing ϵ -FeSi and α -Fe₂Si₅ phases. The XRD pattern of the bulk specimen annealed at 1073 K for 6 h exhibited diffraction peaks of the β -FeSi₂ phase, indicating that annealing is necessary to obtain the β -FeSi₂ phase. These results suggest that mechanical alloying, spark plasma sintering, and subsequent annealing can produce the specimens consisting of the β -FeSi₂ phase.

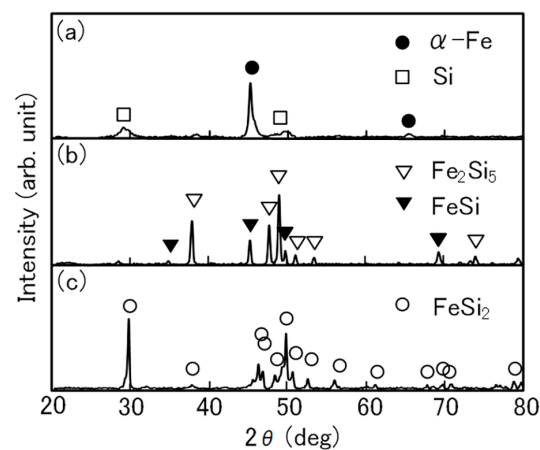


Figure 1. XRD patterns of (a) the mechanically alloyed FeSi₂ powder, (b) the bulk specimen, and (c) the bulk specimen annealed at 1073 K for 6 h.

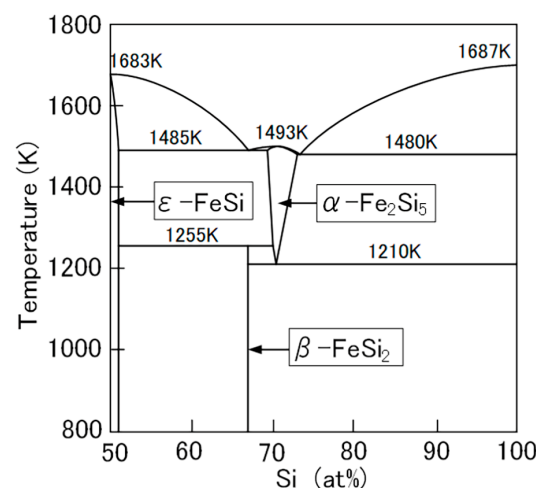


Figure 2. Binary Phase diagram of Fe-Si system alloys [30].

In order to confirm the existence of the β -FeSi₂ phase in the FeSi₂ bulk specimen annealed at 1073 K for 6 h, the thermal properties of the FeSi₂ bulk specimen were examined by DTA. Figure 3 shows the DTA curve of the FeSi₂ bulk specimen annealed at 1073 K for 6 h. The curve shows one large endothermic peak at around 1260 K, corresponding to the peritectoid reaction temperature (β -FeSi₂ phase $\rightarrow$ ϵ -FeSi and α -Fe₂Si₅ phases). This suggests that the FeSi₂ bulk specimen annealed at 1073 K for 6 h consisted of the β -FeSi₂ phase.

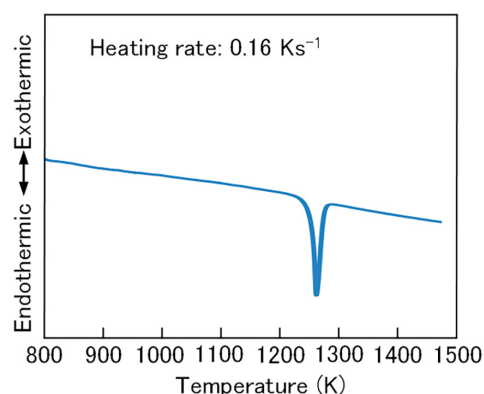


Figure 3. DTA curve of the FeSi₂ bulk specimen annealed at 1073 K for 6 h.

The thermoelectric properties of the FeSi₂ bulk specimens annealed at 1073 K, 1123 K, and 1173 K for 6 h were examined. The Seebeck coefficient and electrical resistivity of the specimens are shown in Figures 4 and 5, respectively. The bulk specimen without annealing is also shown for comparison. These specimens are found to be p-type thermoelectric materials, which are characterized by a positive Seebeck coefficient. The Seebeck coefficient of the bulk specimen without annealing was very small, whereas that of the annealed specimens was quite large. This confirms that the annealed specimens consisting of the β -FeSi₂ phase exhibited a large Seebeck coefficient. Regardless of the ambient temperature, the bulk specimens annealed at higher annealing temperatures showed a higher Seebeck coefficient. The maximum Seebeck coefficient of 356 μVK^{-1} was achieved in the bulk specimen annealed at 1173 K for 6 h. This value is comparable or superior to that of the Bi₂Te₃ compound. The annealed bulk specimens can thus be considered to be promising candidates for thermoelectric materials. A further increase in the annealing temperature may increase the Seebeck coefficient value, but it should be noted that the annealing was performed at temperatures lower than that of the eutectoid reaction ($\text{Fe}_2\text{Si}_3 \rightarrow \beta\text{-FeSi}_2 + \text{Si}$), which takes place at 1210 K.

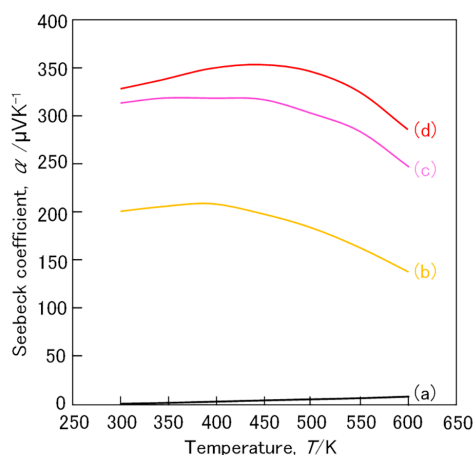


Figure 4. Seebeck coefficient as a function of ambient temperature for (a) the FeSi₂ bulk specimen without annealing and those annealed at (b) 1073 K, (c) 1123 K, and (d) 1173 K.

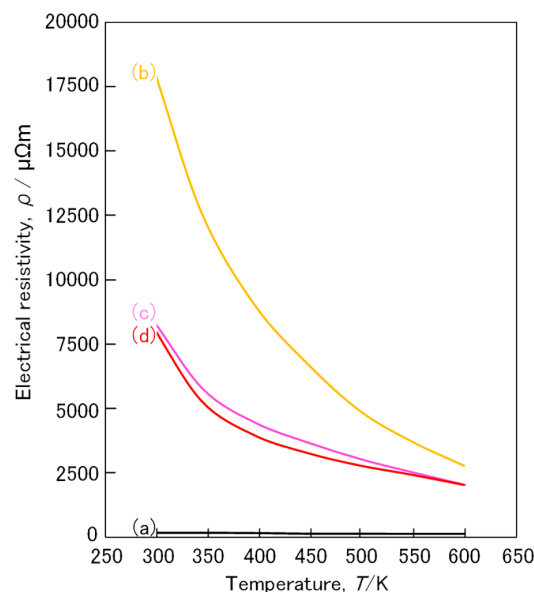


Figure 5. Electrical resistivity as a function of ambient temperature for (a) the FeSi₂ bulk specimen without annealing and those annealed at (b) 1073 K, (c) 1123 K, and (d) 1173 K.

The bulk specimen without annealing had a low electrical resistivity of 64 $\mu\Omega\text{m}$ at room temperature. On the other hand, the annealed bulk specimens consisting of the β -FeSi₂ phase exhibited high electrical resistivity at room temperature, ranging from 17,600 $\mu\Omega\text{m}$ for the specimen annealed at 1073 K to 8000 $\mu\Omega\text{m}$ for the specimen annealed at 1173 K. Furthermore, the electrical resistivity of the annealed bulk specimens drastically decreased as the ambient temperature increased, indicating that the annealed bulk specimens exhibit semiconductor-like temperature dependency. This confirms that the annealed bulk specimens consisted of the semiconducting β -FeSi₂ phase.

The power factors of the FeSi₂ bulk specimen and those annealed at 1073 K, 1123 K, and 1173 K for 6 h were calculated using equation $\text{PF} = S^2 / \rho$, where PF is the power factor, S is the Seebeck coefficient and ρ is electrical resistivity. The results are shown in Figure 6. Unfortunately, the power factors of the annealed bulk specimen were less than 50 $\mu\text{Wm}^{-1}\text{K}^{-2}$, two orders smaller than that of the Bi₂Te₃ compound (around 3000 $\mu\text{Wm}^{-1}\text{K}^{-2}$). This is due to the high electrical resistivity of the annealed bulk specimens. Further studies are therefore necessary to reduce the electrical resistivity of the bulk specimens consisting of the β -FeSi₂ phase.

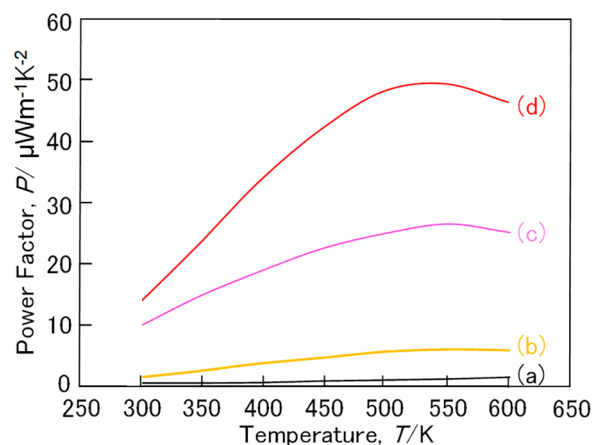


Figure 6. Power factor as a function of ambient temperature for (a) the FeSi₂ bulk specimen without annealing and those annealed at (b) 1073 K, (c) 1123 K, and (d) 1173 K.

3.2. (Fe,Mn)Si₂ and (Fe,Co)Si₂ Compound

In the initial part of the study described above, a β -FeSi₂ specimen with a high Seebeck coefficient was obtained by annealing the bulk specimens at 1173 K for 6 h. Thus, Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) and Fe_{1-x}Co_xSi₂ ($x = 0.2$ – 0.8) bulk specimens were prepared using the same procedure. The (Fe,Mn)Si₂ and (Fe,Co)Si₂ phases were successfully obtained through this process.

First, the thermoelectric properties of Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens annealed at 1173 K for 6 h were compared with those of the FeSi₂ bulk specimen annealed at 1173 K for 6 h. The Seebeck coefficient and electrical resistivity of the specimens are shown in Figures 7 and 8, respectively. The Seebeck coefficient of the annealed FeSi₂ bulk specimen was higher than that of the annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens in the ambient temperature range used in this experiment. The annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens were found to be p-type thermoelectric materials, as was the case for the annealed FeSi₂ bulk specimen. At room temperature, the Seebeck coefficient of the annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens increased from 38.6 μVK^{-1} for Fe_{0.98}Mn_{0.02}Si₂ to 262 μVK^{-1} for Fe_{0.94}Mn_{0.06}Si₂ and then decreased, as the Mn content further increased, to 27.3 μVK^{-1} for Fe_{0.92}Mn_{0.08}Si₂.

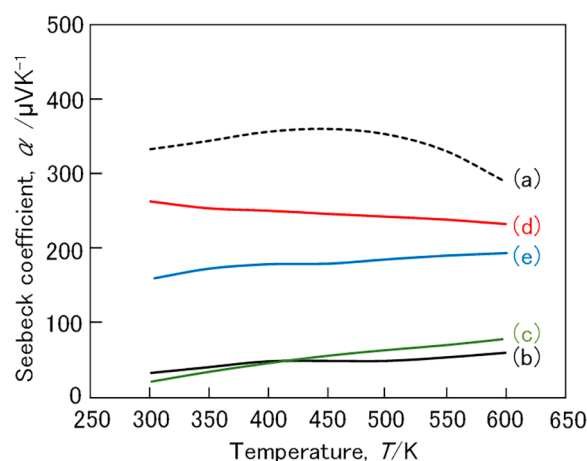


Figure 7. Seebeck coefficient as a function of ambient temperature for the (a) FeSi₂ (dashed line), (b) Fe_{0.98}Mn_{0.02}Si₂, (c) Fe_{0.96}Mn_{0.04}Si₂, (d) Fe_{0.94}Mn_{0.06}Si₂, and (e) Fe_{0.92}Mn_{0.08}Si₂ bulk specimens.

The electrical resistivity of the annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens was also lower than that of the annealed FeSi₂ bulk specimen in the ambient temperature range used in this experiment. At room temperature, the electrical resistivity of the annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens slightly increased from 303 $\mu\Omega\text{m}$ for Fe_{0.98}Mn_{0.02}Si₂ to 1060 $\mu\Omega\text{m}$ for Fe_{0.94}Mn_{0.06}Si₂ and then decreased, as the Mn content further increased, to 134 $\mu\Omega\text{m}$ for Fe_{0.92}Mn_{0.08}Si₂. This suggests that Mn substitution effectively reduces the electrical resistivity of the annealed FeSi₂ bulk specimen. The electrical resistivity of the annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens exhibited a semiconductor-like temperature dependency, as was the case for the annealed FeSi₂ bulk specimen.

The power factor of the annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens was calculated, and the results are shown in Figure 9. It was found that the power factor of the annealed Fe_{1-x}Mn_xSi₂ ($x = 0.2$ – 0.8) bulk specimens also increased as the ambient temperature increased. Regardless of the ambient temperature, the annealed Fe_{0.94}Mn_{0.06}Si₂ bulk specimen showed a higher power factor than the other annealed bulk specimens. The maximum power factor of 339 $\mu\text{Wm}^{-1}\text{K}^{-2}$ was achieved in the annealed Fe_{0.94}Mn_{0.06}Si₂ bulk specimen measured at 600 K. This value is much higher than that of the annealed FeSi₂ bulk specimen but still smaller than that of the Bi₂Te₃ compound.

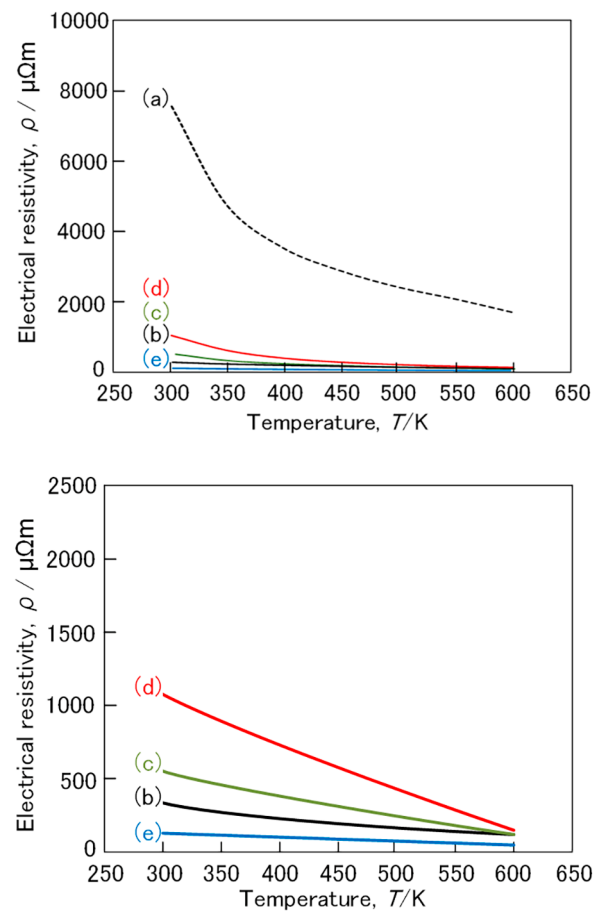


Figure 8. Electrical resistivity as a function of ambient temperature for the (a) FeSi_2 (dashed line), (b) $\text{Fe}_{0.98}\text{Mn}_{0.02}\text{Si}_2$, (c) $\text{Fe}_{0.96}\text{Mn}_{0.04}\text{Si}_2$, (d) $\text{Fe}_{0.94}\text{Mn}_{0.06}\text{Si}_2$, and (e) $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_2$ bulk specimens.

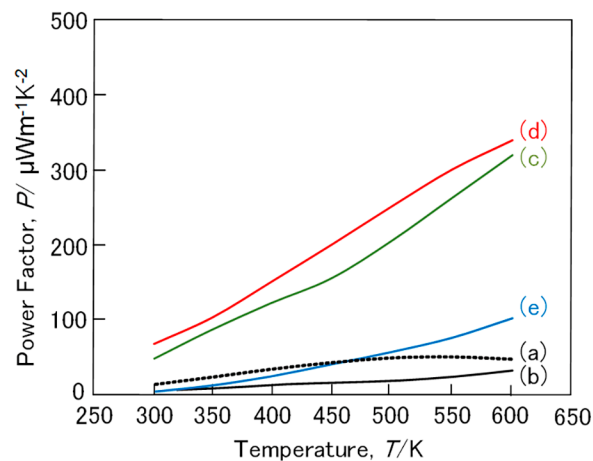


Figure 9. Power factor as a function of ambient temperature for the (a) FeSi_2 (dashed line), (b) $\text{Fe}_{0.98}\text{Mn}_{0.02}\text{Si}_2$, (c) $\text{Fe}_{0.96}\text{Mn}_{0.04}\text{Si}_2$, (d) $\text{Fe}_{0.94}\text{Mn}_{0.06}\text{Si}_2$, and (e) $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_2$ bulk specimens.

Secondly, the thermoelectric properties of $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimens annealed at 1173 K for 6 h were compared with those of the FeSi_2 bulk specimen annealed at 1173 K for 6 h. The Seebeck coefficient and electrical resistivity of the specimens are shown in Figures 10 and 11, respectively. Unlike the annealed $\text{Fe}_{1-x}\text{Mn}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimens, the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimens exhibited a negative Seebeck coefficient. The annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimens were found to

be n-type thermoelectric material. The absolute values of the Seebeck coefficients of the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimens were lower than that of the annealed FeSi_2 bulk specimen. At room temperature, the absolute values of the Seebeck coefficients of the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimens increased from $-64.7 \mu\text{VK}^{-1}$ for $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ to $-180 \mu\text{VK}^{-1}$ for $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$ and then decreased as the Co content further increased, to $-35.2 \mu\text{VK}^{-1}$ for $\text{Fe}_{0.92}\text{Co}_{0.08}\text{Si}_2$.

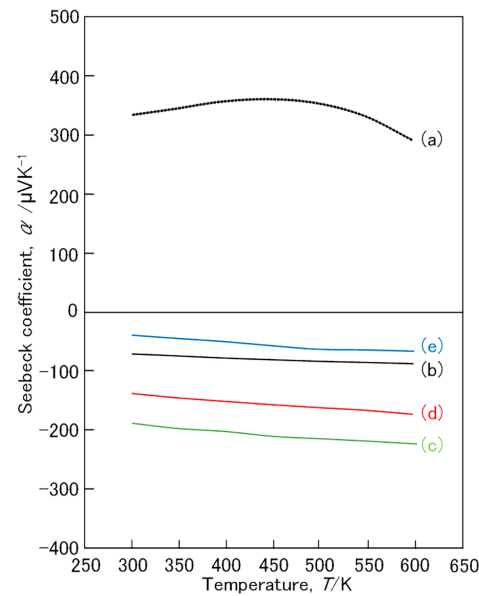


Figure 10. Seebeck coefficient as a function of ambient temperature for the (a) FeSi_2 (dashed line), (b) $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$, (c) $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$, (d) $\text{Fe}_{0.94}\text{Co}_{0.06}\text{Si}_2$, and (e) $\text{Fe}_{0.92}\text{Co}_{0.08}\text{Si}_2$ bulk specimens.

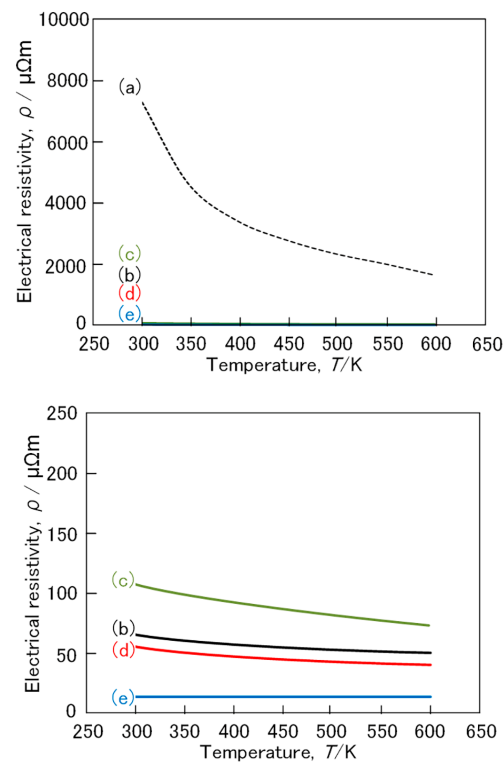


Figure 11. Electrical resistivity as a function of ambient temperature for the (a) FeSi_2 (dashed-line), (b) $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$, (c) $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$, (d) $\text{Fe}_{0.94}\text{Co}_{0.06}\text{Si}_2$, and (e) $\text{Fe}_{0.92}\text{Co}_{0.08}\text{Si}_2$ bulk specimens.

The electrical resistivity of the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2-0.8$) bulk specimens was lower than that of the annealed FeSi_2 bulk specimen, as was the case for the Mn substitution. At room temperature, the electrical resistivity of the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2-0.8$) bulk specimens slightly increased from $64.6 \mu\Omega\text{m}$ for $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ to $108 \mu\Omega\text{m}$ for $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$ and then decreased, as the Co content further increased, to $13.8 \mu\Omega\text{m}$ for $\text{Fe}_{0.92}\text{Co}_{0.08}\text{Si}_2$. This suggests that Co substitution is also effective in reducing the electrical resistivity of the annealed FeSi_2 bulk specimen. The electrical resistivity of the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2-0.8$) bulk specimens also exhibit semiconductor-like temperature dependency, as was the case for the annealed FeSi_2 bulk specimen.

The power factor of the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2-0.8$) bulk specimens was calculated, and the results are shown in Figure 12. It was found that the power factor of the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2-0.8$) bulk specimen also increased as the ambient temperature increased. The annealed $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$ bulk specimen showed a higher power factor than the other bulk specimens. The maximum power factor of $667 \mu\text{Wm}^{-1}\text{K}^{-2}$ was achieved in the annealed $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$ bulk specimen measured at 600 K. This value is higher than that of the annealed $\text{Fe}_{1-x}\text{Mn}_x\text{Si}_2$ ($x = 0.2-0.8$) bulk specimens.

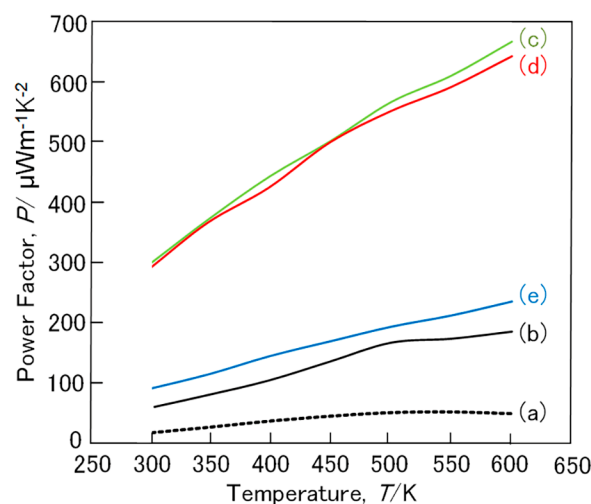


Figure 12. Power factor as a function of ambient temperature for the (a) FeSi_2 (dashed line), (b) $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$, (c) $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$, (d) $\text{Fe}_{0.94}\text{Co}_{0.06}\text{Si}_2$, and (e) $\text{Fe}_{0.92}\text{Co}_{0.08}\text{Si}_2$ bulk specimens.

The Seebeck coefficient of the Mn- and Co-substituted FeSi_2 specimens is almost comparable to the commercial Bi-Te thermoelectric compound ($180-200 \mu\text{VK}^{-1}$). However, the power factor of the Mn- and Co-substituted FeSi_2 specimens is inferior to that of the Bi-Te thermoelectric compound ($2000-3000 \mu\text{Wm}^{-1}\text{K}^{-2}$). Thus, further improvement of the power factor is essential in order to realize thermoelectric materials for thermoelectric generation to achieve waste heat recovery.

4. Conclusions

The FeSi_2 bulk specimens prepared by spark plasma sintering from the mechanically alloyed powder consisted of FeSi and Fe_2Si_3 phases and showed a low Seebeck coefficient. The annealed FeSi_2 bulk specimens consisted of the $\beta\text{-FeSi}_2$ phase and exhibited a high Seebeck coefficient, reaching a maximum of $356 \mu\text{VK}^{-1}$ for the FeSi_2 bulk specimens annealed at 1173 K for 6 h. However, the power factor of the annealed FeSi_2 bulk specimen was less than $50 \mu\text{Wm}^{-1}\text{K}^{-2}$ due to the high electrical resistivity. Thus, Mn- and Co-substituted specimens were prepared using the same procedure to improve the power factor. Although the Mn and Co substitutions decreased the Seebeck coefficient, the substitutions significantly reduced the electrical resistivity and increased the power factor. It was also found that the annealed $\text{Fe}_{1-x}\text{Mn}_x\text{Si}_2$ ($x = 0.2-0.8$) bulk specimens were p-type thermoelectric materials, whereas the annealed $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$ bulk specimens were

n-type thermoelectric materials. Among the annealed $\text{Fe}_{1-x}\text{Mn}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimens, the $\text{Fe}_{0.94}\text{Mn}_{0.06}\text{Si}_2$ bulk specimen exhibited a Seebeck coefficient of $262\ \mu\text{VK}^{-1}$ and a power factor of $339\ \mu\text{Wm}^{-1}\text{K}^{-2}$. Among the annealed $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ ($x = 0.2\text{--}0.8$) bulk specimen, on the other hand, the $\text{Fe}_{0.96}\text{Co}_{0.04}\text{Si}_2$ bulk specimen showed a Seebeck coefficient of $-180\ \mu\text{VK}^{-1}$ and a power factor of $667\ \mu\text{Wm}^{-1}\text{K}^{-2}$.

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