Thermoelectric Properties of p-Type $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with Rare-Earth Oxide Addition

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The effects of rare earth oxide dispersion on the thermoelectric properties of the Mn-doped p-type $\beta\text{-FeSi}_2$ ($\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$) were investigated. The $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ powders were mechanically alloyed with Y_2O_3 powder (0.5–4 mass%) and subsequently hot pressed. The added Y_2O_3 was dispersed in the β phase matrix as a fine particles around 10 nm in size. The thermal conductivity of the sample was significantly reduced by Y_2O_3 addition, which was caused by enhancing phonon scattering due to fine Y_2O_3 dispersion. It was also found that the added Y_2O_3 was partially decomposed in the sample, resulted in solution of elemental Y in the β phase as a p-type dopant. The Seebeck coefficient was slightly improved when a small amount of Y_2O_3 (0.5 and 1 mass%) was added. The improvement of the Seebeck coefficient could not be explained only by the fine dispersion of Y_2O_3 and the Y doping as a p-type dopant. The slight increase in the Seebeck coefficient was also observed in the case of the samples with addition of small amounts of La_2O_3 powder.

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1. Introduction

Thermoelectric power generation, which can directly convert heat energy into electricity, has been more attractive as a clean means of generating electricity. It can generate electrical energy without any exhaust gases, mechanical vibration, or noise, and there is no maintenance required.

Semiconducting iron disilicide, $\beta\text{-FeSi}_2$, is one of the potential candidates for practical use in the high temperature range (up to 1200 K) because of its abundance as a raw material, its good resistance to oxidation and its non-toxicity. However, the performance of $\beta\text{-FeSi}_2$ is still low for practical use compared to other thermoelectric materials, so its thermoelectric properties need to be improved.^{1,2)} The performance of a thermoelectric material is generally evaluated by the figure of merit, Z , which is calculated from the Seebeck coefficient, S , electrical resistivity, ρ , and thermal conductivity, κ , in the equation $Z = S^2/\rho\kappa$. In order to improve the electrical properties of the $\beta\text{-FeSi}_2$, such as Seebeck coefficient and electrical resistivity, the doping of various elements, Co,^{3–9)} Cr,⁸⁾ Ni,^{8,9)} Mn,^{8,10–12)} Al,^{3,4,6,12)} Cu,¹³⁾ B,¹⁴⁾ Nb,¹⁵⁾ Zr,¹⁶⁾ or P,¹⁷⁾ etc., has been attempted during sample preparation. Co and Mn are well known as good dopants for n-type and p-type $\beta\text{-FeSi}_2$ materials, respectively. On the other hand, a decrease in thermal conductivity is also crucial for improving the figure of merit. It was reported that when rare-earth oxides, such as Y_2O_3 etc., were added to the Co-doped n-type $\beta\text{-FeSi}_2$ ($\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$) synthesized by mechanical alloying and hot pressing, small rare earth particles around 10 nm in size were dispersed in the β phase matrix, resulting in significant reduction in the thermal conductivity due to enhancement of phonon scattering.^{18,19)} Besides that, it was also found that the fine dispersion of rare-earth oxides was effective for improving the Seebeck coefficient. For example, Fig. 1 shows that the temperature dependence of (a) the electrical

Fig. 1 Temperature dependence of (a) the electrical resistivity, ρ , and (b) the Seebeck coefficient, S , of the hot-pressed $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ with x mass% Y_2O_3 .¹⁸⁾

resistivity, ρ , and (b) the Seebeck coefficient, S , of the hot-pressed n-type $\beta\text{-FeSi}_2$ ($\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$) with x mass% Y_2O_3 . Although the electrical resistivity increased with increasing amount of Y_2O_3 , the Seebeck coefficient was enhanced by Y_2O_3 addition in the low temperature range (below 900 K), and the enhancement effect was significantly large when the small amount of Y_2O_3 (around 2 mass%) was added. The EDX (energy dispersive X-ray spectroscopy) analysis on the β phase matrix of the samples with Y_2O_3 addition revealed

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that the decomposition of a small amount of the added Y_2O_3 occurred and elemental Y was doped into $\beta\text{-FeSi}_2$ phase.¹⁹⁾ The rare earth element is considered to be substituted for Fe atom in the β phase because of its large atomic radius and behave as a p-type dopant. Additionally, the Hall coefficient measurement showed that the carrier concentration was reduced by Y_2O_3 addition, indicating that the increase in the Seebeck coefficient of the n-type $\beta\text{-FeSi}_2$ was caused by the Y solution as a p-type dopant. From these results, it was also found that the figure of merit of the n-type $\beta\text{-FeSi}_2$ was doubled by the addition of 2 mass% Y_2O_3 . Based on these experimental results described above, in case of the rare earth oxide addition to the p-type $\beta\text{-FeSi}_2$, it is deduced that the solution of rare earth element into the β phase as a p-type dopant due to the decomposition of a small amount of added oxides results in an increase in the carrier concentration of the sample and decreases its Seebeck coefficient. However, the fine dispersion of rare earth oxides is expected to significantly reduce the thermal conductivity of the p-type $\beta\text{-FeSi}_2$, as well as that in the n-type $\beta\text{-FeSi}_2$. On the basis of these considerations, the rare earth oxide dispersion may be an effective process for improvement of the thermoelectric performance even in the case of the p-type $\beta\text{-FeSi}_2$. Therefore, in this study, the Mn-doped p-type $\beta\text{-FeSi}_2$ ($\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$) with Y_2O_3 dispersion was synthesized by mechanical alloying and subsequent hot pressing, and the effects of Y_2O_3 addition on the microstructure and the thermoelectric properties of the p-type $\beta\text{-FeSi}_2$ were investigated.

2. Experimental Procedure

The hot-pressed $\beta\text{-FeSi}_2$ samples with dispersion of Y_2O_3 were prepared by the following process. The composition of the mother sample was the p-type $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$. Mixtures of Fe, Si, Mn powders in the desired mole ratios were arc-melted in an argon atmosphere to form a button composed of the α and ε phases. The argon atmosphere was purified by melting zirconium and allowing it to react with residual oxygen and nitrogen. The buttons were pulverized to -60 mesh using a mortar and pestle. Y_2O_3 powder (0, 0.5, 1, 2, and 4 mass%) was added to the pulverized powder. These powders were mechanically alloyed for 72 ks in an argon atmosphere. The MA powders with or without Y_2O_3 addition were hot pressed at 1173 K for 3.6 ks under 25 MPa in a vacuum using carbon dies. The phases and microstructures of these hot-pressed samples were determined by XRD (X-ray diffraction analysis), TEM (transmission electron microscopy) and EDX. The Seebeck coefficient, S , and the electrical resistivity, ρ , were simultaneously measured from room temperature to about 1100 K by the ordinary four probe dc method in a flowing argon gas atmosphere using a computer-controlled equipment. The thermal diffusivity, D , and the specific heat, C_p , were measured from room temperature to about 1100 K by the laser flash method using the thermal constant analyzer (ULVAC TC-7000). The thermal conductivity, κ , of the hot-pressed samples was calculated from the thermal diffusivity, D , the specific heat, C_p , and the density, d , in the equation $\kappa = D \times C_p \times d$.

Fig. 2 TEM photograph of the hot-pressed $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with 1 mass% Y_2O_3 .

3. Results and Discussion

Figure 2 shows the TEM photograph of the hot-pressed $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with 1 mass% Y_2O_3 . It was found that small Y_2O_3 particles around 10 nm in size were dispersed in the β phase matrix. The EDX analysis revealed that a small amount of Y about 0.5 at.% was detected in the β phase matrix without Y_2O_3 particles, indicating that partial decomposition of the added Y_2O_3 occurred and the elemental Y was slightly dissolved in the β phase matrix. As well as in the case of the n-type $\beta\text{-FeSi}_2$, the elemental Y dissolved in the matrix is considered to be substituted for Fe, not for Si, because of its large atomic radius, and work as a p-type dopant.

Figure 3 shows the temperature dependence of the thermal conductivity, κ , of the hot-pressed samples with x mass% Y_2O_3 dispersion. The κ values significantly decreased with increasing amount of Y_2O_3 over the entire temperature range. Thus, it was found that the fine dispersion of a rare earth oxide was quite effective for reducing the thermal conductivity of the p-type $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$, as well as in the case of the n-type $\beta\text{-FeSi}_2$. When a single sign of charge carrier is predominant, the thermal conductivity of a material can be written as $\kappa = \kappa_{\text{car}} + \kappa_{\text{ph}}$, where κ_{car} is the carrier contribution and κ_{ph} is the lattice contribution regarding phonon scattering.^{1,20)} The κ_{car} was calculated using Wiedemann–Franz relationship $\kappa_{\text{car}} = L\sigma T$, where L is the Lorenz number, σ is the electrical conductivity, and T is the absolute temperature. The Lorenz number is calculated using the reduced Fermi energy, which is estimated from the Seebeck coefficient and the Fermi–Dirac integral.^{21,22)} The κ_{ph} was obtained by subtracting κ_{car} from κ . Figure 4 shows the temperature dependence of the lattice contribution, κ_{ph} , and the carrier contribution, κ_{car} , to the thermal conductivity of the hot-pressed samples with x mass% Y_2O_3 . The κ_{car} values of the n-type and p-type $\beta\text{-FeSi}_2$ are quite small and the κ_{ph} is a dominant component in the total thermal conductivity.^{23,24)} As shown in Fig. 4, although the carrier contribution slightly

Fig. 3 Temperature dependence of the thermal conductivity, κ , of the hot-pressed $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with x mass% Y_2O_3 .

Fig. 4 Temperature dependence of the lattice contribution, κ_{ph} , and the carrier contribution, κ_{car} , to the thermal conductivity of the hot-pressed $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with x mass% Y_2O_3 .

increased with increasing temperature, all the samples with and without Y_2O_3 addition prepared in this study also showed quite small κ_{car} values and the κ_{ph} occupied most part of the total thermal conductivity. Besides that, the Y_2O_3 addition was found to hardly affect the κ_{car} values. On the other hand, κ_{ph} values were significantly reduced with increasing amount of Y_2O_3 because of enhancing phonon scattering, indicating that the decrease in the thermal conductivity shown in Fig. 3 was mostly ascribed to the reduction in the lattice contribution, κ_{ph} . Thus, in the case of the n-type and p-type $\beta\text{-FeSi}_2$, the lattice contribution of which is a main component of the total thermal conductivity, a decrease in the κ_{ph} due to dispersion of fine particles in the β phase matrix is quite

Fig. 5 Temperature dependence of (a) the electrical resistivity, ρ , and (b) the Seebeck coefficient, S , of the hot-pressed $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with x mass% Y_2O_3 .

effective for improving the thermoelectric properties.

Figure 5 shows the temperature dependence of (a) the electrical resistivity, ρ , and (b) the Seebeck coefficient, S , of the hot-pressed samples with x mass% Y_2O_3 . The electrical resistivity slightly increased with increasing amount of Y_2O_3 in the lower temperature range, which is considered to be caused by carrier scattering due to dispersion of fine Y_2O_3 particles. On the other hand, the values of the Seebeck coefficient of the samples with 0.5 and 1 mass% Y_2O_3 were slightly larger than those of the sample without Y_2O_3 . The further increase in the amount of Y_2O_3 resulted in reduction in the S values and the samples with $x = 2$ and 4 showed the Seebeck coefficient smaller than that of the sample without Y_2O_3 . As mentioned above, it was found that a small amount of Y was dissolved in the β phase matrix. This Y solution in the matrix as a p-type dopant is considered to increase the carrier concentration of the sample and reduce the Seebeck coefficient. However, as shown in Fig. 5(b), when a small amount of Y_2O_3 ($x = 0.5$ and 1) was added, the Seebeck coefficient was enhanced as compared to the sample without Y_2O_3 , which is unable to explain only by the change in carrier concentration due to Y solution. This experimental result indicates that the Y_2O_3 addition has another role of enhancing the Seebeck coefficient other than that of the increase in the carrier concentration. The improvement effect on the Seebeck coefficient due to Y_2O_3 addition observed in the p-type sample is small as compared to that of the n-type $\text{Fe}_{0.98}\text{Co}_{0.02}\text{Si}_2$ sample shown in Fig. 1. It is considered that the contribution of Y doping to the p-type sample to the increase in carrier concentration suppressed the enhancement of the Seebeck coefficient. The mechanism of improving the Seebeck coefficient due to addition of a small amount of

Fig. 6 Temperature dependence of the figure of merit, Z , of the hot-pressed $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with x mass% Y_2O_3 .

Y_2O_3 could not be clarified yet in this study, but the lattice strain induced by Y solution or solution of oxygen from Y_2O_3 into the β phase etc., may be associated with the enhancement of the S values.^{25,26)}

Figure 6 shows the temperature dependence of the figure of merit, Z , of the hot-pressed samples with x mass% Y_2O_3 . The sample with 1 mass% Y_2O_3 showed the Z values almost the same as those of the sample without Y_2O_3 . However, the figure of merits of the other samples with Y_2O_3 addition were smaller than that of the non-added sample, in spite of the fact that the Y_2O_3 dispersion was significantly effective for reducing the thermal conductivity. The reason why the figure of merit was not improved by Y_2O_3 addition is that the electrical resistivity increased with increasing amount of Y_2O_3 , and the enhancement of the Seebeck coefficient was small as compared to that of the p-type $\beta\text{-FeSi}_2$ even when the small amount of Y_2O_3 was added ($x = 0.5$ and 1).

In order to investigate effects of dispersion of a rare earth oxide other than Y_2O_3 on the Seebeck coefficient of the p-type $\beta\text{-FeSi}_2$, the samples with La_2O_3 addition were synthesized under the same condition as the samples with Y_2O_3 addition, and their Seebeck coefficient and the electrical resistivity were measured. Figure 7 shows the temperature dependence of (a) the electrical resistivity, ρ , and (b) the Seebeck coefficient, S , of the hot-pressed samples with x mass% La_2O_3 . The electrical resistivity increased with increasing amount of La_2O_3 especially in the lower temperature range because of carrier scattering due to dispersion of fine La_2O_3 particles. Additionally, the Seebeck coefficient was also enhanced when a small amount of La_2O_3 added. The further increase in the amount of La_2O_3 ($x = 4$) deteriorated the S values. As shown in Figs. 5 and 7, these effects of the La_2O_3 addition on the electrical properties were almost the same as those of the Y_2O_3 addition, suggesting that the enhancement of the Seebeck coefficient is also caused by dispersion of other rare earth oxides, such as Nd_2O_3 , Sm_2O_3 , etc. In the future, it is desired that the mechanism of

Fig. 7 Temperature dependence of (a) the electrical resistivity, ρ , and (b) the Seebeck coefficient, S , of the hot-pressed $\text{Fe}_{0.9}\text{Mn}_{0.1}\text{Si}_2$ with x mass% La_2O_3 .

enhancing the Seebeck coefficient of the n-type and p-type $\beta\text{-FeSi}_2$ due to rare earth oxide dispersion will be investigated in detail by using Hall coefficient measurement, etc.

4. Conclusion

The Mn-doped p-type $\beta\text{-FeSi}_2$ with Y_2O_3 addition was synthesized by MA and hot pressing. The effects of the rare earth oxide addition on the thermoelectric properties were investigated. The fine particles of Y_2O_3 around 10 nm in size were dispersed in the β phase matrix by MA. The thermal conductivity was significantly reduced with increasing amount of Y_2O_3 because of enhancement of phonon scattering due to the Y_2O_3 dispersion. The EDX analysis revealed that partial decomposition of added Y_2O_3 occurred and elemental Y was dissolved in the $\beta\text{-FeSi}_2$ as a p-type dopant as well as in the case of the n-type $\beta\text{-FeSi}_2$. In the case of the addition of a small amount of Y_2O_3 ($x = 0.5$ and 1), the Seebeck coefficient was slightly enhanced, which is unable to explain only by the Y solution as a p-type dopant. The enhancement of the Seebeck coefficient was also observed in the samples with addition of small amounts of La_2O_3 . Consequently, the figure of merit of the p-type $\beta\text{-FeSi}_2$ could not be improved by Y_2O_3 addition because of the increase in the electrical resistivity.

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