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

Mikio Ito and Yuta Takiguchi*

Department of Materials Science and Processing, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

The effects of rare earth oxide dispersion on the thermoelectric properties of the Mn-doped p-type β-FeSi$_2$ (Fe$_{0.9}$Mn$_{0.1}$Si$_2$) were investigated. The Fe$_{0.9}$Mn$_{0.1}$Si$_2$ powders were mechanically alloyed with Y$_2$O$_3$ powder (0.5–4 mass%) and subsequently hot pressed. The added Y$_2$O$_3$ 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$_2$O$_3$ addition, which was caused by enhancing phonon scattering due to fine Y$_2$O$_3$ dispersion. It was also found that the added Y$_2$O$_3$ 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$_2$O$_3$ (0.5 and 1 mass%) was added. The improvement of the Seebeck coefficient could not be explained only by the fine dispersion of Y$_2$O$_3$ 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$_2$O$_3$ powder.

(Received October 21, 2004; Accepted April 10, 2005; Published July 15, 2005)

Keywords: p-type β-Fe$_2$Si$_2$, mechanical alloying, rare-earth oxide, nano-particle dispersion, partial decomposition, Seebeck coefficient, thermal conductivity, rare-earth element doping

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, β-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 β-FeSi$_2$ is still low for practical use compared to other thermoelectric materials, so its thermoelectric properties need to be improved. 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, $\rho$, and thermal conductivity, $\kappa$, in the equation $Z = S^2/\rho\kappa$. In order to improve the electrical properties of the β-FeSi$_2$, such as Seebeck coefficient and electrical resistivity, the doping of various elements, Co, Cr, Ni, Mn, Al, Cu, B, Nb, Zr, or P etc., has been attempted during sample preparation. Co and Mn are well known as good dopants for n-type and p-type β-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$_2$O$_3$, were added to the Co-doped n-type β-FeSi$_2$ (Fe$_{0.98}$Co$_{0.02}$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. 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 resistivity, $\rho$, and (b) the Seebeck coefficient, $S$, of the hot-pressed Fe$_{0.98}$Co$_{0.02}$Si$_2$ with $x$ mass% Y$_2$O$_3$. Although the electrical resistivity increased with increasing amount of Y$_2$O$_3$, the Seebeck coefficient was enhanced by Y$_2$O$_3$ addition in the low temperature range (below 900 K), and the enhancement effect was significantly large when the small amount of Y$_2$O$_3$ (around 2 mass%) was added. The EDX (energy dispersive X-ray spectroscopy) analysis on the β phase matrix of the samples with Y$_2$O$_3$ addition revealed...
that the decomposition of a small amount of the added Y$_2$O$_3$ occurred and elemental Y was doped into \( \beta \)-FeSi$_2$ phase.\textsuperscript{19} The rare earth element is considered to be substituted for Fe atom in the \( \beta \) 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$_2$O$_3$ addition, indicating that the increase in the Seebeck coefficient of the n-type \( \beta \)-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 \( \beta \)-FeSi$_2$ was doubled by the addition of 2 mass\% Y$_2$O$_3$. Based on these experimental results described above, in case of the rare earth oxide addition to the p-type \( \beta \)-FeSi$_2$, it is deduced that the solution of rare earth element into the \( \beta \) 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 \( \beta \)-FeSi$_2$, as well as that in the n-type \( \beta \)-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 \( \beta \)-FeSi$_2$. Therefore, in this study, the Mn-doped p-type \( \beta \)-FeSi$_2$ (Fe$_{0.9}$Mn$_{0.1}$Si$_2$) with Y$_2$O$_3$ dispersion was synthesized by mechanical alloying and subsequent hot pressing, and the effects of Y$_2$O$_3$ addition on the microstructure and the thermoelectric properties of the p-type \( \beta \)-FeSi$_2$ were investigated.

2. Experimental Procedure

The hot-pressed \( \beta \)-FeSi$_2$ samples with dispersion of Y$_2$O$_3$ were prepared by the following process. The composition of the mother sample was the p-type Fe$_{0.9}$Mn$_{0.1}$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 \( \alpha \) and \( \varepsilon \) 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$_2$O$_3$ 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$_2$O$_3$ 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, \( \rho \), 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, \( \kappa \), of the hot-pressed samples was calculated from the thermal diffusivity, \( D \), the specific heat, \( C_p \), and the density, \( d \), in the equation \( \kappa = D \times C_p \times d \).

3. Results and Discussion

Figure 2 shows the TEM photograph of the hot-pressed Fe$_{0.9}$Mn$_{0.1}$Si$_2$ with 1 mass\% Y$_2$O$_3$. It was found that small Y$_2$O$_3$ particles around \( 10 \) nm in size were dispersed in the \( \beta \) phase matrix. The EDX analysis revealed that a small amount of Y about 0.5 at\% was detected in the \( \beta \) phase matrix without Y$_2$O$_3$ particles, indicating that partial decomposition of the added Y$_2$O$_3$ occurred and the elemental Y was slightly dissolved in the \( \beta \) phase matrix. As well as in the case of the n-type \( \beta \)-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, \( \kappa \), of the hot-pressed samples with \( x \) mass\% Y$_2$O$_3$ dispersion. The \( \kappa \) values significantly decreased with increasing amount of Y$_2$O$_3$ 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 Fe$_{0.9}$Mn$_{0.1}$Si$_2$, as well as in the case of the n-type \( \beta \)-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 \( \kappa_{\text{car}} \) is the carrier contribution and \( \kappa_{\text{ph}} \) is the lattice contribution regarding phonon scattering.\textsuperscript{1,20} The \( \kappa_{\text{car}} \) was calculated using Wiedemann–Franz relationship \( \kappa_{\text{car}} = L_0 \sigma T \), where \( L \) is the Lorenz number, \( \sigma \) 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.\textsuperscript{21,22} The \( \kappa_{\text{ph}} \) was obtained by subtracting \( \kappa_{\text{car}} \) from \( \kappa \). Figure 4 shows the temperature dependence of the lattice contribution, \( \kappa_{\text{ph}} \), and the carrier contribution, \( \kappa_{\text{car}} \), to the thermal conductivity of the hot-pressed samples with \( x \) mass\% Y$_2$O$_3$. The \( \kappa_{\text{car}} \) values of the n-type and p-type \( \beta \)-FeSi$_2$ are quite small and the \( \kappa_{\text{ph}} \) is a dominant component in the total thermal conductivity.\textsuperscript{23,24} As shown in Fig. 4, although the carrier contribution slightly
increased with increasing temperature, all the samples with and without Y$_2$O$_3$ addition prepared in this study also showed quite small $\kappa_{\text{car}}$ values and the $\kappa_{\text{ph}}$ occupied most part of the total thermal conductivity. Besides that, the Y$_2$O$_3$ addition was found to hardly affect the $\kappa_{\text{car}}$ values. On the other hand, $\kappa_{\text{ph}}$ values were significantly reduced with increasing amount of Y$_2$O$_3$ 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, $\kappa_{\text{ph}}$. Thus, in the case of the n-type and p-type $\beta$-FeSi$_2$, the lattice contribution of which is a main component of the total thermal conductivity, a decrease in the $\kappa_{\text{ph}}$ due to dispersion of fine particles in the $\beta$ phase matrix is quite effective for improving the thermoelectric properties.

Figure 5 shows the temperature dependence of (a) the electrical resistivity, $\rho$, and (b) the Seebeck coefficient, $S$, of the hot-pressed Fe$_{0.9}$Mn$_{0.1}$Si$_2$ with x mass% Y$_2$O$_3$. The electrical resistivity slightly increased with increasing amount of Y$_2$O$_3$ in the lower temperature range, which is considered to be caused by carrier scattering due to dispersion of fine Y$_2$O$_3$ particles. On the other hand, the values of the Seebeck coefficient of the samples with 0.5 and 1 mass% Y$_2$O$_3$ were slightly larger than those of the sample without Y$_2$O$_3$. The further increase in the amount of Y$_2$O$_3$ 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$_2$O$_3$. As mentioned above, it was found that a small amount of Y was dissolved in the $\beta$ 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$_2$O$_3$ ($x = 0.5$ and 1) was added, the Seebeck coefficient was enhanced as compared to the sample without Y$_2$O$_3$, which is unable to explain only by the change in carrier concentration due to Y solution. This experimental result indicates that the Y$_2$O$_3$ 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$_2$O$_3$ addition observed in the p-type sample is small as compared to that of the n-type Fe$_{0.98}$Co$_{0.02}$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
Y$_2$O$_3$ could not be clarified yet in this study, but the lattice strain induced by Y solution or solution of oxygen from Y$_2$O$_3$ 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 Fe$_{0.9}$Mn$_{0.1}$Si$_2$ with x mass% Y$_2$O$_3$. The sample with 1 mass% Y$_2$O$_3$ showed the Z values almost the same as those of the sample without Y$_2$O$_3$. However, the figure of merits of the other samples with Y$_2$O$_3$ addition were smaller than that of the non-added sample, in spite of the fact that the Y$_2$O$_3$ dispersion was significantly effective for reducing the thermal conductivity. The reason why the figure of merit was not improved by Y$_2$O$_3$ addition is that the electrical resistivity increased with increasing amount of Y$_2$O$_3$, and the enhancement of the Seebeck coefficient was small as compared to that of the p-type β-FeSi$_2$ even when the small amount of Y$_2$O$_3$ was added (x = 0.5 and 1).

In order to investigate effects of dispersion of a rare earth oxide other than Y$_2$O$_3$ on the Seebeck coefficient of the p-type β-FeSi$_2$, the samples with La$_2$O$_3$ addition were synthesized under the same condition as the samples with Y$_2$O$_3$ 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 Fe$_{0.9}$Mn$_{0.1}$Si$_2$ with x mass% La$_2$O$_3$. The electrical resistivity increased with increasing amount of La$_2$O$_3$ especially in the lower temperature range because of carrier scattering due to dispersion of fine La$_2$O$_3$ particles. Additionally, the Seebeck coefficient was also enhanced when a small amount of La$_2$O$_3$ added. The further increase in the amount of La$_2$O$_3$ (x = 4) deteriorated the S values. As shown in Figs. 5 and 7, these effects of the La$_2$O$_3$ addition on the electrical properties were almost the same as those of the Y$_2$O$_3$ addition, suggesting that the enhancement of the Seebeck coefficient is also caused by dispersion of other rare earth oxides, such as Nd$_2$O$_3$, Sm$_2$O$_3$, etc. In the future, it is desired that the mechanism of enhancing the Seebeck coefficient of the n-type and p-type β-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 β-FeSi$_2$ with Y$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ because of enhancement of phonon scattering due to the Y$_2$O$_3$ dispersion. The EDX analysis revealed that partial decomposition of added Y$_2$O$_3$ occurred and elemental Y was dissolved in the β-FeSi$_2$ as a p-type dopant as well as in the case of the n-type β-FeSi$_2$. In the case of the addition of a small amount of Y$_2$O$_3$ (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$_2$O$_3$. Consequently, the figure of merit of the p-type β-FeSi$_2$ could not be improved by Y$_2$O$_3$ addition because of the increase in the electrical resistivity.

REFERENCES

