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Thermoelectric properties of hot-pressed β-$FeSi_2$ with yttria dispersion by mechanical alloying

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Abstract

The β-$FeSi_2$ (n-type $Fe_{0.98}Co_{0.02}Si_2$) sintered bodies with dispersion of Y_2O_3 particles were synthesized by mechanical alloying of Fe–Si powder with Y_2O_3 powder and subsequent hot pressing. The effects of Y_2O_3 addition on the thermoelectric properties of the β-$FeSi_2$ were investigated. The thermal conductivity of the β-$FeSi_2$ was significantly reduced by dispersion of fine Y_2O_3 particles on the β phase matrix. On the other hand, the electrical resistivity increased with increasing amount of Y_2O_3. The Seebeck coefficient was enhanced by Y_2O_3 addition, especially below 800 K, corresponding to the extrinsic conductive region of the β-$FeSi_2$. Consequently, the figure of merit was significantly improved by 2 mass% Y_2O_3 addition. The energy dispersive X-ray spectroscopy (EDX) analysis revealed that the added Y_2O_3 was partially decomposed and a small amount of Y was dissolved in the β phase matrix. Based on this fact, the enhancement of the Seebeck coefficient caused by Y_2O_3 addition is considered to be due to reduction in carrier concentration which resulted from this Y solution as a p-type dopant in the β phase matrix, and the behavior of the Seebeck coefficient was found to be well consistent with that of the Y-doped samples synthesized by Y powder addition.

Keywords: Iron disilicide; Mechanical alloying; Seebeck coefficient; Thermal conductivity; Rare-earth oxide dispersion

1. Introduction

Thermoelectric power generation, which can directly convert heat energy into electricity, has been 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 not good for practical use compared to other thermoelectric materials, such as Bi_2Te_3 and $CoSb_3$ systems, etc., so its thermoelectric properties need to be improved [1].

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 β-$FeSi_2$, such as Seebeck coefficient and electrical resistivity, the doping of various elements has been attempted during sample preparation. Co [2–4] and Mn [5–7] 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. Generally, it is considered that second phase dispersion in the β phase matrix is effective for reducing the thermal conductivity due to enhancing phonon scattering. However, when dispersion of ZrO_2, which comparably has a good chemical stability by mechanical alloying (MA), was tried; ZrO_2 decomposed in the β-$FeSi_2$, resulting in deterioration of the thermoelectric performance [8]. This experimental result indicates that a dispersed second phase at least needs

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to be more stable than ZrO_2. Therefore, in the present study, a rare-earth oxide, Y_2O_3, was dispersed in the typical n-type Co-doped β-$FeSi_2$ ($Fe_{0.98}Co_{0.02}Si_2$) by MA, and then the powder was sintered by hot pressing. The microstructure of the sample with Y_2O_3 addition was revealed by transmission electron microscopy (TEM). Additionally, the effects of Y_2O_3 addition on the thermoelectric properties, such as the Seebeck coefficient, electrical resistivity and thermal conductivity were investigated, and their mechanisms were discussed.

2. Experimental procedure

Mixtures of Fe, Si and Co powders in the composition of $Fe_{0.98}Co_{0.02}Si_2$ were arc-melted in an argon atmosphere to form a button composed of the α and ε phases. The argon gas was purified by melting zirconium and allowing it to react with residual oxygen and nitrogen. The buttons were pulverized under 250 μm using a mortar and pestle. Y_2O_3 powder (0–6 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 oxides 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 and EDX (energy dispersive X-ray spectroscopy). The Seebeck coefficient, S, and the electrical resistivity, ρ, were simultaneously measured from room temperature to about 1100 K by the ordinary four-probe d.c. method in a flowing argon gas atmosphere using 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 $\kappa = D \times C_p \times d$.

3. Results and discussion

XRD analysis revealed that all the samples were mostly composed of the β phase with a small amount of residual ε-FeSi phase. Even when 6 mass% Y_2O_3 was added, a peak from Y_2O_3 phase was not observed in the XRD pattern clearly, suggesting that Y_2O_3 was finely dispersed in the β phase matrix. Fig. 1 shows the TEM photograph of the hot-pressed samples with 2 mass% Y_2O_3. The grain size of the β phase was found to be around 50–100 nm. Besides that, it was also found that several small particles around 10 nm in size were dispersed in some β phase grains. These small particles were considered to be Y_2O_3 phase pulverized during MA. For the sample with 4 mass% Y_2O_3, the number of these Y_2O_3 particles in the β phase grains increased as compared to the sample with 2 mass% Y_2O_3.

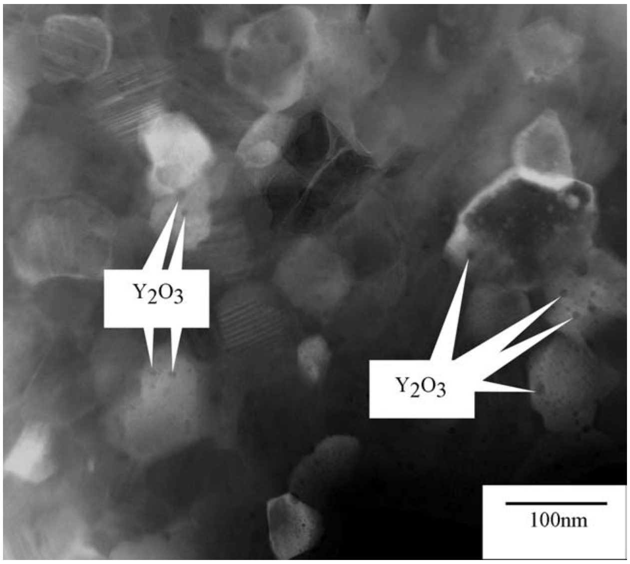

Fig. 1. TEM photograph of the hot-pressed $Fe_{0.98}Co_{0.02}Si_2$ with 2 mass% Y_2O_3.

Fig. 2 shows the temperature dependence of the thermal conductivity, κ, of the hot-pressed samples with x mass% Y_2O_3. The thermal conductivity was significantly reduced by Y_2O_3 dispersion over the entire temperature range. The κ values decreased with increasing amount of Y_2O_3, and the sample with 6 mass% Y_2O_3 showed the κ values about half the values of thermal conductivity of the sample without addition at low temperature range. Additionally, these samples with Y_2O_3 addition showed the κ values by 20% smaller than the samples with the same amount of SiC in the previous study [9], indicating that fine dispersion of a rare-earth

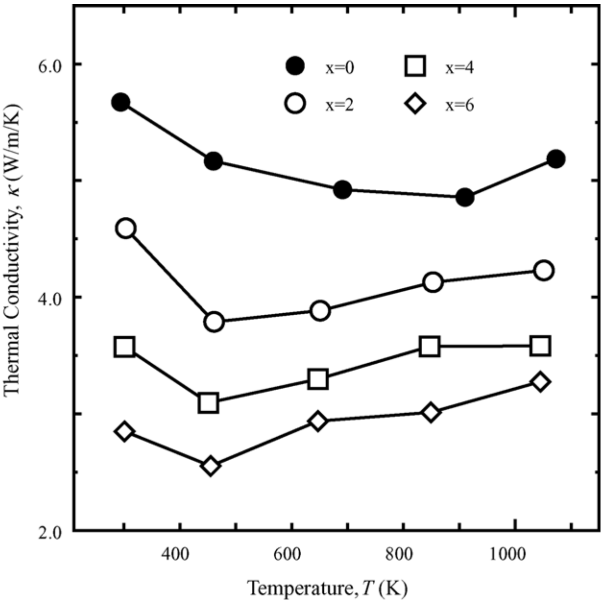

Fig. 2. Temperature dependence of the thermal conductivity, κ, of the hot-pressed $Fe_{0.98}Co_{0.02}Si_2$ with x mass% Y_2O_3.

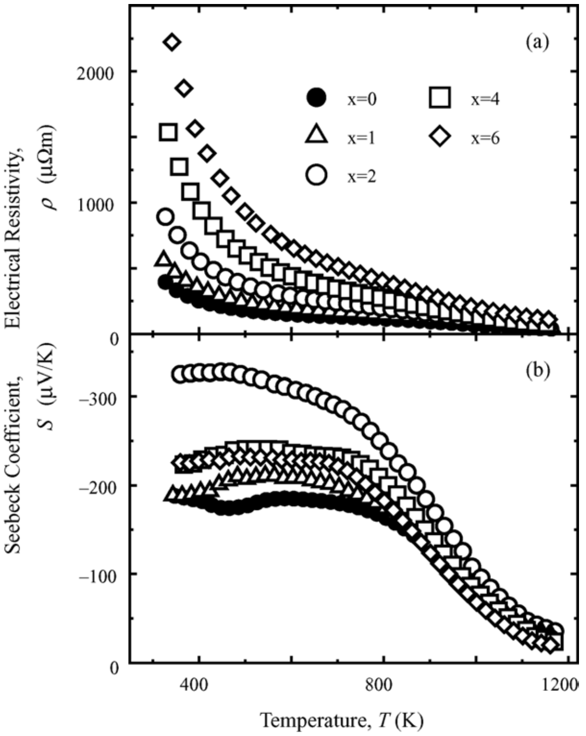

Fig. 3. Temperature dependence of (a) the electrical resistivity, ρ, and (b) the Seebeck coefficient, S, of the hot-pressed $Fe_{0.98}Co_{0.02}Si_2$ with x mass% Y_2O_3.

oxide with low thermal conductivity is effective for reducing thermal conductivity of the β-$FeSi_2$.

Fig. 3 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. As shown in Fig. 3a, the electrical resistivity increased with increasing amount of Y_2O_3, especially in the lower temperature range. This is considered to be due to the enhancement of carrier scattering caused by insulating rare-earth oxide dispersion. On the other hand, the Seebeck coefficient was improved by Y_2O_3 addition below about 800 K in the extrinsic conduction region of β-$FeSi_2$. The maximum Seebeck coefficient was obtained for the sample with 2 mass% Y_2O_3, and then, the samples with 4 and 6 mass% Y_2O_3 showed the $|S|$ values smaller than those of the sample with 2 mass% Y_2O_3, which were still larger than those of the sample without addition. Generally, increase in electrical resistivity and Seebeck coefficient is considered to be caused by a decrease in carrier concentration. However, in this study, such a decrease in carrier concentration is difficult to explain only by the insulating rare-earth oxide dispersion. Although the increase in the electrical resistivity is considered to be mainly caused by enhancing carrier scattering due to dispersion of fine Y_2O_3 particles, the behavior of these electrical transport properties induced by Y_2O_3 addition is similar to a behavior when the carrier concentration decreases. On the other hand, it was reported that when ZrO_2 with a relatively high chemical stability was added to the β-$FeSi_2$, the ZrO_2 phase decomposed and Zr atom was doped into the β phase, resulting in the deterioration of the thermoelectric performance [8]. On the basis of this fact, it is expected that even when Y_2O_3 is added, the Y_2O_3 phase decomposes slightly and a small amount of Y atoms was dissolved in the β phase. This Y solution may be associated with the enhancement of the Seebeck coefficient. Based on this consideration, 1–6 mass% of Y powder was added to the β-$FeSi_2$ and the effects of Y addition on the electrical resistivity and the Seebeck coefficient were investigated.

The hot-pressed samples with Y addition were synthesized through the same preparation process as the samples with Y_2O_3 addition, except for addition of Y powder instead of Y_2O_3 powder. The XRD patterns of the samples with 1–4 mass% Y were almost the same as that of the sample without addition. When 6 mass% Y was added, a small peak from YFe_2 phase was detected in its XRD pattern. EDX analysis revealed that Y content in the β phase varied and was about 0.76–1.85 at.%, supporting the solution of Y in the β phase. In the preparation process, β-$FeSi_2$ was formed from the mixture of the α-Fe_2Si_5 phase and the ε-FeSi phase. The EDX analysis also showed that the ε phase could contain Y only up to 0.4 at.%, and the rest of Y is considered to be dissolved in the α phase. This fact supported that the β phases formed from the ε phase and the α phase contained a small and large amount of Y, respectively, resulting in that variety of the Y amounts. Based on these results, it was found that the Y-doped β-$FeSi_2$ could be obtained by the Y powder addition.

The electrical transport properties were evaluated for the hot-pressed samples with 1–4 mass% Y, which were mostly composed of the β phase without YFe_2 precipitation. Fig. 4 shows the temperature dependence of (a) the electrical resistivity, ρ, and (b) the Seebeck coefficient, S, of these samples. As shown in Fig. 4a, the electrical resistivity of the samples with Y addition was almost the same as that of the sample without addition, and a significant increase in the ρ values shown in the case of the Y_2O_3 addition did not occur. On the other hand, the Seebeck coefficient was improved by addition of a small amount of Y; 1 and 2 mass% Y, especially below 800 K, which is well consistent with the behavior of the S values when Y_2O_3 was added, as shown in Fig. 3b. The increase in $|S|$ values due to Y addition indicates that Y solution in the β phase is effective for enhancing the Seebeck coefficient. Based on this fact, EDX analysis on the β phase matrix of the samples with 2 and 4 mass% Y_2O_3 was also performed on areas where Y_2O_3 particles were not detected in the TEM observation. The β phases of the samples with 2 and 4 mass% Y_2O_3 were found to contain about 0.68 and 1.14 at.% Y, respectively, supporting that even when Y_2O_3 was added, partial decomposition of added Y_2O_3 occurred and a certain amount of Y was dissolved in the β phase. Based on the results of the EDX analysis, it is supported that the improvement of the Seebeck coefficient shown in the case of the Y_2O_3 addition was also caused by the Y solution in the β phase matrix. It is considered that the Y atoms dissolved in

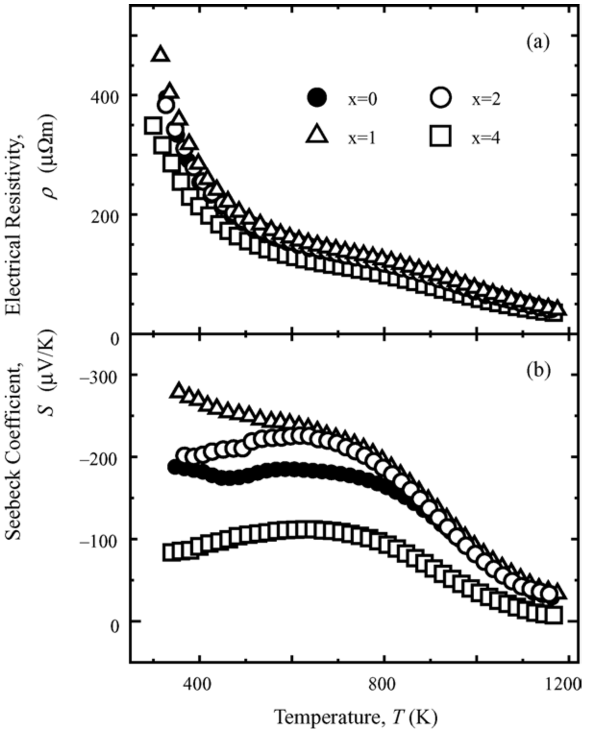

Fig. 4. Temperature dependence of (a) the electrical resistivity, ρ, and (b) the Seebeck coefficient, S, of the hot-pressed $Fe_{0.98}Co_{0.02}Si_2$ with x mass% Y.

the β phase are probably easier to be substituted for Fe atoms than Si atoms because of its atomic radius, and act as a p-type dopant. The solution of Y as a p-type dopant in the n-type $Fe_{0.98}Co_{0.02}Si_2$ causes a reduction in the carrier concentration in the system due to carrier compensation. This is the reason why the Seebeck coefficient was improved by Y_2O_3 addition, especially in the low temperature range, the extrinsic conductive region of the β-$FeSi_2$. Actually, the Hall coefficient measurement performed in the sample with 2 mass% Y_2O_3 showed that the carrier concentration decreased from 2.0×10^{21} to 2.4×10^{20} cm^{-3} of the sample without addition, which also supports the solution of Y as a p-type dopant. The Seebeck coefficient decreased with increasing amount of additives beyond 2 mass% in both samples with Y_2O_3 and Y addition, indicating that addition of a small amount of Y_2O_3 or Y, which is less than or around 1 mass%, is effective for enhancing the Seebeck coefficient.

The figure of merit, Z, of the samples with Y_2O_3 addition was calculated from the Seebeck coefficient, S, the electrical resistivity, ρ, and the thermal conductivity, κ, in the equation $Z = S^2/\rho/\kappa$. Fig. 5 shows the temperature dependence of the figure of merit, Z, of the hot-pressed samples with x mass% Y_2O_3. The figure of merit was significantly improved by addition of 2 mass% Y_2O_3, because the thermal conductivity and the Seebeck coefficient were reduced and enhanced, respectively, in spite of the increase in the electrical resistivity. On the other hand, though the addition of 4 or 6 mass% Y_2O_3 was effective for reducing the thermal conductivity, these samples showed the Z values smaller than those of the sample without addition, because of the significant increase in the electrical resistivity. Thus, it was found that addition of a small amount of Y_2O_3 was effective in improving the thermoelectric performance of the β-$FeSi_2$.

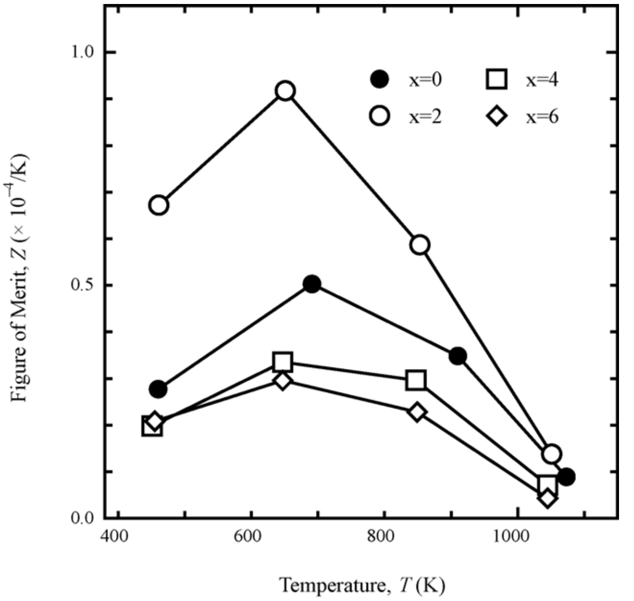

Fig. 5. Temperature dependence of the figure of merit, Z, of the hot-pressed $Fe_{0.98}Co_{0.02}Si_2$ with x mass% Y_2O_3.

4. Conclusion

The effects of Y_2O_3 and Y addition on the thermoelectric properties of $Fe_{0.98}Co_{0.02}Si_2$ were investigated. When Y_2O_3 powder was added, small Y_2O_3 particles around 10 nm in size were dispersed in the β phase matrix by mechanical alloying for 72 ks. The thermal conductivity was significantly reduced with increasing amount of Y_2O_3 over the entire temperature range because of enhancing phonon scattering due to dispersion of fine Y_2O_3 particles. The Y_2O_3 dispersion also enhanced carrier scattering, resulting in the increase in the electrical resistivity with increasing amount of Y_2O_3. The Seebeck coefficient was improved by Y_2O_3 addition, especially below 800 K, in the extrinsic region of the β-$FeSi_2$. In the case of the Y addition to the β-$FeSi_2$, the $|S|$ values of the samples with 1 and 2 mass% Y were also larger than those of the sample without addition below 800 K, indicating that Y doping in $Fe_{0.98}Co_{0.02}Si_2$ was effective for enhancing the Seebeck coefficient. The TEM observation and EDX analysis revealed that when Y_2O_3 was added, partial decomposition of Y_2O_3 occurred and a small amount of Y was doped in the β phase matrix. Therefore, the enhancement of the Seebeck coefficient of the sample with Y_2O_3 addition was considered to be due to reduction in its carrier concentration because of the Y solution as a p-type dopant in the n-type $Fe_{0.98}Co_{0.02}Si_2$.

From these results, the figure of merit was found to be significantly improved by 2 mass% Y_2O_3 addition.

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