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Thermoelectric properties of β-$FeSi_2$ with B_4C and BN dispersion by mechanical alloying

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The B_4C- and BN-dispersed β-$FeSi_2$ thermoelectric materials were synthesized by mechanical alloying and subsequent hot pressing. The effects of the B_4C and BN dispersion on the thermoelectric properties, such as Seebeck coefficient, electrical resistivity and thermal conductivity etc., of the β-$FeSi_2$ were investigated. For the sample with B_4C and BN addition, a larger amount of the residual ε phase was detected in the X-ray diffraction patterns than the sample without addition. In the case of the BN addition, the Seebeck coefficient was enhanced by BN addition above 700 K, and the electrical resistivity also increased with increasing amount of BN. This is considered to result from doping of a small amount of B into the β phase due to partial decomposition of the BN phase. The fine dispersion of BN particles in the β phase matrix was quite effective for reducing the thermal conductivity as compared to the B_4C addition over the entire temperature range. The figure of merit, Z, of the β-$FeSi_2$ was significantly enhanced by BN addition.

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 required maintenance.

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 low cost of raw materials, its good resistance to oxidation and its non-toxicity. However, the thermoelectric performance of β-$FeSi_2$ is still low for practical use compared to other thermoelectric materials, such as PbTe or $CoSb_3$ etc., so its thermoelectric properties need to be improved [1, 2]. Generally, the performance of thermoelectric materials is evaluated by figure of merit, Z, which is calculated from Seebeck coefficient, S, electrical resistivity, ρ, and thermal conductivity, κ, using the equation $Z = S^2/\rho/\kappa$. In order to increase the figure of merit of β-$FeSi_2$, mechanical alloying, mechanical grinding and doping of various elements, such as Co [3–9], Cr [8], Ni [8, 9], Mn [8, 10–12], Al [3, 4, 6, 12], Cu [13], B [14], Nb or Zr [15], etc., have been applied to sample preparation. On the other hand, as well as optimizing the Seebeck coefficient and the electrical resistivity due to doping of various elements, reduction on the thermal conductivity is also effective for increasing the figure of merit. The thermal conductivity of the β-$FeSi_2$ is expected to be reduced by dispersion of a second phase in the β phase matrix because of enhancing phonon scattering. On the basis of this consideration, in this study, B_4C and BN powders were dispersed in the hot-pressed β-$FeSi_2$ matrix as a second phase by mechanical alloying, and the effects of the B_4C and BN dispersion on the reduction in the thermal conductivity were investigated. Additionally, the Seebeck coefficient and the electrical resistivity were also measured and the figure of merit of the B_4C- and BN-dispersed β-$FeSi_2$ was evaluated.

2. Experimental procedure

The hot-pressed β-$FeSi_2$ samples with B_4C and BN dispersion were prepared by the following process. Mixtures of Fe and Si 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. B_4C and BN powders (1, 2, 4 and 6 mass%) were added to the pulverized powder. These mixed powders were mechanically alloyed for 72 ks in an argon atmosphere. The MA powders with or without B_4C and BN 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 X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). The Seebeck coefficient,

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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 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

Fig. 1 shows X-ray diffraction patterns of the hot-pressed samples with and without 4 mass% B_4C and BN. All the samples were mostly composed of the β phase with a small amount of the residual ε phase. However, the amount of the ε phase in the sample with 4 mass% B_4C was larger than that of the sample without addition. The sample with 4 mass% BN also showed a slightly larger peak from the ε phase compared to the sample without addition. The powder after mechanical alloying, which was composed of the α-Fe_2Si_5 + ε-FeSi phase, is transformed into the β phase through the hot pressing at 1173 K for 3.6 ks under 25 MPa [15]. The dispersion of the second phase, such as B_4C or BN particles, is considered to suppress the β phase formation because of preventing Fe or Si atoms from diffusing between the α phase and the ε phase. The peaks corresponding to B_4C and BN were hardly detected even in the patterns of the samples with 6 mass% B_4C and BN, respectively.

Fig. 2 shows SEM photographs of the hot-pressed samples (a) without addition, (b) with 4 mass% B_4C and (c) with 4 mass% BN. For the sample without addition (a), several black Si particles with 2–5 μm in size were dispersed in the β phase matrix. There were also small pores, which size were around or smaller than 1 μm. The relative density of this sample was 99.8%, indicating that the quite densely sintered body could be obtained through the hot pressing. In the case of the sample with 4 mass% B_4C (b), B_4C was also black particle, which was difficult to be distinguished from the Si particles in the SEM photograph. However, the number of these black phases increased compared to those of the sample (a). Based on this observation and EDX analysis, it was found that B_4C particles with 2–5 μm in size were dispersed in the β phase matrix by mechanical alloying. Because B_4C compound has a significantly high strength and abrasion resistance, fine dispersion of submicron B_4C particles was considered to be difficult on the mechanical alloying condition in this study. As shown in this SEM photograph, there were also many small pores compared to the sample (a), indicating that the B_4C addition suppressed sample densification. The relative density of the sample with B_4C

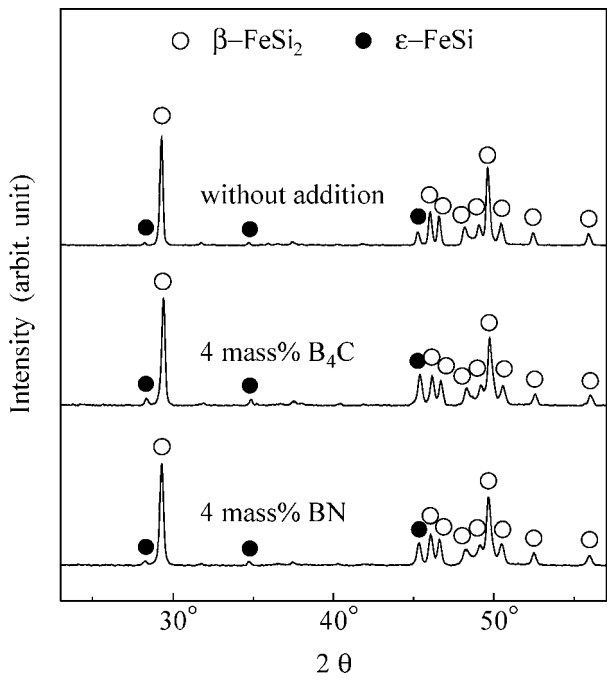

Figure 1 X-ray diffraction patterns of $FeSi_2$ alloys with and without 4 mass% B_4C and BN, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

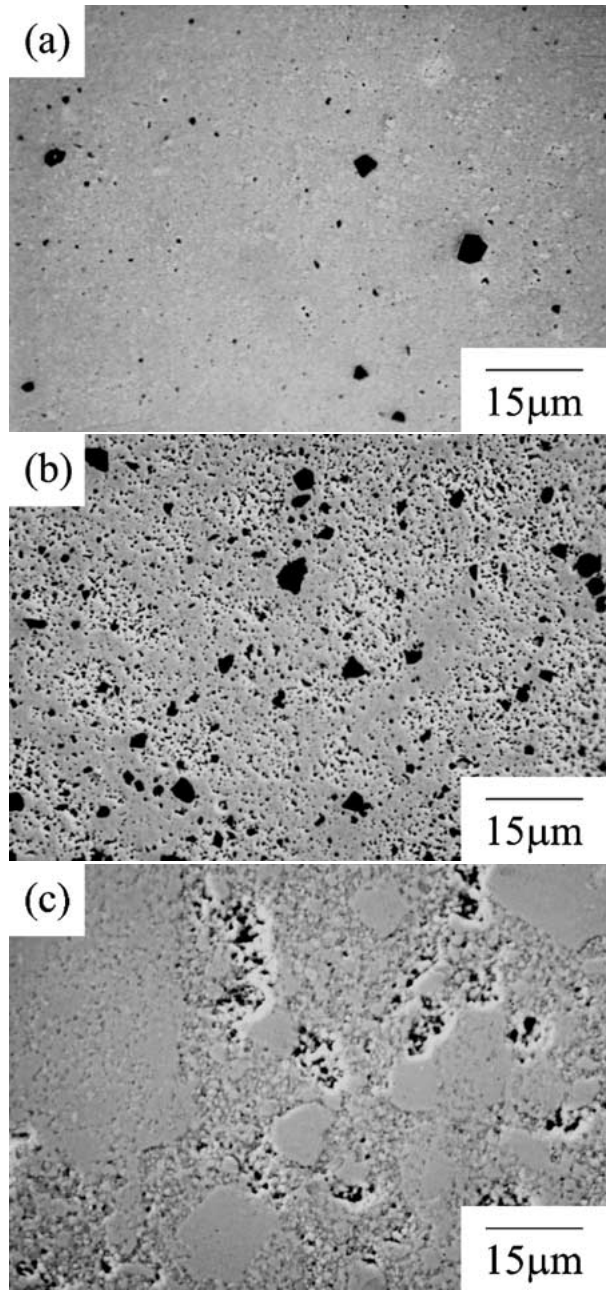

Figure 2 SEM photographs of $FeSi_2$ alloys (a) without addition, (b) with 4 mass% B_4C and (c) with 4 mass% BN, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

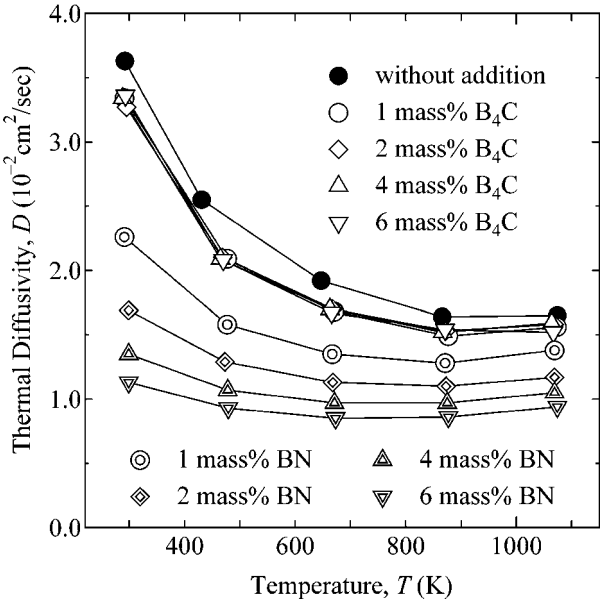

Figure 3 Temperature dependence of the thermal diffusivity, D, of $FeSi_2$ alloys with and without B_4C and BN, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

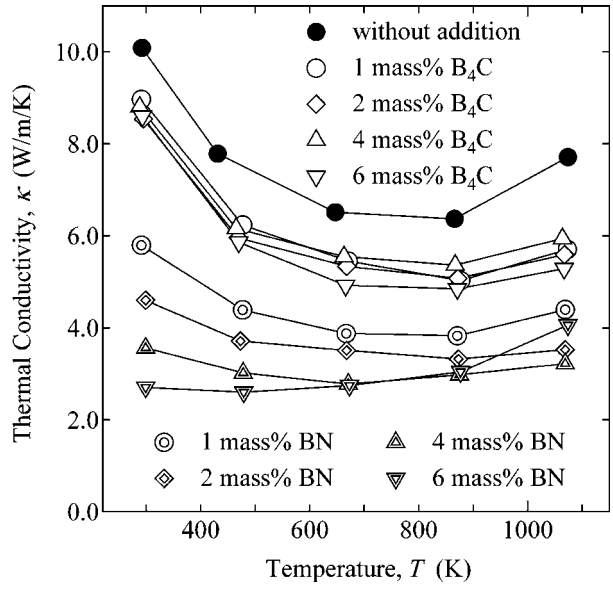

Figure 4 Temperature dependence of the thermal conductivity, κ, of $FeSi_2$ alloys with and without B_4C and BN, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

addition decreased with increasing amount of B_4C, and that of this sample shown in Fig. 2b was 97.1%. For the sample with 4 mass% BN (c), not only small pores, several coarse pores were also observed, and the sample densification was found to be smaller than that of the sample (b). The relative density of the BN-added samples decreased with increasing amount of BN, and that of this sample (c) was 93.9 %. The dispersed BN particles were hardly detected in the SEM photographs of the BN-added samples. From this fact, it is considered that fine dispersion of submicron BN particles in the β phase matrix was caused by mechanical alloying. This fine dispersion of the BN particles may prevent Fe or Si atoms from diffusing between $FeSi_2$ particles, resulting in the smaller sample densification.

Thermal conductivity, κ, is calculated using the equation $\kappa = D \times C_p \times d$. In order to obtain high thermoelectric performance, thermal diffusivity, D, is needed to decrease. Fig. 3 shows the temperature dependence of the thermal diffusivity, D, of the hot-pressed samples with and without B_4C and BN. Except for high temperature range, the thermal diffusivity of all the samples was reduced with increasing temperature. This is attributable to enhancing phonon scattering due to strengthening lattice vibration. For the samples with B_4C addition, the thermal diffusivity was lower than that of the sample without addition over the entire temperature range. However, as shown in Fig. 3, the effect for reducing the thermal diffusivity was small as compared to that of the samples with BN addition. Besides that, the values of thermal diffusivity for the samples with B_4C addition scarcely depended on the amount of B_4C in spite of the fact that the number of the dispersed particles definitely increased with increasing amount of B_4C. These findings are considered to result from a higher thermal diffusivity of B_4C than that of the β-$FeSi_2$. On the other hand, BN addition was significantly effective for reducing the thermal diffusivity. Even in the case of the sample with 1 mass% BN, values of the thermal diffusivity were lower than those of the sample with 6 mass% B_4C over the entire temperature range. The thermal diffusivity of the samples with BN addition monotonously decreased with increasing amount of BN, and especially for the sample with 6 mass% BN, the low values around 1.0×10^{-2} sm^2/sec could be obtained.

The thermal conductivity, κ, of all the samples was calculated from D in Fig. 3, C_p and d as described above. Fig. 4 showed the temperature dependence of the thermal conductivity of the hot-pressed samples with and without B_4C and BN. As described above, the samples with B_4C and BN addition had the densities lower than that of the sample without addition. On the other hand, C_p did not have any significant dependence on the amount of B_4C and BN. Therefore, the effect of B_4C and BN addition for reducing κ became greater than that for decreasing D. Especially for the samples with 4 and 6 mass% BN, values of the thermal conductivity were about 1/2–1/3 of those of the sample without addition over the entire temperature range. Thus, it was found that BN addition was significantly effective for reducing thermal conductivity.

When a single sign of the charge carrier is predominant, the thermal conductivity, κ, of a material can be written as $\kappa = \kappa_{car} + \kappa_{ph}$, where κ_{car} is the carrier contribution and κ_{ph} is the lattice contribution. The carrier contribution to the thermal conductivity, κ_{car}, is calculated using the Wiedemann-Franz relationship $\kappa_{car} = L\sigma T$, where L is the Lolentz number, σ is the electrical conductivity, and T is the absolute temperature. The Lorentz number was calculated using the reduced Fermi energy, which was estimated from the Seebeck coefficient and the Fermi-Dirac integral. Figs 5 and 6 show the temperature dependence of κ_{ph} and κ_{car} of the hot-pressed samples with and without B_4C and BN, respectively. The values of κ_{car} for the sample without addition slightly increased with increasing temperature, because excitation due to temperature rise increased carrier concentration. However, their values are quite small as compared to those of κ_{ph}. This is a

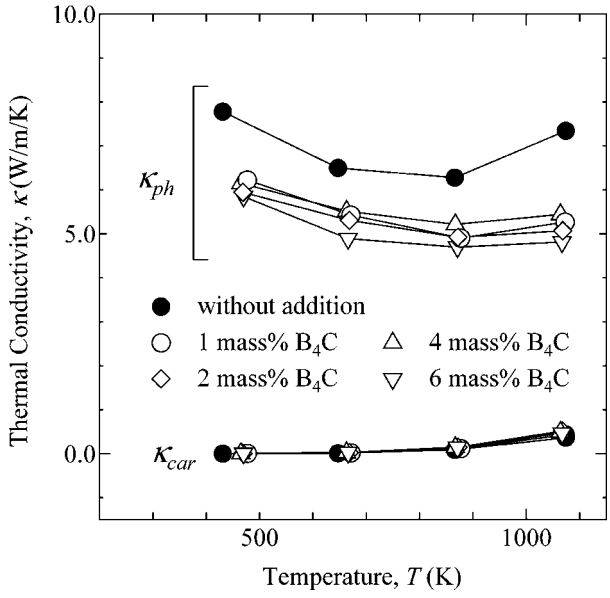

Figure 5 Temperature dependence of κ_{car} and κ_{ph} of $FeSi_2$ alloys with and without B_4C, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

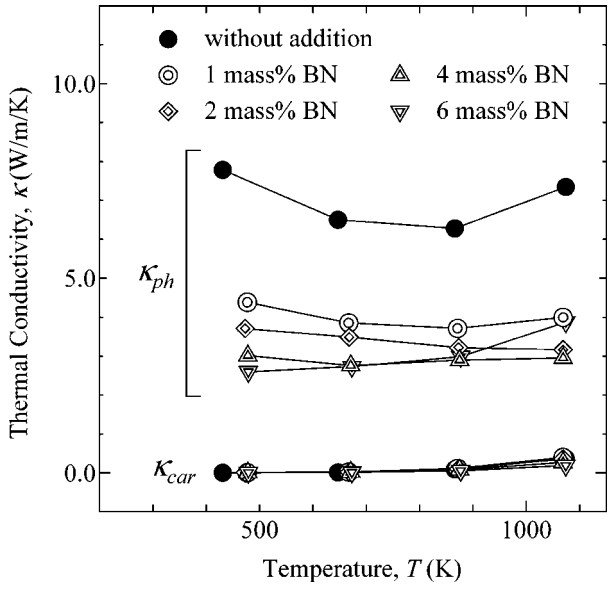

Figure 6 Temperature dependence of κ_{car} and κ_{ph} of $FeSi_2$ alloys with and without BN, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

phenomenon similar to that in the case of Mn-, Co- and P-doped β-$FeSi_2$ [16, 17]. Thus, the lattice contribution, κ_{ph}, is a major component of the thermal conductivity for the β-$FeSi_2$. The values of κ_{car} scarcely varied with the amount of B_4C and BN. Therefore, the reduction in the thermal conductivity due to B_4C and BN addition was mostly ascribed to the decrease in κ_{ph}. The values of κ_{ph} for the samples with BN addition were significantly lower than those of the samples with B_4C addition over the entire temperature range. From these results, it is evident that in the case of the β-$FeSi_2$, fine dispersion of a second phase in the β phase matrix is significantly effective for reducing the lattice contribution, κ_{ph}.

Fig. 7 shows the temperature dependence of the Seebeck coefficient, S, and the electrical resistivity, ρ, of the hot-pressed samples with and without B_4C addition. The Seebeck coefficient of all the samples was low above 800 K, in the intrinsic conductive range, and the values scarcely varied with the amount of B_4C in this temperature range. On the other hand, in the lower temperature range, the Seebeck coefficient decreased with increasing tempetarure. As described above, in the samples with B_4C addition, a larger amount of the metallic ε phase remained present after hot pressing as compared to the sample without addition, and the amount of the residual ε phase slightly increased with increasing amount of B_4C. Therefore, the decrease in the Seebeck coefficient is considered to result from the increase in the amount of the ε phase. The electrical resistivity of all the samples monotonously decreased with increasing temperature, indicating a semiconducting behavior. In the intrinsic conductive range above 800 K, the electrical resistivity of all the samples was quite low and their values scarcely varied with the amount of B_4C, a phenomenon similar to that of the Seebeck coefficient. On the other hand, below 800 K, in the impurity conductive range, the electrical resistivity was reduced by B_4C addition. This is also due to the presence of the metallic ε phase, as described above.

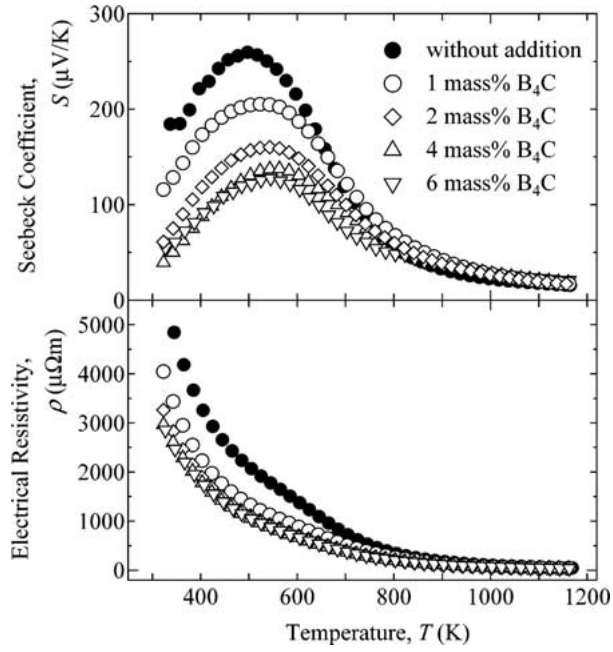

Figure 7 Temperature dependence of the Seebeck coefficient, S, and the electrical resistivity, ρ, of $FeSi_2$ alloys with and without B_4C, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

Fig. 8 shows the temperature dependence of the Seebeck coefficient, S, and the electrical resistivity, ρ, of the hot-pressed samples with and without BN addition. Below 700 K, the Seebeck coefficient decreased with increasing amount of BN up to 2 mass%, which is considered to be due to the increase in the amount of the ε phase, as well as in the case of the sample with B_4C addition. On the other hand, further increase in the amount of BN hardly reduced the Seebeck coefficient. Besides that, above 700 K, the Seebeck coefficient of the samples with BN addition was slightly enhanced compared to the sample without addition. These behaviors were not observed in the case of the samples with B_4C addition, as seen in Fig. 7. It has been reported that

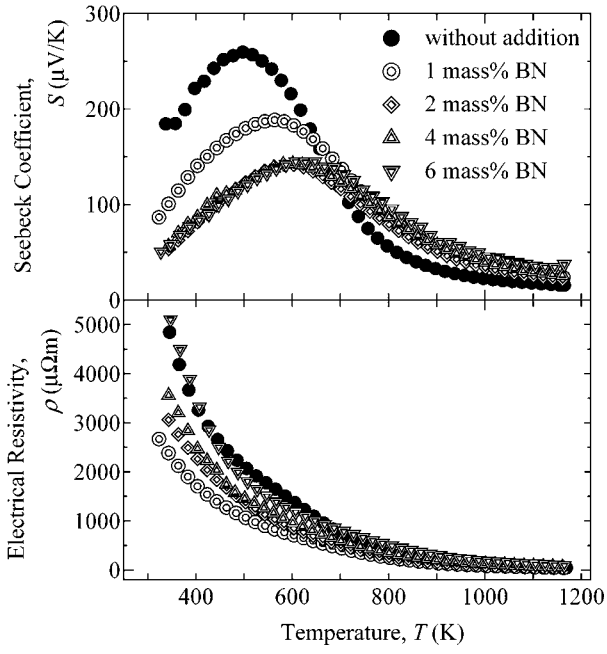

Figure 8 Temperature dependence of the Seebeck coefficient, S, and the electrical resistivity, ρ, of $FeSi_2$ alloys with and without BN, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

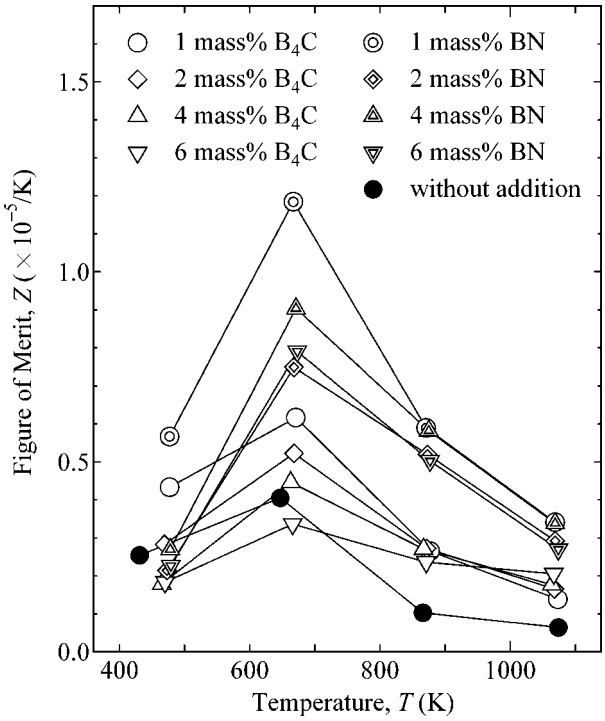

Figure 9 Temperature dependence of the figure of merit, Z, of $FeSi_2$ alloys with and without B_4C and BN, hot-pressed at 1173 K for 3.6 ks under 25 MPa.

in the case of the B-doped β-$FeSi_2$, B was substituted for Fe as an n-type dopant [14]. It is considered that doping of a small amount of B atoms into the β phase causes a decrease in carrier concentration due to carrier compensation because the non-doped β-$FeSi_2$ is a p-type thermoelectric material. The decrease in the carrier concentration is considered to enhance the Seebeck coefficient. Based on this consideration, the specific behavior in the Seebeck coefficient of the sample with BN addition, in spite of the slight increase in the amount of the ε phase with increasing amount of BN, is deduced to be caused by B doping into the β phase matrix due to partial decomposition of the BN phase. On the other hand, although the electrical resistivity was reduced by the addition of 1 mass% BN, the larger amount of BN resulted in an increase in the values of ρ. This behavior of the electrical resistivity is consistent with the decrease in carrier concentration due to doping of a small amount of B, as described above. In the case of the B_4C addition, taking a quite high stability of B_4C and the behaviors in the Seebeck coefficient and the electrical resistivity shown in Fig. 7 into consideration, it is suggested that B doping into the β phase did not occur.

The figure of merit, Z, is calculated using the equation $Z = S^2/\rho/\kappa$. Fig. 9 shows the temperature dependence of the figure of merit, Z, of the hot-pressed samples with and without B_4C and BN addition. For the samples with B_4C addition, below 700 K, the figure of merit was enhanced by 1 mass% addition, and then, decreased with increasing amount of B_4C in spite of the reduction in the electrical resistivity and the thermal conductivity. This is due to the significant decrease in the Seebeck coefficient. In the higher temperature range, above 800 K, the reduction in the thermal conductivity due to the B_4C dispersion resulted in the increase in the values of Z, though the Seebeck coefficient and the electrical resistivity were scarcely affected by B_4C addition. In the case of the samples with BN addition, the figure of merit was markedly enhanced by BN addition above 600 K. This is attributable to the significant reduction in the thermal conductivity due to BN addition. Especially above 800 K, the Seebeck coefficient was also enhanced by BN addition, resulting in the figure of merit 3–6 times as large as that of the sample without addition. Thus, the BN dispersion in the β-$FeSi_2$ by mechanical alloying was found to be significantly effective for enhancing the thermoelectric performance. The maximum figure of merit, 1.18×10^{-5} K^{-1}, was obtained for the sample with 1 mass% BN addition at 667 K.

4. Conclusion

The effects of B_4C and BN addition on the thermoelectric properties of the β-$FeSi_2$ were investigated. The samples with B_4C and BN addition showed the larger peaks from the metallic ε phase than the sample without addition in the X-ray diffraction patterns. The presence of larger amount of the ε phase decreased both the Seebeck coefficient and the electrical resistivity. However, in the case of the BN addition, the Seebeck coefficient was enhanced by BN addition above 700 K, and the electrical resistivity also increased with increasing amount of BN. This is considered to result from doping of a small amount of B due to partial decomposition of the BN phase. The dispersion of B_4C and BN particles in the β phase matrix was effective for decreasing the lattice contribution to the thermal conductivity, κ_{ph}, over the entire temperature range. Especially for the samples with BN addition, the thermal conductivity was significantly reduced because of the dispersion of submicron BN particles and the low density. From these results, the figure of merit was enhanced by B_4C and BN addition, and the maximum figure of merit, 1.18×10^{-5} K^{-1}, was obtained for the sample with 1 mass%

BN at 667 K. Thus, the BN dispersion in the β-$FeSi_2$ by mechanical alloying was found to be significantly effective for enhancing the thermoelectric properties.

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