



Thermoelectric properties of higher boride-intermetallics composite materials made from MgAlB_{14} by spark plasma sintering

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ABSTRACT

We investigated thermoelectric properties of higher boride-intermetallics composite materials. They were prepared by sintering MgAlB_{14} powder with up to 20 vol% of metals, Co and Ni, using spark plasma sintering (SPS). The composite materials exhibited non-metallic but highly electrically conductive behavior from room temperature to over 1000 K. Furthermore, most the samples had negative Seebeck coefficient that was rare for higher-borides and large power factor. The results indicate this composition is a useful method to tune and improve thermoelectric properties of higher boride materials.

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1. Introduction

Depleting fossil fuels as an energy source has been a serious energy issues for years, which strongly stimulates development of clean energy sources. Thermoelectric generation system, which converts thermal energy to electrical energy, can be a solution for these problems [1–3]. The performance of a thermoelectric material is evaluated by a dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ , T and κ are electrical conductivity, temperature and thermal conductivity, respectively. The numerator in Z , $S^2\sigma$, is called power factor that is used for the evaluation of electrical output power. A high efficiency thermoelectric material requires large S , high σ and low κ . A practical thermoelectric module consists of thermoelectric materials of n-type with negative S and of p-type with positive one that are connected electrically in series and thermally in parallel [4].

Higher borides are promising thermoelectric materials in high temperature due to their high-temperature stability, intrinsic low thermal conductivity [5–10] and large Seebeck coefficient. Because few higher-boride materials of the n-type have been reported so far

other than p-type ones [8,11,12], there has been considerable interest in higher boride thermoelectric materials having a negative S .

MgAlB_{14} , which is one of the higher borides, was reported to have an extremely-large negative S of $-6500 \mu\text{V/K}$ [13], though subsequent works reported positive values [14,15]. Thus, MgAlB_{14} is gathering attention as both n- and p-type materials. One of important topics on the material is improvement of its low σ .

T. Goto et al. reported that $\text{B}_4\text{C}-\text{TiB}_2$ composite had considerably large σ in comparison with single-phase B_4C without decreasing S . This revealed highly conductive TiB_2 phase locally connected in the material to increase the bulk conductivity [16]. This report indicated that making composite with metallic material possibly improve σ of non-metallic base material without reducing S . This methodology has a significant advantage over usually used lower-level doping because the usual compound has a trade-off relation between S and σ against performance tuning by the doping.

We, in this report, explored MgAlB_{14} -based thermoelectric materials with large S and high σ by making multi-phase MgAlB_{14} composites with large amount of metals, Co and Ni.

2. Experiment

The starting powders were amorphous-B (95.6% purity, H.C. Starck Ltd.), Mg (99.5% purity, Kojundo Chemical Lab Co. Ltd.), Al

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(99.9% purity, Kojundo Chemical Lab Co. Ltd.), Co (99.7% purity, OMG Kokkola Chemicals Oy.) and Ni (99.8%, Vale Inco Ltd.). We first mixed Mg with B and Al with B with a metal/boron atomic ratio of 1/7 by V-shape mixer to heat-treat at 873 K for 1 h in an Ar atmosphere. The heat-treated powders were mixed in equal amount then heat-treated at 1473 K for 1 h in an Ar atmosphere to get pre-alloyed MgAlB_{14} powder.

The pre-alloyed powder was sintered by spark plasma sintering (SPS) method under a pressure of 30 MPa with and without metal mixture. Up to 20 vol% of a metal powder, Co and Ni, was mixed with the pre-alloyed MgAlB_{14} powder by V-shape mixer then sintered at 1573 K and 1523 K, respectively. The pre-alloyed powder was also sintered without metal at 1773 K to obtain sintered pre-alloy for comparison with the metal composites.

Microstructures and constituent element of sintered bodies were examined by electron probe X-ray microanalysis (EPMA: JEOL Ltd., JXA-8200) with a wavelength-dispersive x-ray spectroscopy (WDS). The pre-alloyed powder and the sintered bodies were characterized by X-ray diffraction (XRD: Bruker AXS Ltd., D8 Advance) with $\text{CuK}\alpha$ radiation. Seebeck coefficient and electrical conductivity up to 1073 K were measured by ZEM-1 (ULVAC-RIKO, Inc.).

3. Results and discussion

3.1. Characterization

In Fig. 1, we show the backscattered electron images of the sintered bodies. The sintered pre-alloy (a) contained small pores and grain smaller than ca. 5 μm in matrix phase. EPMA revealed that the matrix mainly consisted of B, and the small grains contained Mg, Al, and O. Consequently, the matrix and the small grain were a higher boride phase and MgAl_2O_4 , respectively. The metal-added samples (b–e) contained two phases: a bright phase and a dark one. EPMA showed that the bright phase mainly consisted of metal and the dark one did B. That is, the dark phase was a boron-rich phase.

XRD pattern of pre-alloyed powder and sintered bodies are shown in Fig. 2. The pre-alloyed powder and sintered pre-alloy exhibited quite similar patterns that were identified as MgAlB_{14} , $\alpha\text{-AlB}_{12}$, and MgAl_2O_4 . This oxide has been reported as a by-product of MgAlB_{14} [17]. All metal-added samples mainly consisted of intermetallics, metal boride and MgAl_2O_4 .

The XRD patterns for Co-added samples included high background noise caused by fluorescent X-ray from Co excited by the $\text{CuK}\alpha$ radiation. Thus diffraction peaks of MgAlB_{14} looked so weakened. Though we did not put corresponding markers on the patterns for the samples, the boron-rich phase in the Co-added samples was identified as MgAlB_{14} .

As for the Ni-added samples, EPMA revealed that the dark phase in Fig. 1 contained Mg, Al, Ni and B. This result indicated that Mg and Ni were dispersed in AlB_{31} that seemed to be derived from MgAlB_{14} about Ni 10% added sample, and Mg in $\text{Ni}_{20}\text{AlB}_{14}$ about Ni 20% added sample.

3.2. Thermoelectric properties

The temperature dependence of S for the samples is shown in Fig. 3. The sintered pre-alloy showed large positive S . This value is comparable to previous research about single-phase MgAlB_{14} [15]. The metal-added samples exhibited smaller absolute value of S than sintered pre-alloy.

While Ni 20% added sample exhibited positive S as sintered pre-alloy, the other metal-added samples did negative one. Both Co-added samples showed coequal value of S in the range up to 723 K. As Co 10% added sample changed its S between n- and p-type at 1023 K, other samples possibly change their sign of S outside our measurement temperature range.

The temperature dependence of σ for the samples is shown in Fig. 4. The sintered pre-alloy exhibited a comparable σ value to the previous report [15] as in the case of S . Thus the by-product in the sintered pre-alloy did not have strong influence on thermoelectric properties of the material. The metal-added samples exhibited σ value obviously superior to that of the sintered pre-alloy.

The Co-added samples slightly increased σ with increasing temperature, that indicated the materials had a non-metallic conduction mechanism in spite of intermetallic composition. This behavior is typical for semiconductors due to thermal excitation of carriers and so are the higher borides including MgAlB_{14} . Though Ni added samples slightly decreased σ with increasing temperature, the thermal constant was much smaller than typical metals. That is, the Ni added materials could have intermediate conduction mechanism between metallic and of semiconductors.

The temperature dependence of power factor calculated from S and σ for the sintered samples is shown in Fig. 5. The Co 20% added

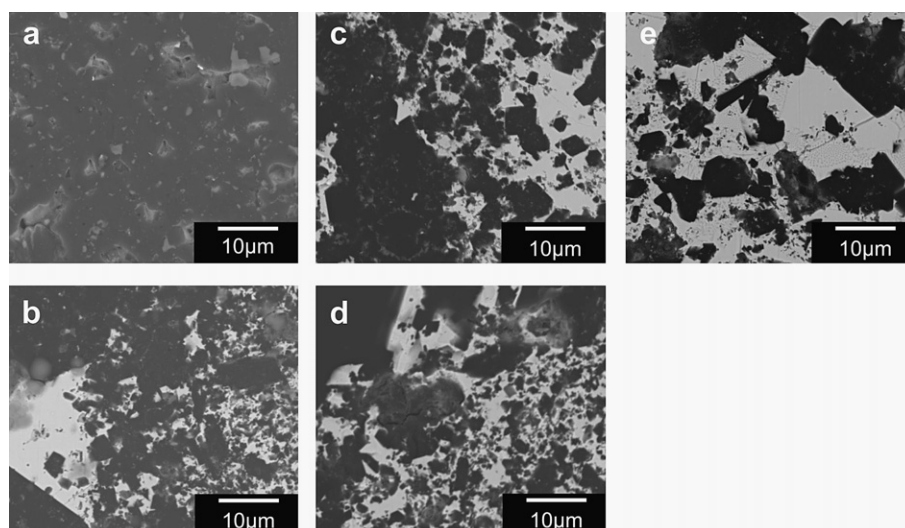


Fig. 1. Backscattered electron images for (a) sintered pre-alloy, (b) Co 10% added sample, (c) Co 20% added one, (d) Ni 10% added one, (e) Ni 20% added one.

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