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Thermal expansion and melting temperature of the half-Heusler compounds: MNiSn (M = Ti, Zr, Hf)

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ABSTRACT

Half-Heusler compounds: MNiSn (M = Ti, Zr, Hf) are considered as a candidate of environmentally friendly and low-cost thermoelectric (TE) materials. Although the thermomechanical properties are quite important when utilizing the half-Heusler compounds in TE devices, such properties have been scarcely reported. In the present study, we tried to collect the data of the thermal expansion coefficient and the melting temperature (T_m) of MNiSn. The thermal expansion coefficient was evaluated by means of two methods: the dilatometer measurement and the high temperature X-ray diffraction analysis. The T_m was evaluated from the differential thermal analysis. The relationship between the thermal expansion coefficient and the T_m of the half-Heusler compounds was studied.

1. Introduction

Thermoelectric (TE) conversion is a technology to transform waste heat to usable electric energy [1,2]. This technology, which can apply in any type of heat sources, is expected to play a major role in reusing the waste heat that accounts for approximately 66% of the entire energy. The efficiency of a TE device depends on material properties, which in turn depend on the figure of merit ZT, where $Z = S^2/\rho\kappa$, S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, and T is the absolute temperature. Because all these parameters are linked and mutually influence in inverse way, it is very difficult to enhance the value of ZT. The ZT value of the materials used in current TE devices is approximately 1.

Degenerate semiconductors composed of heavy elements such as Bi_2Te_3 and PbTe have been studied for many years as highly efficient TE materials. However, these compounds include toxic and scarce elements such as tellurium and lead, so alternative high ZT materials that contain no such elements should be developed. MNiSn and MCoSb type half-Heusler compounds (M = Ti, Zr, Hf) are one of the candidates for non-toxic and inexpensive TE materials [3–10]. It has been reported that the half-Heusler compounds exhibit relatively high ZT values in both n- and p-type materials. For example, the ZT values of the n-type $Zr_{0.98}Nb_{0.02}NiSn$ and p-type $ZrCoSb_{0.9}Sn_{0.1}$ have been reported to be 0.7 at 973 K [9] and 0.45 at 950 K [10], respectively.

When utilizing such half-Heusler compounds in the TE generator devices, not only the TE properties but also the thermomechanical properties are very important. However, the thermomechanical properties such as thermal expansion, elastic modulus, and melting temperature of the half-Heusler compounds have been scarcely reported. In the present study, therefore, we investigated the thermal expansion and melting temperature of the MNiSn type half-Heusler compounds. We evaluated the thermal expansion coefficient by means of two different methods: the dilatometer measurement and the high temperature X-ray diffraction (HT-XRD) analysis. We studied the relationship between the thermal expansion coefficient and the melting temperature of the half-Heusler compounds.

2. Experiment

Ingots of the MNiSn type half-Heusler compounds were prepared by an arc melting from pure metal flakes. The obtained ingots were crushed to fine powders and then ball milled for 2 h using WC pot and balls. The obtained powders were packed into a graphite die and pelletized using a spark plasma sintering (SPS) technique. The SPS temperature was 1200 K for TiNiSn and 1400 K for ZrNiSn and HfNiSn. The sintering pressure was 100 MPa. Note that here the densification was finished in 10 min, but the sintering time

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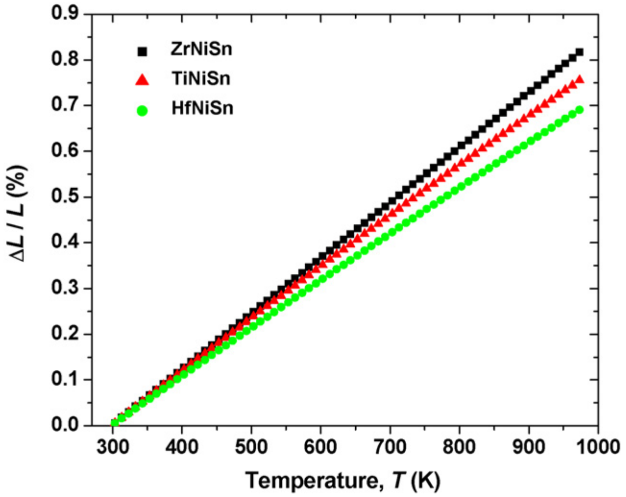

Fig. 1. Thermal expansion of MNiSn (M = Ti, Zr, Hf) obtained from the dilatometer measurements.

was set to be 2 h for improvement of the sample homogeneity. The sintered pellets were sealed in quartz tubes and annealed at temperatures ranging between 1073 and 1173 K for several days. The crystal structure and the phase state were examined by powder XRD using Cu Kα radiation. The polished surface of the samples was observed by scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis.

Table 1
Thermal expansion coefficient and melting temperature of *M*NiSn (*M* = Ti, Zr, Hf).

Average linear thermal expansion coefficient, α_{ave} ($\times 10^{-6}$ K^{-1})	Melting temperature, *Tm* (K)		
Method	Dilatometer	HT – XRD	*DTA*
Temperature range	313–963 K	323–673 K	–
ZrNiSn	12.1	11.0	1708
TiNiSn	11.3	10.5	1453[a]
HfNiSn	10.2	9.6	1760

[a] TiNiSn: decomposition temperature.

The thermal expansion was measured by a dilatometer for rectangular-shaped samples cut from the sintered pellets in the temperature range between room temperature and 973 K in an argon atmosphere, with the heating rate 5 K/min. From the obtained thermal expansion curves, the average linear thermal expansion coefficient, α_{ave}, between room temperature T_{RT} and temperature T, was calculated from the following equation:

$$\alpha_{ave} = \frac{1}{L_{RT}} \frac{L(T) - L_{RT}}{T - T_{RT}}, \quad (1)$$

where L_{RT} is the sample length at room temperature. The HT-XRD patterns for the powder samples were collected from room temperature to 673 K in a helium atmosphere. The linear thermal expansion coefficient was calculated from the temperature dependence of the lattice parameter. The melting temperatures of the samples were checked by using a system of differential thermal analysis (DTA) in an argon atmosphere.

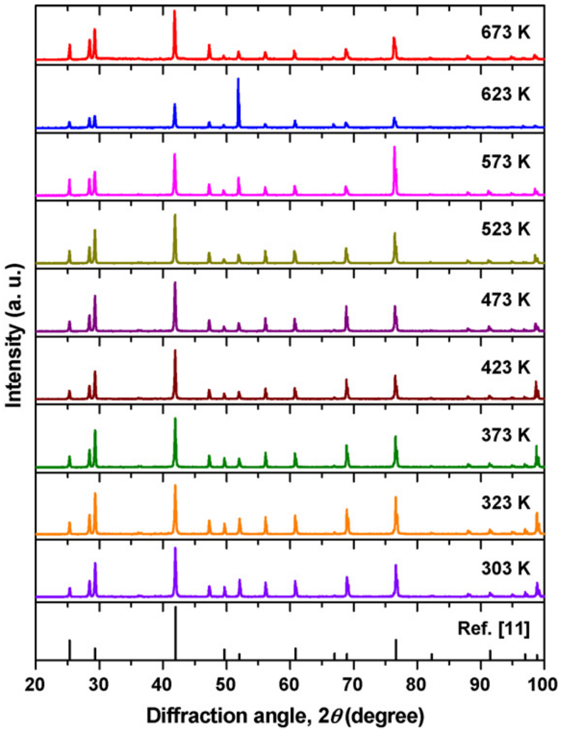

Fig. 2. Power XRD patterns of HfNiSn at elevated temperatures, together with the peak positions of HfNiSn [11].

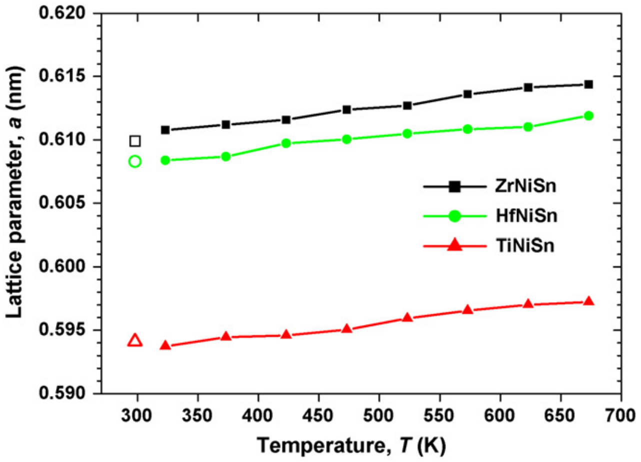

Fig. 3. Temperature dependences of the lattice parameters of MNiSn (M = Ti, Zr, Hf). Open marks represent the literature data [11,12].

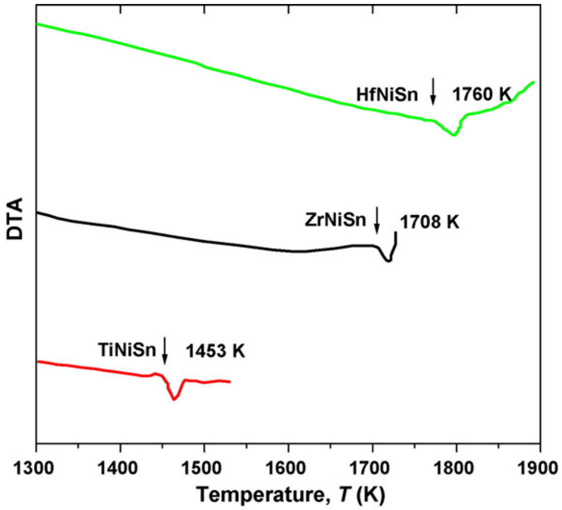

Fig. 4. DTA curves of MNiSn (M = Ti, Zr, Hf).

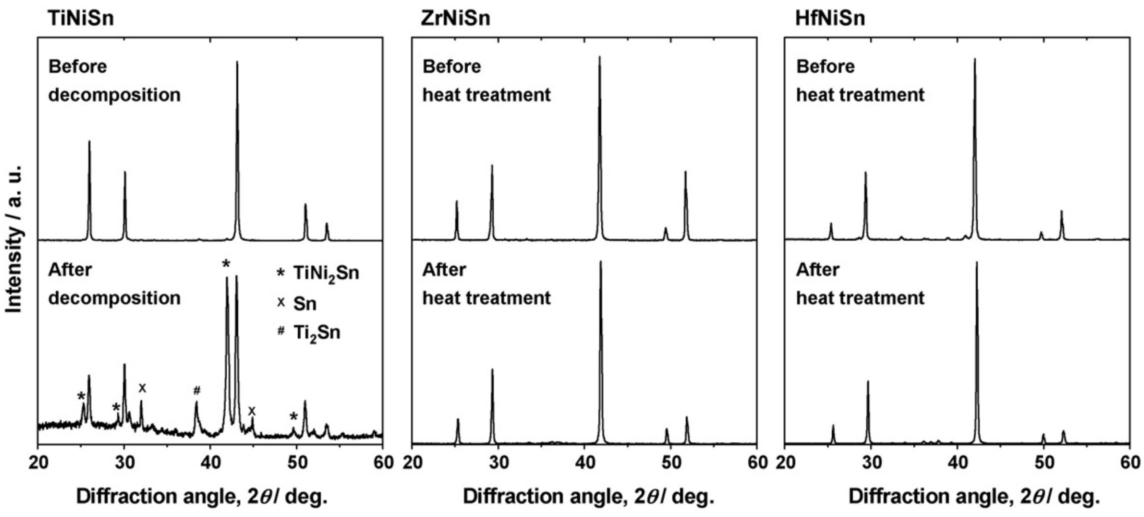

Fig. 5. Power XRD patterns of MNiSn (M = Ti, Zr, Hf). For TiNiSn, the XRD patters were collected before and after the DTA measurement. For ZrNiSn and HfNiSn, the XRD patterns were collected before and after the heat treatments. The ZrNiSn and HfNiSn samples were heated at just below the melting temperature in an Ar atmosphere.

3. Results and discussion

From the XRD and SEM/EDX analyses, it was confirmed that the samples prepared in the present study were pure MNiSn type half-Heusler phase with no impurities. The details of the sample characteristics were reported in Ref. [9].

The thermal expansion data obtained by using the dilatometer are shown in Fig. 1. The thermal expansion curves of all the three samples increased nearly linearly with increasing temperature. However, the thermal expansion trend slightly deviated from the linear relationship at high temperatures. This non-linear characteristic may manifest an anharmonic effect. In the temperature range from 313 to 963 K, the α_{ave} was calculated based on Eq. (1), as summarized in Table 1. The α_{ave} values for TiNiSn, ZrNiSn, and HfNiSn determined by the dilatometer method were 11.3×10^{-6}, 12.1×10^{-6}, and $10.2 \times 10^{-6}\ K^{-1}$, respectively.

The HT-XRD patterns of HfNiSn are shown in Fig. 2, together with the reported peak positions of HfNiSn [11]. It was confirmed that the peaks shifted to lower angle at elevated temperatures. The lattice parameters at high temperatures were calculated from the HT-XRD patterns for all the three samples, and the data were plotted in Fig. 3. The lattice parameters increased with increasing temperature, indicating positive thermal expansion coefficient. In this figure, literature values of the lattice parameters at room temperature [11,12] are also plotted for comparison. A good agreement between our data and the literature data can be confirmed. From the temperature dependences of the lattice parameters, the α_{ave} in the temperature range from 323 to 673 K was calculated as summarized in Table 1. The α_{ave} values for TiNiSn, ZrNiSn, and HfNiSn determined by the HT-XRD method were 10.5×10^{-6}, 11.0×10^{-6}, and $9.6 \times 10^{-6}\ K^{-1}$, respectively. These values were slightly lower than the values obtained from the dilatometer measurements. One of the reasons of this difference would be the difference of the temperature range in each measurement. However, the tendency of the magnitude of α_{ave} was consistent each other, that is the α_{ave} values were large in order of ZrNiSn, TiNiSn, and HfNiSn. Next, in order to understand the magnitude relation of the α_{ave} values in the MNiSn type half-Heusler compounds, we collected the melting temperature by means of DTA.

Fig. 4 shows the DTA curves of the MNiSn samples. We determined the phase transition temperature as a beginning point of an endothermic peak, as shown by arrows in Fig. 4. After the DTA measurements, it was visually confirmed that the ZrNiSn and HfNiSn samples completely melted, whereas the TiNiSn sample did not melt. So, we checked the XRD patterns of the TiNiSn samples before and after the DTA measurement, as shown in Fig. 5. In this figure, the XRD patterns of the ZrNiSn and HfNiSn samples after heating are also shown for comparison. The ZrNiSn and HfNiSn samples were heated at just below the melting temperatures under an Ar atmosphere followed by furnace cooling down to room temperature. It was confirmed that TiNiSn was decomposed into $TiNi_2Sn$, Ti_2Sn, and Sn, whereas ZrNiSn and HfNiSn were not decomposed into other phases and the half-Heusler phases were retained. Therefore, it can be concluded that ZrNiSn and HfNiSn melted at 1708 and 1760 K, respectively, whereas TiNiSn decomposed at 1453 K, as summarized in Table 1.

Generally, the thermal expansion coefficient (α) varies inversely as the melting temperature (T_m), and it is empirically confirmed that the product αT_m is a constant for many substances [13]. This means that a material with high T_m should exhibit low α. Here, let us consider the a_{ave} and the T_m values for ZrNiSn and HfNiSn. (Unfortunately, since TiNiSn decomposed before melting as described in the previous paragraph, we were not able to evaluate the T_m of TiNiSn.) In the present study, we confirmed that HfNiSn indicated higher T_m (1760 K) than ZrNiSn (1708 K), and for this reason, the smaller a_{ave} of HfNiSn than that of ZrNiSn will be expected. And, indeed, the a_{ave} value of HfNiSn was smaller than that of ZrNiSn, which was confirmed from both the dilatometer and the HT-XRD methods. Hence, it can be said that the data obtained in the present study were reasonable, and α_{ave} varied inversely as the T_m in the system of ZrNiSn and HfNiSn.

In fabricating a thermoelectric generator, similar values of the thermal expansion coefficient should be required for *n*-type and *p*-type thermoelectric materials in order to reduce the thermal stress arising across the temperature gradient. Therefore, we compared the data of the α_{ave} for the *n*-type MNiSn with the reported data for *p*-type half-Heusler compounds: ErPdSb, ErPdBi, and ZrCoSb. It was reported that the α_{ave} of ErPdSb [14], ErPdBi [14], and ZrCoSb [10] were 10.4×10^{-6}, 10.6×10^{-6}, and $8.9 \times 10^{-6}\ K^{-1}$, respectively. The α_{ave} of MNiSn were similar to those of ErPdSb and ErPdBi, whereas they were slightly larger than that of ZrCoSb. Therefore, from the viewpoint of thermal expansion, it can be said that MNiSn have better compatibility with ErPdSb and ErPdBi than ZrCoSb.

4. Summary

In the present study, the average linear thermal expansion coefficient (α_{ave}) and melting temperature (T_m) of the half-Heusler compounds: MNiSn (M = Ti, Zr, Hf) were collected, as summarized in Table 1. The values of the α_{ave} were large in order of ZrNiSn, TiNiSn, and HfNiSn. ZrNiSn and HfNiSn melted at 1708 and 1760 K, respectively, whereas TiNiSn was decomposed into $TiNi_2Sn$, Ti_2Sn, and Sn at 1453 K. As for ZrNiSn and HfNiSn, the magnitude relation of α_{ave} was explained from the viewpoint of T_m, that is the α_{ave} varied inversely as the T_m in the system of ZrNiSn and HfNiSn.

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