Substitution Effect on Thermoelectric Properties of ZrNiSn Based Half-Heusler Compounds

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Thermoelectric properties of ZrNiSn based half-Heusler compounds, $\text{Zr}_{0.7}\text{X}_{0.3}\text{NiSn}$ ($\text{X} = \text{Ti}, \text{Hf}$), $\text{ZrNi}_{0.7}\text{Y}_{0.3}\text{Sn}$ ($\text{Y} = \text{Pd}, \text{Pt}$), and $\text{ZrNi}_{1.05}\text{Sn}$ were investigated from room temperature to 1000 K. All the substitutions and addition of the excess nickel drastically decreased the thermal conductivity. The experimental values at room temperature were in good agreement with those estimated by the disorder scattering theory. The thermal conductivity exhibited considerable increase above 700 K for all the samples. It was corresponding to the transition of electrical properties, indicating that the generated hole conduction at high temperatures provided the increase. The additional electronic thermal conductivity caused by the ambipolar diffusion effect is discussed. [doi:10.2320/matertrans.47.1453]

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1. Introduction

ZrNiSn and the isoelectronic half-Heusler compounds such as $(\text{Ti}, \text{Zr}, \text{Hf})\text{NiSn}$,¹⁻⁷⁾ $(\text{Ti}, \text{Zr}, \text{Hf})\text{CoSb}$,⁸⁾ and LnPdSb ⁹⁾ were promising thermoelectric materials because of the high power factor and the thermal stability. However, the thermal conductivity was two or three times higher than those of conventional materials, which decreased the material performance. Many efforts were focused on the reduction of the thermal conductivity, by introducing the phonon-point defect scattering by alloying,¹⁻⁷⁾ phonon-grain scattering by reduction of the grain size¹⁰⁾ and nano-particle addition.¹¹⁾ Among them the alloying of zirconium and/or nickel were effective for reduction of the thermal conductivity without large deterioration of power factor. Recently partially antimony doped $\text{Ti}_{0.5}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{NiSn}$ was reported to have very large dimensionless figure of merit, about 1.5 at 700 K.⁷⁾ The alloying by hafnium together with titanium results in a strong reduction of the thermal conductivity. The lattice thermal conductivity of such alloys can be estimated by using a point defect scattering theory derived by Klemens and Callaway.^{12,13)} It has already been applied for thermoelectric materials such as Skutterudites¹⁴⁾ and the half-Heusler compounds.^{15,16)} However, the obtained adjustable parameter for ZrNiSn based compounds, ε , that means a ratio of phonon scatterings caused by mass fluctuation and strain field fluctuation, was different for each alloying element and concentration. Hence the thermal conductivity of the alloyed compounds cannot be predicted from their values. In this study, several ZrNiSn based compounds were prepared in a consistent way and common parameters for prediction of the thermal conductivity of the multi-alloyed compounds were determined. In addition, the compounds have been known to show unexplainable increase of thermal conductivity at high temperature. This study attempted to explain the increase by taking into the account an ambipolar diffusion effect.

2. Experimental Procedure

The pure constituents were arc melted at argon atmosphere for 5 times. The ingots were crashed and grained in steel mortar, the powders with a diameter of about 50 μm were obtained. Then the powders were sintered for two hours at about 1373 K by SPS technique, using graphite die under argon flow. It is noted that samples with the theoretical density were obtained for several minutes sintering, however, the sintering time was expanded for the sample homogeneity. The sintered pellets were sealed in quartz tube and annealed at 1073 K for one week. The crystal structure and sample phase were evaluated by XRD measurement, SEM observation and EDX analysis.

The electrical conductivity and the Seebeck coefficients were measured simultaneously from room temperature to about 1000 K using ULVAC ZEM-1 equipment at helium atmosphere. The thermal conductivity, κ , was evaluated as $\kappa = \lambda d C_p$, λ is thermal diffusivity, d is the experimental density at room temperature, and C_p is a heat capacity of the sample. In this study, the thermal conductivity was measured by a laser flash method using ULVAC TC-7000 equipment in vacuum. The sound velocity was measured at room temperature by ultrasonic pulse echo method for calculation of the Debye temperature¹⁷⁾ and estimation of the lattice thermal conductivity.

3. Results and Discussion

3.1 Sample characteristics and electrical properties

All the samples were confirmed as single phase of half-Heusler structure by XRD measurement. No pore and crack were observed from SEM analysis. The 5 at% excess nickel addition generated no impurity phase, which indicated that ZrNiSn based compounds can include some of the excess nickel probably in the nickel sublattice. Table 1 shows lattice parameter, phonon velocity, and Debye temperature of the samples estimated from XRD measurement and sound velocities. The Debye temperatures are higher than those of conventional thermoelectric materials of Bi_2Te_3 (165 K) and

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Table 1 Lattice parameter, Phonon velocity, and Debye temperature of samples. Phonon velocity and Debye temperature are calculated from sound velocities.

sample	Lattice parameter, a [nm]	Phonon velocity, v [ms ⁻¹]	Debye temperature, θ [K]
ZrNiSn	0.6110	3498	390
Zr _{0.7} Ti _{0.3} NiSn (30%Ti)	0.6059	3407	382
Zr _{0.7} Hf _{0.3} NiSn (30%Hf)	0.6098	3367	376
ZrNi _{1.05} Sn (+5%Ni)	0.6118	3481	388
ZrNi _{0.7} Pd _{0.3} Sn (30%Pd)	0.6191	3335	367
ZrNi _{0.7} Pt _{0.3} Sn (30%Pt)	0.6194	3260	359

Fig. 1 Temperature dependence of electrical conductivity. Lines are fitted above 700 K for estimation of band gap.

Fig. 2 Temperature dependence of Seebeck coefficient.

PbTe (160 K).¹⁸⁾ The high values confirm the intrinsic high thermal conductivity of the compounds. The alloying of zirconium site and excess nickel addition appeared to have a small influence on the phonon velocity and the Debye temperature. On the other hand, alloying by palladium and platinum slightly decreased those values. The lattice parameter changed according to the differences of metallic radius of the elements.¹⁹⁾

Figures 1 and 2 show temperature dependence of the electrical conductivity and the Seebeck coefficient. All the samples showed n-type semiconducting behavior. The excess nickel addition increased the electrical conductivity and decreased the Seebeck coefficient in magnitude. The result

indicates carrier generation by the excess nickel. The temperature dependence of the electrical conductivity appeared to change about 700 K for most of samples. The Seebeck coefficient decreased in magnitude at same temperatures, indicating that electron-hole generation occurred and the compounds were considered to be intrinsic semiconductor above the temperature. The band gap energy can be estimated from the temperature dependence of electrical conductivity in this region according to the following formula;

$$\sigma = \sigma_0 \exp\left(-\frac{E_g}{2k_B T}\right).$$

The estimated value for ZrNiSn was about 0.2 eV, corresponding to the reported value.²⁰⁾ However, the higher temperature measurement appeared to be necessary for evaluation of the band gap energy for the sample. The change of temperature dependence was more clearly seen for ZrNi_{0.7}Pd_{0.3}Sn and ZrNi_{0.7}Pt_{0.3}Sn probably due to the lower electron concentration. The estimated band gap energies of the two samples were about 0.5 eV, larger than those of other samples. The higher value of 0.5 eV appeared to be more probable for the compounds as a band gap energy. On the other hand, the temperature dependence of electrical conductivity was nearly equal for alloyed samples below 700 K. It indicates that there were common impurity donor levels in the electronic structure, probably caused by the Zr-Sn exchange or excess nickel.

3.2 Estimation of thermal conductivity

The experimental thermal conductivity was shown in Fig. 3. The alloying and the excess nickel addition drastically decreased the thermal conductivity. Among the samples, platinum alloying most effectively decreased the thermal conductivity due to the strong disorder scattering because of the large differences of atomic mass and radius compared to those of the matrix element, nickel. In spite of the difference of atomic mass the thermal conductivity of titanium substituted sample was almost equal to that of hafnium alloyed sample in the measured temperature range. They were about a half of that of the pure ZrNiSn at room temperature. The lattice thermal conductivity of such alloys can be estimated using a point defect scattering theory. Only phonon-phonon scattering (Umklapp process) and phonon-point defect scattering caused by lattice disorders were taking into considered.¹²⁾ In this study the boundary scattering can be neglected because of the high sintering temperature and the large diameter (about 50 μm) of particles. It is reported

Fig. 3 Temperature dependence of experimental thermal conductivity.

that both electron and phonon are not scattered strongly by grain boundary when the particle diameter is larger than $10\mu\text{m}$ for the half-Heusler compounds.^{10,21)} In this case, the lattice thermal conductivity at high temperature was expressed by,¹³⁾

$$\kappa = \frac{k_B}{2\pi^2 v} \int_0^{k_B\theta/T} \tau_{\text{total}} \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2} \omega^2 d\omega$$

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_D} + \frac{1}{\tau_P}$$

$$\frac{1}{\tau_D} = A\omega^4, \quad \frac{1}{\tau_P} = CT\omega^2.$$

Where k_B , v , $\hbar$, ω are Boltzmann constant, phonon velocity, Planck constant divided by 2π , and phonon frequency, respectively. The two phonon scattering processes were assumed to be represented by frequency-dependent relaxation time, τ_D and τ_P . τ_D is a relaxation time for scatterings by point defects of the lattice. The value of A is considered to be independent of the temperature, which can be expressed by²²⁾

$$A = \frac{\delta^3}{4\pi v^3} \sum_i x_i(1-x_i) \left[\left(\frac{\Delta M}{M} \right)^2 + \varepsilon \left(\frac{\Delta r}{r} \right)^2 \right].$$

Where δ^3 is average atom volume and x_i is fractional concentration of the component i . The mass fluctuation ($\Delta M/M$) is expressed by average atomic mass M in the site and the difference $\Delta M = M_i - M$, M_i is atomic mass of substituted element. The strain field fluctuation ($\Delta r/r$) is also represented by average and balance of atomic radius. However, there is no data of the average r for excess nickel added sample. Hence, in this study the parameter is estimated from the lattice parameter of XYSn ($X = \text{Ti, Zr, Hf}$, $Y = \text{Ni, Pd, Pt}$) and ZrNi_2Sn .²³⁾ The Fig. 4 shows the relation between ($\Delta r/r$) and balance of the lattice parameters of the compounds. There is linear relation for the four cases, hence ($\Delta r/r$) of the excess nickel added sample can be estimated. The parameter ε is related to elastic constants and average anharmonicity of the bonds of the lattice²²⁾ and generally regarded as adjustable parameter. The isoelectrical alloying has small influence on the bonding of the compounds as seen in Table 1, hence the parameter is considered to be nearly equal. Almost same values of ε have been obtained for several thermoelectric materials.^{14,16)} The phonon-phonon

Fig. 4 Relation between lattice strain term $\Delta r/r$ and difference of lattice parameter of XYSn ($X = \text{Ti, Zr, Hf}$ and $Y = \text{Ni, Pd, Pt}$) and ZrNi_2Sn .

Table 2 Phonon scattering parameters, estimated and experimental lattice thermal conductivity of samples. The strain field fluctuation parameter Γ_S is estimated from the adjustable parameter of $\varepsilon = 39$.

sample	C , [$10^{-19} \text{ s K}^{-1}$]	Γ_{total}	Γ_M	Γ_S	κ_{Lattice} , [$\text{Wm}^{-1} \text{ K}^{-1}$]	κ_{calc} , [$\text{Wm}^{-1} \text{ K}^{-1}$]
ZrNiSn	3.39	—	—	—	10.1	10.1
30% Ti	3.40	0.0606	0.0215	0.0232	5.4	5.0
30% Hf	3.40	0.0594	0.0387	~ 0	5.6	4.9
+5% Ni	3.39	0.0239	0.0158	0.0049	6.9	6.6
30% Pd	3.34	0.0414	0.0299	0.0322	5.0	5.6
30% Pt	3.34	0.1688	0.131	0.0382	3.3	3.3

scattering relaxation time is derived by parameter C , expressed as;

$$C = \frac{k_B^2 \theta}{2\pi^2 v \hbar T} \cdot \frac{1}{\kappa_{\text{ZrNiSn}}}$$

where θ is Debye temperature and κ_{ZrNiSn} is thermal conductivity of pure ZrNiSn. Using these parameters, the lattice thermal conductivity is expressed by Ref. 12);

$$\kappa_{\text{Lattice}} = \frac{k_B}{2\pi^2 v (ACT)^{1/2}} \tan^{-1} \left[\frac{k_B \theta}{\hbar} \left(\frac{A}{CT} \right)^{1/2} \right].$$

The lattice thermal conductivity is estimated from the experimental values of v , θ , δ and adjustable parameter ε . The parameters and lattice thermal conductivity are listed in Table 2. The average of adjustable parameter ε is determined to 39. The estimated lattice thermal conductivities using this value were in good agreement with the experimental results. The major phonon scattering was caused by mass fluctuation for hafnium or platinum alloyed and excess nickel added samples. The C values related to the phonon-phonon scattering were almost equal for all the samples. Hence the thermal conductivity of multi-alloyed ZrNiSn based compounds can be estimated from the obtained common ε and C parameters.

3.3 Ambipolar diffusion effect on thermal conductivity

Figure 5 shows temperature dependence of calculated and experimental thermal conductivity of ZrNiSn. The dashed

Fig. 5 Experimental and calculated thermal conductivity of ZrNiSn. Dashed line is drawn by assuming that Lorenz number is $1.6 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$. The solid line takes into account ambipolar diffusion effect.

line represents sum of the calculated lattice thermal conductivity and electronic thermal conductivity estimated by using a normal Lorenz number. The Lorenz number is estimated from Hall measurement by assuming that the scattering parameter is equal to $-1/2$. It is nearly independent of the temperature and about $1.6 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$. The estimated thermal conductivity was lower than the experimental value at high temperatures, hence there should be additional contribution of the carriers. Above 700 K the compounds is considered to be intrinsic semiconductor from the electrical properties measurement. In this region hole conduction occurred, which mean that it is necessary to consider the ambipolar diffusion effect on the thermal conductivity. In this case, the Lorenz number is represented by Ref. 24);

$$L = \frac{k_B^2}{e^2} \left(r + \frac{5}{2} \right) + \frac{k_B^2}{e^2} \frac{\sigma_h \sigma_e}{\sigma^2} \times \left[2 \left(r + \frac{5}{2} \right) + \frac{E_g}{k_B T} \right]^2 = L_0 + L_{am}$$

The σ_h and σ_e were electrical conductivity carried by holes and electrons. r is the scattering parameter and assumed to be equal for both carriers in this formula. The 2nd term expresses the ambipolar diffusion effect, which was caused by the generation and re-combination of electron-hole pair in the material. The electron-hole pair additionally carries energy that is equal to the band gap energy. Hence the carrier contribution to the thermal conduction increases. The solid line in Fig. 5 represents estimated thermal conductivity taking into account the ambipolar diffusion effect. The band gap energy is assumed to 0.5 eV from the temperature dependence of electrical conductivities. The estimated thermal conductivity of ZrNiSn was in good agreement with the experimental results. Therefore, it is concluded that the increase of the thermal conductivity above 700 K in the compounds was caused by the ambipolar diffusion. According to the formula, the effect strongly depends on the ratio of electron and hole conductivity. The 2nd term can be reduced to

Table 3 Estimated b values at 300 K and 873 K from temperature dependences of electrical and thermal conductivity. The band gap energy is fixed to 0.5 eV.

sample	$b = n_e \mu_e / n_h \mu_h$	
	300 K	873 K
ZrNiSn	1.5×10^3	24
30% Ti	2.9×10^3	22
30% Hf	1.1×10^3	15
+5% Ni	1.1×10^3	42
30% Pd	5.5×10^2	13
30% Pt	1.9×10^3	10

$$L_{am} = \frac{b}{(1+b)^2} (|S_e| + |S_h|)^2, \quad b = \frac{\sigma_e}{\sigma_h} = \frac{n_e \mu_e}{n_h \mu_h}$$

where n and μ are carrier concentration and mobility, respectively. The subscript of h and e express the hole and electron. This term depends on b and absolute values of the Seebeck coefficient. The large $n_h \mu_h = \sigma_h / e$ and $|S_h|$ enhanced the ambipolar diffusion effect. It means high “p-type” power factor induces the large additional electronic thermal conductivity. From the band calculation, the MNiSn ($M = \text{Ti, Zr, Hf}$) based half-Heusler compounds were found to be also prospective as a p-type thermoelectric material. It is corresponding to the strong ambipolar diffusion effect of the compounds. The estimated b values were listed in Table 3. The values at room temperature are order of 10^3 , therefore the ambipolar diffusion effect can be neglected. However, they decreased with increasing the temperature. According to the estimated results, several percent of electrical conduction was carried by hole at high temperature, which cause the considerable increase of the thermal conductivity. The titanium substituted and excess nickel added sample had large b due to the increased electron concentration. On the other hand, the value decreased by palladium and platinum substitution. It means the alloying in nickel site promotes hole conduction in the samples. The result qualitatively agrees with the p-type behavior of ZrPdSn and ZrPtSn.²⁵⁾ Figure 6 shows the estimated electronic thermal conductivity taking into account the ambipolar diffusion effect as function of b values. When $b = 20$, the contribution exceeded $2 \text{ Wm}^{-1} \text{ K}^{-1}$ at 900 K, significantly large as thermoelectric materials. It is important to reduce the additional electronic thermal conductivity since the compounds exhibit maximum performance in the temperature range. This result indicates that it is necessary to decrease the hole conduction for not only the optimization of power factor, but also the suppression of the electronic thermal conductivity.

4. Conclusion

Common parameters to predict the lattice thermal conductivity of ZrNiSn based alloyed compounds were determined from the experimental values of $\text{Zr}_{0.7}\text{X}_{0.3}\text{NiSn}$ ($X = \text{Ti, Hf}$), $\text{ZrNi}_{0.7}\text{Y}_{0.3}\text{Sn}$ ($Y = \text{Pd, Pt}$), and $\text{ZrNi}_{1.05}\text{Sn}$. All the substitutions and addition of excess nickel effectively decreased the thermal conductivity. Increase of the thermal conductivity at high temperature of the compounds can be

Fig. 6 Electronic thermal conductivity $L_{am}\sigma T$ caused by ambipolar diffusion for different b ($=\sigma_e/\sigma_h=n_e\mu_e/n_h\mu_h$) values. Electrical conductivity is assumed to $10^5 \Omega^{-1} \text{m}^{-1}$.

explained by ambipolar diffusion effect. The effect depends on the hole transport properties, which indicates that it is necessary to disturb the hole conduction (or electronic conduction as a p-type material) for reduction of the additional electronic thermal conductivity.

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