The effect of an isoelectronic Ti-Zr substitution on Heusler nanoprecipitation and the thermoelectric properties of a $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ half-Heusler alloy

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Abstract

The microstructure and thermoelectric properties of an **off-stoichiometric** quaternary $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ half-Heusler (HH) alloy was investigated in three heating cycles. A high density of coherent nanoprecipitates with an average diameter of ~13 nm and an interprecipitate spacing of ~6 nm was observed in the alloy. Formation of the extremely fine nanoprecipitates, most likely to be the **‘full’ Heusler (FH) phase**, was not only strongly related to the degree of excess Ni concentration ratio in the alloy, but also appeared to be affected by the Ti-Zr substitutions. We noticed the behaviour of both electrical resistivity (ρ) and Seebeck coefficient (S) of the alloy was closely associated with the microstructure evolution of the **FH**-nanoprecipitates, which depended on their phase instability at elevated temperature and the cyclic heating process. The ρ and S reduced after the 1st heating cycle and stabilised thereafter in the subsequent heating cycles. Despite the presence of the metallic **FH**-nanoprecipitates, the stabilised S maintained similar magnitudes to S of the ZrNiSn (without **FH**-nanoprecipitates) and did not show degradation of S as previously seen in the $\text{ZrNi}_{1.1}\text{Sn}$ containing relatively much larger **FH**-nanoprecipitates. The high density of **FH**-nanoprecipitates and the presence of Ti-Zr point defects were responsible for the significant reduction of thermal conductivity (κ) of the alloy, about 30% and 20% less than κ of the ZrNiSn and $\text{ZrNi}_{1.1}\text{Sn}$ alloys, respectively. Moreover, further reduction of κ was noticed due to formation of the diffuse HH/FH interfaced **FH**-nanoprecipitates from the cyclic heating process. Consequently, the alloy has shown a maximum dimensionless figure of merit (ZT) up to 0.81 at 870 K.

1. Introduction

Recently, the introduction of a nanoscale microstructure has increasingly attracted attention as a promising approach for the further improvement of thermoelectric performance in bulk thermoelectric materials [1-6]. The performance of thermoelectric materials can be characterised by the dimensionless figure of merit $ZT = (S^2/\rho\kappa)T$, where the S , ρ , κ and T are the Seebeck coefficient, the thermal conductivity, the electrical resistivity and the absolute temperature, respectively. For bulk half-Heusler (HH) thermoelectric alloys, MNiSn (where M= Ti,Zr,Hf), **similar approach utilizing various**

types of nanostructure has also been attempted, see several recent reviews [7-9]. One approach based on the precipitation of nanoscale ‘full’ Heusler (FH) phase within the HH matrix to improve the thermoelectric properties of the alloys is particular interest in the current study [10-16]. This approach is simple, as the formation of the FH phase can occur easily in HH alloys primarily because of their similarity in crystal structure [11]. The FH-nanoprecipitates in the MNiSn alloys have been reported as being capable of improving S via a so-called carrier filtering mechanism at the HH/FH interface [17] while simultaneously providing a high number of phonon scattering centres that result in the reduction of κ . However, direct experimental evidence of the beneficial effect of the FH-nanoprecipitates in HH alloys remains elusive. Often, the reduction of κ in the alloys may not always be accompanied by an improvement of S , as demonstrated explicitly in our recent investigation in a $\text{ZrNi}_{1.1}\text{Sn}$ HH alloy [18]. The phenomenon appeared to originate from the significant microstructure changes of the FH-nanoprecipitates from the cyclic heating process, which was closely related to their phase stability at an elevated temperature. To further elucidate such a microstructure evolution of the FH-nanoprecipitates and its effect on thermoelectric properties, we have extended our investigations in a $(\text{Ti}_{0.2},\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ HH alloy. The quaternary alloy was fabricated with a similar off-stoichiometric HH composition (i.e. excess Ni concentration ratio) to the previously studied ternary $\text{ZrNi}_{1.1}\text{Sn}$ HH alloy. As will be shown later, the results are interesting as the isoelectronic substitution between the Ti and Zr solute atoms not only led to a further reduction of κ in the $(\text{Ti}_{0.2},\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ compared with the $\text{ZrNi}_{1.1}\text{Sn}$, as one would expect due to the introduction of Ti-Zr disorders, but the isoelectronic substitution might also involve in the modification of the FH-nanoprecipitates microstructure and, thereby, the electrical and thermal transport properties of the alloy. The microstructure modification through the isoelectronic Ti-substitution is important and can be utilised for designing future high thermoelectric performance HH alloys. For simplicity, discussion of the microstructure and thermoelectric properties of the alloy have been made in conjunction with those of the $\text{ZrNi}_{1.1}\text{Sn}$ [18] and ZrNiSn [19] alloys.

2. Experimental procedure

An off-stoichiometric quaternary $(\text{Ti}_{0.2},\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ half-Heusler alloy, i.e. molar ratio $(\text{Ti}+\text{Zr})\text{:Ni}\text{:Sn} = 1\text{:}1.1\text{:}1$, was prepared by arc-melting followed by a directional solidification process using an optical floating zone method [19,20]. The phase constituents of the alloy were determined by powder X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The microstructure of the alloy was observed

using scanning electron microscopy (SEM), a scanning transmission electron microscope (STEM) equipped with energy-dispersive spectroscopy (EDS) and a high resolution TEM (HRTEM) operated at 200 kV. Preparation of the TEM specimens has been described elsewhere [14]. For comparison, the microstructure of a quaternary ($\text{Ti}_{0.2}\text{Zr}_{0.8}\text{NiSn}$) alloy (i.e. without excess Ni concentration ratio) and heat-treated at 1273 K for 2 weeks has also been observed by the STEM instrument. The temperature dependent ρ and S of the alloy were measured using the ULVAC ZEM-3, and the measurements were repeated for three consecutive heating cycles. **Measurement uncertainties of the ρ and S have been estimated to be 2% and 3%, respectively.** After the heating cycles, the microstructure of the alloy was again observed using the STEM. The carrier concentrations (n) and carrier mobility (μ_H) of the alloy, before and after the heating cycles, were measured at room temperature using Hall effect measurements with a DC four-probe van der Pauw subject to a 0.6 T magnetic field. The temperature dependence, κ , of the alloy was calculated based on the relationship $\kappa = d \times \alpha \times C_p$, where d is the density, α is the thermal diffusivity and C_p is the specific heat capacity. The three parameters, d , α and C_p , were estimated based on Archimedes principle, the laser flash method (ULVAC TC-1200RH) and differential scanning calorimetry (ULVAC DSC-9400), respectively. **The measurement uncertainty of the κ was estimated to about 3%.** The phase stability of the alloy was evaluated using differential thermal analysis (DTA; SETARAM, SETSYS Evolution, France).

3. Results and discussion

3.1. Initial microstructure and phase constituents

Fig. 1(a) is a SEM-backscattered electron (SEM-BE) image revealing that the initial microstructure of the as-grown ($\text{Ti}_{0.2}\text{Zr}_{0.8}\text{Ni}_{1.1}\text{Sn}$) alloy has a rather large grain size, with an average grain size of approximately 235 μm in diameter, and contains significantly fewer impurity phases. The alloy is a nearly single HH phase, as suggested by composition analysis using EPMA showing an average composition of (Ti+Zr):Ni:Sn = (2.2 + 29.2):36.9:31.8 (± 0.3 at%). **The alloy, with a molar ratio (Ti+Zr):Ni:Sn = 0.99:1.16:1, shows a relatively higher Ni concentration ratio than the initial nominal composition.** The alloy of a nearly single HH phase alloy was further confirmed by XRD analysis, as shown Fig. 1(b). The lattice parameter of the HH alloy (a_{HH}) was estimated to be 0.6104 (± 0.0001) nm. **The slightly one-side distorted 220_{HH} XRD peak towards the lower 2θ may be indication of overlapping XRD peaks between a secondary phase and the HH matrix (see inset in Fig. 1(b)).** Under a STEM observation, it was confirmed that a high density of extremely small precipitates was indeed embedded

110 within the HH matrix of the alloy as revealed in Fig. 1(c). These nanoscale precipitates
 111 were primarily spherical, with an average size of only approximately 13 nm in diameter;
 112 see the higher magnification image in Fig. 1(d). The spacing between the
 113 nanoprecipitates was even smaller, average of about 6 nm. Their volume fraction was
 114 estimated to be approximately 11 ± 2 %. Based on the STEM-EDS analysis, the
 115 nanoprecipitates were slightly rich in their Ni-concentration ratio, with an average
 116 composition of (Ti+Zr):Ni:Sn = (5+27):36:32 (± 4 at%). However, we were unable to
 117 conclusively determine their phase identity due to their extremely small size, which led
 118 to the overlapping of the X-ray interaction volume between the HH matrix and the
 119 nanoprecipitates. Therefore, the lattice structure of the Ni-rich nanoprecipitates was
 120 further investigated using HRTEM observation. Fig. 2(a) reveals the lattice structure of
 121 the spherical Ni-rich nanoprecipitates within the HH matrix of the alloy (some of them
 122 have been indicated by arrows). The figure is looking along the $[110]_{\text{HH}}$ direction as
 123 evident by the fast Fourier transform (FFT) diffraction pattern, see inset in Fig. 2(a). In
 124 the $[110]_{\text{HH}}$ FFT pattern, no other appreciable diffraction spots was observed apart from
 125 the diffraction spots from the HH matrix. However, the HH matrix diffraction spots
 126 were found to be considerably diffuse (see example of the enlarged $\overline{222}_{\text{HH}}$ spot in the
 127 inset of the FFT pattern). For ease of analysis, the square area in Fig. 2(a) containing the
 128 Ni-rich nanoprecipitates, labelled as L, M and N, was taken for image filtering process
 129 by an inverse fast Fourier transform (IFFT) analysis. The results are shown in Figs. 2(b)
 130 and 2(c), which correspond to IFFT processed images with and without indication of
 131 strain contrast (dark contrast), respectively. The Ni-rich nanoprecipitates, L, M and N,
 132 have been highlighted by broken lines for ease of visualization. One can see clearly the
 133 Ni-rich nanoprecipitates are coherent with the surrounding HH matrix and coherency
 134 strain (dark contrast) is mostly distributed in the vicinity of the nanoprecipitates/HH
 135 interface and within the nanoprecipitates, Fig. 2(b). These coherent Ni-rich
 136 nanoprecipitates within the HH matrix may well be responsible for the overlapping
 137 XRD peaks with the HH matrix, as seen previously in Fig. 1(b). For further analysis, the
 138 lattice structure of the L, M and N nanoprecipitates with the strain contrast filtered (Fig.
 139 2(c)) has been enlarged as shown in Fig. 2(e). Both of the lattice configuration of both
 140 the L and M nanoprecipitates was strongly resembled to the ordered FH lattice (see Fig.
 141 2(d)), where the structural vacancies of the HH were thought to be occupied by the
 142 excess Ni atoms. The Ni-antisites, as shown in Fig. 2(e), are point defects that formed
 143 from the structural vacancies occupation by the excess Ni atoms in the HH alloy. During
 144 the lattice structure analyses of the Ni-rich nanoprecipitates, only the Ni-antisites and
 145 the vacancies originated from the swapping sites between the Ni atoms and structural

vacancies of the HH structure [14] were considered because of their formations have been predicted to be energetically more favourable than other point defects at absolute temperature [21,22]. Nevertheless, at finite temperature particularly at temperature during the HRTEM observation, the observation of other point defects could be possible [23], as suggested by the presence of Ti/Zr vacancies within the Ni-rich nanoprecipitates, indicated by N, in Fig. 2(e). In Fig. 2(e), lattice structure of the HH matrix is also presented for comparison with those of the Ni-rich nanoprecipitates. Based on all the experimental indications in Figs. 1 and 2, as well as a reference to the phase equilibrium of HH and FH phases with respect to the Ni concentration ratio in a TiNiSn ternary phase diagram [22,24], the Ni-rich nanoprecipitates in the alloy were most likely to be FH-phase. The extremely small size and spherical FH-nanoprecipitates could well suggest they were at the initial formation stage in the FH-phase precipitation process, similar to those previously observed in the TiNiSn HH alloys [13,14]. For ease of discussion, hereafter, we termed these coherent Ni-rich nanoprecipitates as FH-nanoprecipitates. We noticed that the morphology, the HH/FH interfacial coherency, the size and the interprecipitate spacing of the H-nanoprecipitates in the quaternary $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ HH alloy were quite different from the precipitates observed in the ternary $\text{ZrNi}_{1.1}\text{Sn}$ HH alloy, despite they were fabricated by the same process [18]. For instance, the FH-nanoprecipitates in Fig. 2 are mostly spherical and coherent, with an average size of ~ 13 nm in diameter, whereas those observed in the ternary $\text{ZrNi}_{1.1}\text{Sn}$ were mostly semicoherent platelets and had a much larger size: ~ 330 nm long, ~ 100 nm wide and ~ 20 nm thick. The interprecipitate spacing of the FH-nanoprecipitates, as shown in Fig. 2, was also much smaller (i.e., ~ 6 nm), which is approximately 15 times smaller than the spacing in the $\text{ZrNi}_{1.1}\text{Sn}$ (i.e., ~ 90 nm). This is an important finding as the size of the FH-nanoprecipitates is closely related not only by the degree of excess Ni concentration ratio in the HH alloys [10-16] but also by the isoelectronic Ti-Zr substitution. The reason will be discussed in more detail in section 3.4.1.

In addition to the FH nanoprecipitation, we are also aware that other phase transformation process involved a phase separation of the HH phase itself according to a miscibility gap could also occur in the quaternary $(\text{Ti}_x, \text{Zr}_{1-x})\text{NiSn}$ HH alloys and thereby affect their thermoelectric properties [25-28]. The transformation process would result in the formation of a HH microstructure containing mixtures of Ti-rich and Zr-rich HH phases when the molar ratio x in the quaternary $(\text{Ti}_x, \text{Zr}_{1-x})\text{NiSn}$ HH alloys exceeds the solid solubility limit ~ 0.17 (i.e., Ti concentration $> \sim 5.5$ at %) [25,26]. An example revealing the microstructure of the HH phase separation process in a $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{NiSn}$ alloy heat-treated at 1273 K for 2 weeks is shown in Fig. 3(a). Two regions

of HH phases with clear phase contrast, indicated as HH_I and HH_{II}, can be clearly distinguished in the microstructure in Fig. 3(a). They were Zr-rich and Ti-rich HH phases, respectively, with composition (Ti+Zr):Ni:Sn, determined by EPMA as (3.5+28.8):34.4: 3.2 (± 0.3 at%) and (16.1+16.5):34.2:33.1 (± 0.3 at%). Noted that both of the HH_I and HH_{II}, although were identified as HH phase, their Ti/Zr ratio, calculated to be 0.12 and 0.98, respectively, were markedly different. Such a microstructure of HH phase separation process has been further confirmed by the STEM-EDS analyses, as shown in Figs. 3(b) and 3(c). The figures reveal two HH phases regions, indicated by HH_I and HH_{II}, are differentiated mainly on the different of Ti and Zr concentration contrast. The localised variation of the Ti, Zr, Ni and Sn concentrations across the HH_I and HH_{II} is indicated in the line composition analysis in Fig. 3(d). Besides the Ti/Zr ratio, it is further learnt that the HH phase separation microstructure may be differentiated by a relative different of dislocation density, where dislocation density within the HH_I (i.e. Zr-rich HH phase with relatively lower Ti/Zr ratio) often tended to be relatively higher than the HH_{II} (i.e. Ti-rich HH phase with relatively higher Ti/Zr ratio), see Fig. 3(b). In the current off-stoichiometric (Ti_{0.2}Zr_{0.8})Ni_{1.1}Sn HH alloy, however, we were unable to observe such a HH phase separation microstructure despite the Ti concentration exceeding the solid solubility limit. This could be caused by a depletion of the Ti concentration in the HH matrix to less than the Ti solid solubility limit (~ 5.5 at % [25,26]) due to a preference partitioning of Ti solute atoms from the HH matrix into FH-nanoprecipitates, hence avoid the formation of Ti-rich and Zr-rich HH phase separation in the alloy. Evidence of the preference partitioning of Ti solute atoms into the FH phase is shown later in Fig. 5 and discussed in section 3.4.1.

3.2. Electrical resistivity (ρ)

The temperature dependence, ρ , of the quaternary (Ti_{0.2}Zr_{0.8})Ni_{1.1}Sn HH alloy over three heating cycles is shown in Figs. 4(a) and 4(b). The alloy exhibits a semiconducting behaviour as the ρ value decreased with an increasing temperature over the three heating cycles. In the 1st heating cycle, the ρ values of the (Ti_{0.2}Zr_{0.8})Ni_{1.1}Sn were not reduced much from those of the ZrNiSn (i.e., containing no FH-nanoprecipitates) compared with the ρ values in the ZrNi_{1.1}Sn. This result was surprising as the presence of metallic FH-nanoprecipitates in the (Ti_{0.2}Zr_{0.8})Ni_{1.1}Sn would result in an increase in the carrier concentrations (n) and lead to a reduction in ρ compared with the ZrNiSn following the relationship below [29]

$$\rho = \frac{1}{n e \mu} , \quad (1)$$

where e is the electron charge and μ is carrier mobility. This result was suggested by the relatively larger n in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$, i.e., $12.1 (\pm 1) \times 10^{25} \text{ m}^{-3}$ (at room temperature), compared with the n in the two ternary alloys $\text{ZrNi}_{1.1}\text{Sn}$ and ZrNiSn , which were $10.1 (\pm 0.8) \times 10^{25} \text{ m}^{-3}$ and $9.5 (\pm 0.8) \times 10^{25} \text{ m}^{-3}$, respectively. The μ_H of the alloy at room temperature was not changed much compared with the ternary alloys, i.e., $18.5 (\pm 1.5) \times 10^{-4}$, $19.9 (\pm 1.6) \times 10^{-4}$ and $19.0 (\pm 1.5) \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. This result could be due to the reduction of ρ , which was also compensated for by an increase in ρ as a result of the increase in the energy band gap (E_g) by the substitution of Ti-Zr in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$. ρ and E_g were related through the following [30]

$$\rho \propto \exp\left(\frac{E_g}{2 k_B T}\right), \quad (2)$$

where k_B is the Boltzmann constant and T is the absolute temperature. E_g was highest in the quaternary $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$, i.e., 0.17 eV compared with the 0.12 eV and 0.10 eV of the $\text{ZrNi}_{1.1}\text{Sn}$ and ZrNiSn alloys, respectively. The estimations of E_g were carried out based on the ρ values within 800 to 1073 K during the 1st heating cycle, as seen in Fig. 4(a).

In the subsequent 2nd and 3rd heating cycles, however, the alloy shows a considerable reduction in ρ from that of the ZrNiSn , particularly in the lower temperature range $< 800 \text{ K}$, as seen in Fig. 4(b). For instance, the ρ values in the 2nd and 3rd cycle were measured to be $\sim 29 \times 10^{-6}$ and $\sim 25 \times 10^{-6} \Omega \text{m}$ at room temperature, respectively. There was an approximately 40% reduction from the ρ values of the ZrNiSn . The reduction of ρ in the quaternary $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ should be caused by a further increase in n from the 1st heating cycle, as indicated by measurement of n at room temperature of $15.9 (\pm 1.3) \times 10^{25} \text{ m}^{-3}$ after the three heating cycles. Upon heating, the reduction of ρ in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ decreased relatively slower with an increase in the temperature compared with the $\text{ZrNi}_{1.1}\text{Sn}$, i.e., the ρ of the alloy increased from values similar to those in the $\text{ZrNi}_{1.1}\text{Sn}$ at a lower temperature range to values similar to the ZrNiSn at temperatures $> 800 \text{ K}$. The relatively greater increment of ρ in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ at a higher temperature range indicates that the Ti-Zr substitution could introduced a relatively larger thermally carrier excitation effect than that observed in the $\text{ZrNi}_{1.1}\text{Sn}$. This result may be confirmed by the relatively greater reduction of E_g in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ than the reduction in the $\text{ZrNi}_{1.1}\text{Sn}$; the E_g of the former reduced from 0.17 eV (1st cycle) to 0.14 eV (2nd cycle) and 0.12 eV (3rd cycle), whereas the E_g of the latter reduced from 0.12 eV (1st cycle) to 0.11 eV (2nd cycle) and 0.10 eV (3rd cycle). The estimations were carried out using the ρ values obtained in the temperature range between 800 and 1073K in the 3 heating cycles, as seen in Figs. 4(a) and 4(b). The

results in Figs. 4(a) and 4(b), suggest the Ti-Zr substitution in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ is not effective in reducing ρ .

254

255 3.3. Seebeck coefficient (S)

256 The temperature dependence, S , of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ HH alloys in the 1st, 2nd
 257 and 3rd heating cycles are shown in Figs. 4(c) and 4(d), respectively. The negative sign
 258 of the S values indicates that the alloy is an n-type semiconductor. At approximately
 259 room temperature, the magnitude of S for the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ in the 1st heating cycle
 260 was measured to be approximately $-229 \mu\text{VK}^{-1}$, which was $\sim 35\%$ greater than that of
 261 the ZrNiSn (i.e., $170 \mu\text{VK}^{-1}$) and $\sim 20\%$ greater than the $\text{ZrNi}_{1.1}\text{S}$ (i.e., $-208 \mu\text{VK}^{-1}$).
 262 Such a large improvement of S , despite having the greatest n among the alloys, has been
 263 attributed to the so-called energy filtering mechanism where electrons with lower
 264 energy were filtered by the band bending potential (V_B) at the HH/FH interfaces [17].
 265 Compared with the $\text{ZrNi}_{1.1}\text{Sn}$, the relatively greater magnitude of S for the $(\text{Ti}_{0.2},$
 266 $\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ was also related to the size factor of the FH-nanoprecipitates, as a greater
 267 carrier filtering probability would occur as the relatively smaller FH-nanoprecipitate in
 268 the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ would create a greater V_B according to equation (3) below [17]

$$269 \quad C \propto V_B^2 x / R, \quad (3)$$

270 where C is a constant, x and R are the volume fraction and the radius of the
 271 nanoprecipitates, respectively. The x value of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ and the $\text{ZrNi}_{1.1}\text{Sn}$
 272 were similar in magnitude: $\sim 11\%$. The gradual reduction of the magnitudes of S for the
 273 $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ with an increase in temperature during the 1st heating cycle was due
 274 to an increase in the thermally excited carriers in the alloy.

275 The temperature dependence of the S of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ in the subsequent 2nd
 276 and 3rd heating cycles was rather different from that in the 1st heating cycle, as seen in
 277 Fig. 4(d). The large S improvement, as previously observed in the 1st cycle, vanished
 278 with the magnitude of S , which almost decreased to the values observed in the ZrNiSn .
 279 Such behaviour has also previously been observed in $\text{ZrNi}_{1.1}\text{Sn}$. In Fig. 4(d), both the
 280 magnitude and the variation trend of S were very similar for both heating cycles, and
 281 this result indicates that the FH-nanoprecipitates in the alloy must be stabilised in the 1st
 282 heating-cooling cycle. A similar behaviour has also been observed previously in
 283 $\text{ZrNi}_{1.1}\text{Sn}$. Despite the decrease in the improvement of S , the present $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$
 284 out performed $\text{ZrNi}_{1.1}\text{Sn}$, as it did not show the degradation of S where the magnitudes
 285 of S did not decrease below the values of the ZrNiSn , as seen in Fig. 4(c). In fact, a
 286 small increment in the magnitude of S in the ZrNiSn , i.e., up to 5%, could be noticed at
 287 temperatures from 400 to 950 K, as seen in Fig. 4(d). Moreover, the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$

has a magnitude of S of approximately $209 \mu\text{VK}^{-1}$, which is 16% greater than that of the $\text{ZrNi}_{1.1}\text{Sn}$ (Fig. 4(d)), which may even suggest a partially remaining carrier filtering effect. Nevertheless, the effect was lost completely at temperatures above 950 K as the magnitude of S of the alloy decreased below the value of the ZrNiSn .

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293 3.4. Power factor (S^2/ρ)

294 The temperature dependence of the power factor (S^2/ρ) of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$
 295 alloy in the 1st, 2nd and 3rd heating cycles is shown in Figs. 4(e) and 4(f), respectively. In
 296 the 1st heating cycle, as seen in Fig. 4(e), the S^2/ρ values of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ were
 297 mostly greater than in the ZrNiSn from room temperature up to approximately 1000 K,
 298 with a maximum value estimated up to $3.8 \text{ mWK}^{-2}\text{m}^{-1}$ at 840 K. This was an
 299 approximate 15% improvement from the ZrNiSn , *i.e.*, $3.3 \text{ mWK}^{-2}\text{m}^{-1}$ at 900 K. The S^2/ρ
 300 values dropped slightly in the subsequent heating cycles but remained relatively greater
 301 than the values in the ZrNiSn (Fig. 4(f)). The maximum S^2/ρ values in the 2nd and 3rd
 302 heating cycle were approximately 3.5 and $3.3 \text{ mWK}^{-2}\text{m}^{-1}$ at 840 K, respectively.
 303 Compared with the $\text{ZrNi}_{1.1}\text{Sn}$, the maximum S^2/ρ values of the alloy in all three heating
 304 cycles were still relatively less than the values for the $\text{ZrNi}_{1.1}\text{Sn}$ over the whole
 305 temperature range primarily due to the relatively greater values of ρ in the $(\text{Ti}_{0.2},$
 306 $\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ despite the improvements in S . For ease of the reader, the changes of
 307 thermoelectric properties of the alloy with respect to the cyclic heating process have
 308 been summarised in Table 1.

309

310 3.4.1. Microstructure of the post-heating cycled H-nanoprecipitates

311 The microstructure of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ alloy after undergoing the three
 312 heating cycles is shown in Fig. 5. As seen in Fig. 5(a), the microstructure of large grain
 313 size, up to several hundred μm in diameter, and with significant less impurity phases is
 314 still observed in the post-heating cycled microstructure. Similarly, no significant change
 315 of composition was found in the post-heating cycled alloy, which was determined by
 316 EPMA to be $(\text{Ti}+\text{Zr})\text{:Ni:Sn} = (2.4+28.7)\text{:36.8:32.1} (\pm 0.3 \text{ at}\%)$. A subsequent XRD
 317 analysis as shown in Fig. 5(b) has confirmed the post-heating cycled alloy remained as
 318 the HH phase, but with slightly larger lattice parameter, estimated to be $0.6107 (\pm$
 319 $0.0001) \text{ nm}$. However, the enlarged 220_{HH} XRD peak in the inset of Fig. 5(b) has
 320 revealed that a small amount of FH phase was also present in the alloy. The two phase
 321 microstructure containing the HH and FH in the post-heating cycled alloy was further
 322 confirmed by STEM observation as shown in Figs. 5(c) and 5(d). Note that Figs. 5(c)
 323 and 5(d) have been taken at the same magnifications as those in Figs. 1(c) and 1(d),

324 respectively. Some significantly large precipitates with diameter measuring up to several
325 hundred nm in size were often observed randomly distributed throughout the HH matrix
326 (indicated by arrows in Fig. 5(c)). They were identified as the FH-phase, with an
327 average composition (Ti + Zr):Ni Sn estimated to be (9 + 18): 48: 25 (± 4 at %) as
328 determined by STEM-EDS. Most of these relatively large FH-precipitates were
329 semicoherent with misfit dislocations easily observed at the HH/FH interface.
330 Additionally, further microstructure investigations revealed that the large
331 FH-precipitates were actually surrounded by a high density of extremely fine of
332 nanoscale precipitates that were also embedded within the HH matrix, some of the
333 nanoscale precipitates have been highlighted by arrows in Fig. 5(d). These mostly
334 spherical post-heating cycled nanoprecipitates were much more diffuse compared to
335 those pre-heating cycled FH-nanoprecipitates (see Figs. 1(d)). Their average size was
336 estimated to approximately 8 nm in diameter with interprecipitate spacing of less than 5
337 nm has also indicated their relatively higher density than FH-nanoprecipitates before the
338 heating cycles. They should correspond to the FH-nanoprecipitates in the pre-heating
339 cycled microstructure. The post-heating cycled FH-nanoprecipitates have been further
340 analysed by the HRTEM as shown in Fig. 6. Fig. 6(a) shows the lattice structure of the
341 post-heating cycled nanoprecipitates that embedded within the HH matrix (some of the
342 nanoprecipitates have indicated by arrows). It is observed along the $[110]_{\text{HH}}$, see inset of
343 FFT pattern. The nanoprecipitates, some of them have been highlighted by arrows, are
344 coherent with the HH matrix. The presence of coherency strain (dark contrast)
345 surrounding the HH/FH interface may also be indicated more clearly in IFFT image in
346 Figs. 6(b). This coherency strain may also be responsible to the diffuse HH diffraction
347 spots in the $[110]_{\text{HH}}$ FFT pattern, see the enlarged $\overline{222}_{\text{HH}}$ spot in the inset of the FFT
348 pattern. Moreover, as seen in Fig. 6(b), the coherency strain was found to be more
349 spread out from the HH/H interface and therefore, resulted in the nanoprecipitates to be
350 relatively more diffuse compared to those in the pre-heating cycled alloy. The length
351 scale of the coherency strain field (dark contrast), which was approximately on the order
352 of the interprecipitate spacing, *i.e.*, less than 5 nm, was relatively larger than the length
353 scale of coherency strain field previously observed in the pre-heating cycled
354 nanoprecipitates, as seen in Fig. 2. The lattice structure of the diffuse P and Q
355 nanoprecipitates in Fig. 6(c) has been enlarged for further analyses as shown in Fig. 6(d).
356 Similarly, they were most likely corresponded to the FH phase due to their strong
357 resemblance to the H lattice. The observation of these diffuse FH-nanoprecipitates and
358 those significantly larger H-precipitates within the HH matrix (in Figs. 5 and 6) has
359 further suggested an Ostwald ripening process, where some of the initially sharp

H-nanoprecipitates coarsen at the expense of the surrounding H-nanoprecipitates during the cyclic heating process. The formation of diffuse H-nanoprecipitates in the alloy after the heating cycles is very similar to the particles observed previously in the $\text{ZrNi}_{1.1}\text{Sn}$ HH alloy and has been reasoned to be the main factor causing the loss of S improvement after undergoing the 1st heating cycle [18]. The diffuse HH/FH interfacial structure might result in the reduction of V_B and hence the carrier filtering effect at the interface.

In order to elucidate the origin of the formation of the diffuse H-nanoprecipitates in the alloy, the phase stability of the FH-nanoprecipitates at an elevated temperature has been evaluated by DTA analyses in three consecutive heating (solid line) and cooling (dotted line) cycles, as shown in Fig. 7. The exothermic and endothermic peaks corresponding to the dissolution and formation of the FH-nanoprecipitates, respectively, were identified in each of the heating and cooling cycles in the figure. One should notice that the onset peak temperature of the FH-phase dissolution (exothermic) and the formation (endothermic) processes were almost unchanged regardless of the number of heating and cooling cycles, i.e., approximately 1067 and 1061 K, respectively (see insets of the enlarged peaks in Fig. 7). The temperatures were located just at the higher end of the temperature range for the ρ and S measurements in Fig. 4. Therefore, repetition of the H-phase dissolution and formation would occur during the measurements and, consequently, resulted in the formation of diffuse FH-nanoprecipitates in the alloy, as seen in Figs. 5 and 6[31]. Indication of microstructure stabilization from the cyclic DTA measurements could also be noticed in Fig. 7 as the large variation of heat flow in the 1st heating cycle vanished after the alloy was heated to above the FH-phase dissolution temperature. After that, the heat flow variation trends in the subsequent 1st cooling cycle (as well as those in the heating cycles) behave similarly in the 2nd and 3rd cycles.

In Fig. 5(c), we noticed composition of the large FH-precipitates have a much greater Ti solid solubility than the HH matrix. Their respective average composition (Ti+Zr):Ni:Sn, estimated by STEM-EDS to be (3+31):33:33 (± 4 at%) and (8+18):48:25 (± 3 at%), have shown the large H-precipitates contained approximately five times greater of the Ti/Zr ratio than the surrounding HH matrix, i.e. ~ 0.5 and ~ 0.1 , respectively. This indicates a preferential partitioning of Ti solute atoms occurs from the HH matrix into the FH phase. We anticipated that a similar preferential partitioning of Ti solute atoms would also occur in those relatively smaller FH-nanoprecipitates in the alloy before (see Figs. 1 and 2) and after (Figs. 5 and 6) the heating cycles. Consequently, the FH-nanoprecipitates would be expected to show a relatively higher

396 Ti/Zr ratio than the surrounding HH matrix. Interestingly, we observed that both the
 397 onset temperatures for the FH-phase dissolution and formation in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$
 398 were also almost unchanged from those platelet and disc FH-nanoprecipitates in the
 399 ternary $\text{ZrNi}_{1.1}\text{Sn}$, *i.e.*, 1067 and 1062 K, respectively [15]. In addition, the degree of
 400 excess Ni concentration ratio were more or less similar in both alloys (*i.e.* 1.16 and 1.17,
 401 respectively based on the EPMA), and the volume fraction of the FH-nanoprecipitates
 402 were also similar in both alloys, *i.e.* $\sim 11 (\pm 2) \%$, these indications have suggested that
 403 the effect of Ti-Zr substitutions on the refining size of the FH-nanoprecipitates should
 404 be related more to a reduction of the coarsening kinetic than an increment of the driving
 405 force for the nucleation of the FH-nanoprecipitates. At this stage, systematic
 406 investigations into the coarsening kinetic of the FH-nanoprecipitates in the alloy have
 407 not been evaluated systematically. Intuitively, it is anticipated that the overall diffusion
 408 for the coarsening of the FH-nanoprecipitates from the substitution Ti-Zr and
 409 ‘interstitial’-like nature of the structural vacancy occupation by the excess Ni atoms in
 410 the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ is likely to be less than only the ‘interstitial’-like diffusion of the
 411 excess Ni in the $\text{ZrNi}_{1.1}\text{Sn}$. As a consequence, the size of FH-nanoprecipitates in the
 412 quaternary $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ alloy is relatively smaller than the nanoprecipitates in the
 413 $\text{ZrNi}_{1.1}\text{Sn}$, as seen in the current case. The preferential partitioning of the Ti solute
 414 atoms to the FH-nanoprecipitates would also result in the depletion of the Ti
 415 concentration in the HH matrix to less than the solid solubility limit for the HH phase
 416 separation, and this might explain the absence of Ti-rich and Zr-rich HH phases in the
 417 alloy, as mentioned previously in section 3.1.

418 Apart from the significant impact on S , we also observed that the carrier mobility
 419 (μ_H) of the alloy was significantly affected by changes in the HH/FH interfacial
 420 characteristics of the FH-nanoprecipitates in the alloy. For instance, the μ_H of the alloy
 421 at room temperature was found to be reduced from $18.5 (\pm 1.5) \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ before
 422 the cyclic process to $13.3 (\pm 1.1) \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ after the heating cycles. The reduction
 423 was not caused by changes in the interfacial coherency (*i.e.* semicoherent or coherent)
 424 because the FH-nanoprecipitates in the alloy were primarily coherent before and after
 425 the heating cycles. Therefore, the 28% reduction in μ_H must have been caused by an
 426 increase in carrier scattering primarily to the relatively larger length scale of the
 427 coherency strain field from the FH-nanoprecipitates with the diffuse HH/FH interface
 428 (Figs. 5 and 6) compared with the sharp HH/FH interface (Figs. 1 and 2). Additionally,
 429 an increase in n from $12.1 (\pm 1) \times 10^{25} \text{ m}^{-3}$ to $15.9 (\pm 1.3) \times 10^{25} \text{ m}^{-3}$ was also observed in
 430 the alloy after the cyclic heating process. This increase may be due to an increase in the
 431 point defects (*e.g.*, Ni-antisites and Ti-Zr disorders) that were generated during the

FH-phase dissolution/formation processes in the alloy. The coherency strain field (dark contrast as indicated in Fig. 6(b)) that spread from the diffuse HH/FH interface into the HH matrix may be indicative of diffusion paths containing a large number of Ni-antisites and Ti-Zr disorders.

3.5. Thermal transport properties

The temperature dependence, κ , of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ over the two heating cycles, the 1st and 2nd, are shown in Figs. 8(a) and 8(b), respectively. Each of the κ values in the figures has been deduced from the temperature dependence thermal diffusivity (α) and specific heat (c_p) as shown in the supporting information. Density of the alloy was estimated to be 7.59 gcm^{-3} . The κ of the alloy in the 3rd cycle, however, was anticipated to be similar than κ of the 2nd heating cycle as the microstructure stabilization of the H-nanoprecipitates occurred after the 1st heating-cooling cycle, as indicated in Fig. 4. In Fig. 8(a), the room temperature κ of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ in the 1st heating cycle was estimated to be $\sim 4.5 \text{ Wm}^{-1}\text{K}^{-1}$, which was $\sim 31\%$ and $\sim 21\%$ less than κ of the ZrNiSn and the $\text{ZrNi}_{1.1}\text{Sn}$, which were ~ 6.5 and $\sim 5.7 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. The significant reduction in κ of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ was attributed to enhanced phonon scattering by the introduction of the point defects, particularly the Ti-Zr disorders and the presence of a high density FH-nanoprecipitates (*i.e.*, $\sim 13 \text{ nm}$ in diameter) with a shorter interprecipitate spacing (*i.e.*, $\sim 6 \text{ nm}$), see Fig. 1(c). The κ values of the alloy remained more or less constant at approximately $4.5 \text{ Wm}^{-1}\text{K}^{-1}$ as the temperature increased up to approximately 850 K . Beyond 850 K , however, κ increased rapidly to values even larger than that of the ZrNiSn and $\text{ZrNi}_{1.1}\text{Sn}$ alloys at temperatures above 950 K . Such a rapid increase in κ at temperatures beyond 850 K could be caused by the so-called ambipolar diffusion effect [32,33]. In the subsequent heating cycle, the alloy exhibited a further reduction of κ . For instance, the room temperature κ , which was estimated to be $\sim 3.9 \text{ Wm}^{-1}\text{K}^{-1}$, was $\sim 13\%$ less than κ in the 1st heating cycle. The reduction was even larger when it compared with the κ of the two ternary ZrNiSn and $\text{ZrNi}_{1.1}\text{Sn}$ HH alloys, *i.e.* $\sim 40\%$ and $\sim 20\%$, respectively. Such a further reduction in κ should originate from an additional enhancement of the phonon scattering due to formation of the diffuse FH-nanoprecipitates during the heating-cooling process (see Figs. 5 and 6). As the temperature increased, the variation trend of κ in the 2nd heating cycle was very similar to the variation in the 1st heating cycles. To evaluate the variation in κ of the alloy in more detail, its electronic (κ_e) and lattice (κ_l) components in the two heating cycles were calculated, as shown in Figs. 8(c) and 8(d), respectively. The calculations were based on the Wiedemann-Franz law:

$$\kappa = \kappa_l + \kappa_e, \quad (4)$$

where the κ_e that was closely related to ρ

$$\kappa_e = \frac{LT}{\rho}. \quad (5)$$

The Lorentz number L was assumed to be $1.6 \times 10^{-8} \text{ W}\Omega \text{ K}^{-2}$ [34] and T is the absolute temperature. The figures revealed that the reduction in κ for the alloy primarily originated from the reduction of κ_l , as the κ_e values appeared not to increase much despite the presence of FH-nanoprecipitates. In both heating cycles, the κ_l values increased slightly with an increasing temperature and decreased again to a minimum value, i.e. $\sim 3.5 \text{ W m}^{-1} \text{ K}^{-1}$, at approximately 800 K in the 1st heating cycle (Fig. 8(c)) and $\sim 2.5 \text{ W m}^{-1} \text{ K}^{-1}$ at 830 K in the 2nd heating cycle (Fig. 8(d)). As the temperature increased further, the greater increasing rate of κ_l of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ compared with the rate of the ZrNiSn and $\text{ZrNi}_{1.1}\text{Sn}$ indicated that the Ti-Zr substitution could have favoured the ambipolar diffusion effect. The enhanced phonon scattering that resulted in the reduction of κ_l was attributed to the similar order of the phonon mean free path (l_{ph}) to the microstructure in the alloy, such as the length scale of the coherency strain field, the interprecipitate spacing and the size of the FH-nanoprecipitates. The l_{ph} in the present alloy has been estimated to be approximately 1.8 nm (1st cycle) and 1.5 nm (2nd cycle) based on the expression adapted from the kinetic theory of gas [35]

$$l_{ph} = \frac{3 \kappa_l}{C_v v_m}, \quad (6)$$

where κ_l is the lattice component of κ , C_v is the specific heat per unit volume and v_m is the mean speed of sound. At 300 K, the $C_v (= d \times C_p)$ of the alloy in the 1st and 2nd cycles was determined to be 2.1×10^6 and $2.2 \times 10^6 \text{ J/m}^3 \text{ K}$, respectively. The alloy density d was 7.59 g cm^{-3} , whereas C_p for the 1st and 2nd heating cycles was 0.28 and $0.24 \text{ J g}^{-1} \text{ K}^{-1}$, respectively. v_m was assumed to be equal to 3407 m/s [32].

3.6. Dimensionless figure of merit, ZT .

The temperature dependence of the dimensionless figure of merit, ZT , of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ in the 1st and 2nd heating cycles is shown in Figs. 9(a) and 9(b), respectively. A maximum ZT of 0.70 at 850 K was noted in the 1st heating cycle, as seen in Fig. 9(a). This ZT values was up to a 30% improvement from the ZT value of the ZrNiSn and the $\text{ZrNi}_{1.1}\text{Sn}$, i.e., 0.54 at 800 K and 900 K, respectively. An even larger increment in ZT was observed in the 2nd heating cycle, with the maximum ZT estimated to be 0.81 at 870 K. This was $\sim 50\%$ and $\sim 10\%$ greater than the ZT values for the ZrNiSn and $\text{ZrNi}_{1.1}\text{Sn}$, respectively. The improvement of the ZT values was primarily

due to the reduction of κ without significantly sacrificing the electrical transport properties, S^2/ρ . The improvement showed that the introduction of H-nanoprecipitates and Ti-Zr point defects could be a promising approach to improve the thermoelectric properties of HH alloys. Nevertheless, the issue of the ambipolar effect that resulted in the rapid increment of κ and thereby the rapid decrease in ZT at temperatures greater than 850 K in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ remains an issue that must be addressed in the future. Table 1 also summarises the changes of κ and ZT of the alloy with respect to the cyclic heating process.

510

511 4. Conclusions

512 Several important findings have been concluded as follows:

- 513 1) A high density of coherent FH-nanoprecipitates with an average diameter of
514 approximately 13 nm and an interprecipitate spacing of approximately 6 nm was
515 observed in the quaternary $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ HH alloy. The size and interprecipitate
516 spacing were much smaller than in the $\text{ZrNi}_{1.1}\text{Sn}$ suggesting that the Ti-Zr
517 substitutions played an important role in refining the precipitate size and spacing.
- 518 2) The alloy exhibits a reduction of electrical resistivity (ρ) in the 2nd and 3rd heating
519 cycles from the ρ of the ZrNiSn due to the presence of the FH-nanoprecipitates in
520 the alloy. However, the ρ reduction was only found in the lower temperature range
521 of the two cycles and degree of the ρ reduction was comparatively smaller than
522 those in the $\text{ZrNi}_{1.1}\text{Sn}$ suggesting the Ti-Zr substitution is not effective in reducing ρ
523 in the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$.
- 524 3) A large improvement in the magnitude of S was observed in the alloy, but only
525 during the 1st heating cycle. The improvement in S decreased significantly in the
526 subsequent 2nd heating cycle. Nevertheless, the magnitude of S for the alloy was still
527 relatively greater than the two ternary ZrNiSn and $\text{ZrNi}_{1.1}\text{Sn}$ alloys. Stabilization of
528 S was noticed after the 1st heating-cooling cycles.
- 529 4) The maximum power factor (S^2/ρ) of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ was $\sim 3.8 \text{ mW m}^{-1} \text{ K}^{-2}$ at
530 840 K in the 1st cycle and it decreased to approximately 3.5 and 3.3 $\text{mW m}^{-1} \text{ K}^{-2}$ at
531 840 K in the subsequent 2nd and 3rd heating cycles, respectively. The maximum S^2/ρ
532 in the three cycles were comparatively less than the S^2/ρ of the $\text{ZrNi}_{1.1}\text{Sn}$ primarily
533 due to the greater ρ despite the relatively larger S .
- 534 5) The κ of the alloy was $\sim 4.5 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature in the 1st heating cycle.
535 This was approximately 31% less than the κ of the ZrNiSn and 12% less than the κ
536 in the $\text{ZrNi}_{1.1}\text{Sn}$. The reduction was attributed to the enhanced phonon scattering due
537 to the introduction of Ti-Zr disorders and the high density of FH-nanoprecipitates.

- 538 6) A further reduction in κ was observed in the subsequent 2nd heating cycle in the
 539 $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$. This reduction was caused by an additional enhancement of the
 540 phonon scattering through the formation of the diffuse FH-nanoprecipitate, which
 541 had a relatively smaller size, a shorter interprecipitate spacing and a relatively larger
 542 length scale of the coherency strain field from the HH/FH interface compared with κ
 543 prior to the heating-cooling process. A rapid increase in κ was observed in the
 544 $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ at temperatures greater than 850 K possibly due to the ambipolar
 545 effect.
- 546 7) The maximum ZT of the $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ was observed to be 0.81 at 870 K in the
 547 2nd heating cycle. This was a ~50% and 8% improvement from the ZT of the ZrNiSn
 548 and ZrNi_{1.1}Sn, respectively. However, the ZT values decreased rapidly at higher
 549 temperature due to the rapid increase of κ .

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Fig. 1. (a) SEM-backscattered electron (SEM-BE) image revealing an overall microstructure of the quaternary $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ alloy before the cyclic heating process. (b) XRD profile shows the alloy contains a nearly single HH phase alloy. (c) and (d) correspond to bright-field (BF)-STEM images taken at low and high magnifications, respectively, revealing a high density of spherical and nanosized precipitates embedded within the HH matrix (see arrows).

Fig. 2. (a) HRTEM image shows the lattice structure of the Ni-rich nanoprecipitate (see L, M and N) within the HH matrix in the pre-heating cycled $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ alloy. The image is looking along a $[110]_{\text{HH}}$ direction, see inset of fast Fourier transform (FFT) pattern. (b) and (c) Inverse fast Fourier transform (IFFT) filtered images reveal the presence and absence of strain contrast (dark contrast) in the vicinity of the Ni-rich nanoprecipitates, respectively. (d) Schematic diagrams show an ordered lattice structure of FH, (i.e. $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{Ni}_2\text{Sn}$) and HH (i.e. $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{NiSn}$) looking along an $[110]_{\text{HH}}$. (e) Enlarged IFFT filtered images from the square area in (c) showing lattice structure of the Ni-rich nanoprecipitates (L, M and N) and the HH matrix. The schematic diagrams below reveal the analyses of their lattice configurations.

Fig. 3. (a) SEM-BE image revealing a microstructure of HH phase separation in a $(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{NiSn}$ alloy heat-treated at 1273K for 2 weeks. Regions of Zr-rich and Ti-rich HH phases are indicated as HH_I and HH_II , respectively. (b) and (c) are BF-STEM image and STEM-EDS composition mapping analysis of the HH_I and HH_II . (d) Line composition analysis by STEM-EDS showing variations of each Ti, Zr, Ni and Sn concentration

across the HH_I and HH_II in (b).

Fig. 4. Temperature dependence of the electrical resistivity (ρ), Seebeck coefficient (S) and power factor (S^2/ρ) of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ HH alloy in three consecutive heating cycles. The alloy is shown in (a) and (b), (c) and (d), (e) and (f), respectively. Graphs in the 1st column represent the 1st heating cycle and graphs in the 2nd column represent the 2nd and 3rd heating cycles. Lines are guides to the eye.

Fig. 5. (a) SEM-BE image reveals an overall microstructure of the quaternary $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ alloy after three heating cycles. (b) XRD profile indicates the presence of two phases, HH and FH (solid blue triangle in the inset), in the post-heating cycled HH alloy. (c) and (d) are BF-STEM images showing the HH matrix is embedded with some relatively large FH precipitates and a large density of extremely fine and diffuse nanoprecipitates (pointed by arrows).

Fig. 6. (a) HRTEM image showing lattice structure of the diffuse FH nanoprecipitates embedded within the HH matrix of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ alloy (see arrows). The image is looking along the $[110]_\text{HH}$ direction as shown by the FFT pattern in the inset. (b) and (c) are IFFT filtered images indicating the presence and absence of strain contrast (dark contrast) surrounding the two diffuse FH-nanoprecipitates, P and Q, respectively. (d) Enlarged IFFT images from Fig. 6(c) revealing the lattice configurations of the P and Q nanoprecipitates. Schematic diagrams indicate their similarity to the FH lattice.

Fig. 7. DTA analyses showing onset exothermic peak temperature for the dissolution of FH-phase upon heating (solid red lines) and onset endothermic peaks temperature for the formation of FH-phase upon cooling (broken blue lines) in three consecutive heating and cooling cycles. The insets correspond to the enlarged exothermic and endothermic peaks of the three heating and cooling cycles, respectively.

Fig. 8. Temperature dependent thermal conductivity (κ) of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ HH alloy in (a) 1st and (b) 2nd heating cycles. (c) and (d) the corresponding lattice (κ_l) and electronic (κ_e) components of κ in the 1st and 2nd heating cycles, respectively. Lines are guides to the eye.

Fig. 9. Temperature dependent dimensionless figure of merit (ZT) for the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$ HH alloy in the (a) 1st and (b) 2nd heating cycles. Error bars show experimental measurement uncertainty of about 11%. Lines are guides to the eye.

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717 List of Table caption

718 Table 1. Summary indicates the effect of heating cycles, i.e. room temperature (RT) to
719 1073 K, on the thermoelectric properties of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$, $\text{ZrNi}_{1.1}\text{Sn}$ and
720 ZrNiSn half-Heusler alloys. The values are taken at room temperature except stated
721 otherwise.

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Table 1. Summary indicates the effect of heating cycles, i.e. room temperature (RT) to 1073 K, on the thermoelectric properties of the $(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$, $\text{ZrNi}_{1.1}\text{Sn}$ and ZrNiSn half-Heusler alloys. The values are taken at room temperature except stated otherwise.

Thermoelectric properties	$(\text{Ti}_{0.2}, \text{Zr}_{0.8})\text{Ni}_{1.1}\text{Sn}$			$\text{ZrNi}_{1.1}\text{Sn}$			ZrNiSn
	Heating cycles			Heating cycles			Heating cycle
	1st	2nd	3 rd	1st	2 nd	3 rd	1st
ρ ($\times 10^{-6} \Omega\text{m}$)	40	29	25	-28	-26	-25	42
S ($\times 10^{-6} \text{VK}^{-1}$)	-229	-170	-165	-208	-178	-175	-170
S^2/ρ ($\times 10^{-3} \text{Wm}^{-1}\text{K}^{-2}$)	3.8 @ 840 K	3.5 @ 840 K	3.3 @ 840 K	4.1 @ 900 K	4.0 @ 900 K	3.9 @ 900 K	3.3 @ 900 K
E_g (eV)	0.17	0.14	0.12	0.12	0.11	0.10	0.10
n ($\times 10^{25} \text{m}^{-3}$)	12.1	-	15.9	10.1	7.1	-	9.5
μ_H ($\times 10^{-4} \text{m}^2\text{V}^{-1}\text{s}^{-1}$)	18.5	-	13.3	19.9	22.8	-	19.0
κ ($\text{Wm}^{-1}\text{K}^{-1}$)	4.5	3.9	-	5.7	5.2	-	6.3
ZT	0.7 @ 850 K	0.81 @ 850 K	-	0.54 @ 900 K	0.75 @ 900 K	-	0.53 @ 800 K

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Fig. 1 (Revision 1)

Figure 2

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Fig. 2 (Revision 1)

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Fig. 3 (Revision 1)

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Fig. 4 (Revision 1)

Figure 5

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Fig. 5 (Revision 1)

Figure 6

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Fig. 6 (Revision 1)

Figure 7

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Fig. 7(Revision 1)

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Fig. 8 (Revision 1)

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Fig. 9 (Revision 1)

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Figure abstract (revision 1)