Microstructure and thermoelectric properties of a $\text{ZrNi}_{1.1}\text{Sn}$ half-Heusler alloy

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Abstract

The microstructure and thermoelectric properties of a $\text{ZrNi}_{1.1}\text{Sn}$ half-Heusler alloy have been investigated. The alloy was found to contain a high density of nanosized Heusler precipitates that appeared as platelets and discs. These Heusler nanoprecipitates were responsible for a large improvement of the Seebeck coefficient of the alloy at room temperature compared with the ZrNiSn , which contained no Heusler nanoprecipitates. However, the improvement reduced with increasing temperature due to the phase instability of the Heusler nanoprecipitates. Nevertheless, the reduction of the Seebeck coefficient could be stabilised after heating and cooling the alloy from beyond the precipitate dissolution temperature to below the phase decomposition temperature due to stabilisation of the Heusler nanoprecipitates. The size of the stabilised precipitates was significantly reduced to < 20 nm in diameter. A reduction in the electrical resistivity was observed and resulted in an overall improvement of the power factor to 20% higher than that of the ZrNiSn . Similarly, a reduction in the thermal conductivity was observed due to the reduction of the size and inter-precipitate spacing, as well as to the relatively larger length scale of the coherency strain field around the diffuse interface between the half-Heusler matrix and stabilised Heusler nanoprecipitates that enhanced phonon scattering. The dimensionless figure of merit ZT of the $\text{ZrNi}_{1.1}\text{Sn}$ was 0.75 at 900 K, which was an approximately 40% improvement from that of the ZrNiSn .

1. Introduction

Half-Heusler (HH) alloys, XYZ (where X= Ti, Zr, Hf; Y=Ni, Co; Z= Sn, Sb), have increasingly attracted attention as potential candidates for thermoelectric applications at high temperatures because they often exhibit maximum Seebeck coefficients between 600 to 1000K [1]. The alloys are also environmental friendly and can be used in large-scale production, compared with other thermoelectric materials such as Pb-Te, Pb-Se and skutterudites because they usually do not contain toxic elements (*e.g.*, Pb) or rare earth metals [2]. The performance of energy conversion for thermoelectric materials can be characterised by the dimensionless figure of merit $ZT = (S^2/\rho\kappa)T$, where the S , ρ , κ and T represent the Seebeck coefficient, thermal conductivity, electrical resistivity and absolute temperature, respectively. The S^2/ρ value is often referred to as the power factor. Thermoelectric half-Heusler alloys usually exhibit rather

large S values, as high as 340 $\mu\text{V/K}$ at 700K [3]. This value is comparable to other thermoelectric materials that perform best in the field [4,5]. Nevertheless, the overall ZT of HH alloys is still comparatively unsatisfactory, mainly because of their rather high κ value.

In the past decade, a promising approach has been proposed as capable of improving the ZT of thermoelectric materials through the introduction of a nanoscale microstructure that could simultaneously reduce the κ and improve the S^2/ρ [6-12]. A similar approach has also been used in HH alloys by compositing with nanoinclusions such as $\gamma\text{-Al}_2\text{O}_3$, ZrO_2 [13-15] and InSb [16,17]. Lately, introducing Heusler (H) nanoprecipitates as a secondary phase within a HH matrix in HH alloys has also been reported as capable of reducing the κ without comprising (or even improving) the power factor, S^2/ρ [18-24]. This latter approach is of particular interest in the present study. The reduction of the κ of the HH alloys containing H-nanoprecipitates has been attributed to enhanced phonon scattering at the HH/H interfaces. However, the effect of the H-nanoprecipitates on the electrical properties S and ρ of HH alloys is still rather ambiguous. Often, improvement of the S in HH alloys was attributed to the carrier filtering mechanism at the HH/H interfaces, as theoretically envisaged by Faleev *et al.* [25]. However, direct experimental evidence of the energy filtering mechanism by the H-nanoprecipitates within an HH matrix is still lacking. More often, difficulties in quantitatively evaluating the effect of the H-nanoprecipitates in HH alloys occurred due to other interference factors, such as the existence of other impurity phases, Sn, oxides, carbides and X_5Sn_3 (where X= Ti, Zr, Hf) that are usually observed in HH alloys prepared by arc-melting and/or powder metallurgy. The impurity phases could strongly affect the electrical properties of the alloys [26]. Owing to this feature, current research is aimed at quantitatively investigating the microstructure of the H-nanoprecipitates and their effect on the thermoelectric properties of HH alloys that were prepared by a direct solidification process using the optical floating zone method. Alloys prepared using this method have been shown to produce significantly less impurity phases and large grain sizes ($> 300 \mu\text{m}$), and they were suitable for this study [26-28]. The evaluation and comparison of the thermoelectric properties was carried out in HH alloys with and without the H-nanoprecipitates. The stability of the thermoelectric properties upon heating and cooling cycles are discussed together with the corresponding microstructure evolution of the H-nanoprecipitates in the alloy. Additionally, the interfacial characteristics of the H-nanoprecipitates and their effect on the thermoelectric properties of the alloy at elevated temperatures will also be discussed in this study.

74 2. Experimental procedure

75 A slightly off-stoichiometric ternary $\text{ZrNi}_{1.1}\text{Sn}$ half-Heusler alloy, *i.e.*, a
76 concentration ratio having excess Ni, was chosen in this investigation. The alloy was
77 first prepared by arc-melting followed by a directional solidification process using the
78 optical floating zone method. Details of the fabrication processes can be found in
79 manuscripts by Kimura *et al.* [27,28]. The phase identification of the alloys was
80 determined by powder X-ray diffraction (XRD, RINT2100, Rigaku, Japan) using
81 $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406$ nm) and electron probe microanalysis (EPMA, Jeol
82 JXA-8900, Japan). The microstructure investigations were performed using scanning
83 electron microscopy (SEM, Jeol JSM-6510, Japan). The observation of the
84 H-nanoprecipitates in the HH alloy and identification of its phase was performed using
85 a scanning transmission electron microscope (STEM, Jeol-2100F, Japan) equipped with
86 energy-dispersive spectroscopy (EDS, Jeol JED-2300T, Japan) and a high-resolution
87 TEM (HRTEM, Jeol-2100F, Japan) operated at 200 kV. The specimens for TEM were
88 first thinned by standard metallography methods to a thickness of 100-150 μm and then
89 further thinned by twin-jet electropolishing using 10-15 V at ~ 233 K (Tenupol-5, Struer,
90 Denmark) in a solution containing methanol and perchloric acid (in a ratio of 8:2).

91 The electrical transport properties of the alloy, *i.e.*, ρ and S , were measured from
92 room temperature to 1073K using a DC four-probe method (ZEM-3, Ulvac-Riko,
93 Japan) under a low pressure of He atmosphere. To evaluate the stability of the electrical
94 transport properties with heating cycles, the measurements were repeated in three
95 consecutive heating and cooling cycles; however, only measurements of the heating
96 cycles were recorded. The cooling rate was estimated to be approximately 0.6 K/s. After
97 the three cycles, the alloy was observed again under STEM-EDS to observe any
98 microstructure changes with respect to the heating-cooling cycles. Differential thermal
99 analysis (DTA, SETARAM, SETSYS Evolution, France) was performed with three
100 heating-cooling cycles to evaluate the possible phase transition in the alloy. The
101 temperature dependence thermal conductivity (κ) of the alloy was deduced based on the
102 relationship $\kappa = d \times \alpha \times C_p$, where d is the density of the alloy, C_p is the specific heat
103 capacity and α is the thermal diffusivity. The d was estimated based on the Archimedes
104 principle, α was measured by the laser flash method (LF, Ulvac-Riko, TC-1200RH,
105 Japan), and C_p was evaluated using differential scanning calorimetry (DSC, Ulvac-Riko,
106 DSC-9400, Japan). The carrier concentration (n) and mobility (μ_H) of the alloy were
107 evaluated at room temperature by the Hall effect measurement using DC four-probe van
108 der Pauw under a 0.6 T magnetic field. The microstructure of ZrNiSn (prepared by the
109 same processes) and its thermoelectric properties [26,27] were also included in this

study for comparison and discussion. The measurement uncertainties for both ρ and S were estimated to about 2 and 3%, respectively. The combined measurement uncertainty for calculating the κ was about 3%. Hence, this yielded to total measurement uncertainty for the ZT to less than 11%.

3. Results and discussion

3.1. Phase identity and microstructure of the ZrNiSn and ZrNi_{1.1}Sn

The XRD profile of the ZrNi_{1.1}Sn is shown in Fig. 1(a). For comparison, the XRD profile of the ZrNiSn half-Heusler alloy has been included in Fig. 1(b). The ZrNi_{1.1}Sn was found to contain mainly two phases, HH as a major phase and H as a minor phase, whereas the ZrNiSn was a nearly single HH phase alloy (with only a small amount of Zr₅Sn₃). Based on the XRD profiles in Fig. 1, lattice parameters of the ZrNi_{1.1}Sn and ZrNiSn alloys for the HH and H phases were estimated, as shown in Table 1. We observed that the a_{HH} of the alloys, 0.6118 and 0.6115 nm, were similar in magnitude. Lattice parameter of the H phase in the ZrNi_{1.1}Sn was relatively larger, $a_H = 0.6267$ nm. The difference between a_{HH} and a_H in the ZrNi_{1.1}Sn resulted in a misfit strain (δ) of 2.4%. SEM observation further confirmed significantly less amounts of other common impurity phase types, *e.g.*, Sn, oxides, carbides and Zr₅Sn₃, as shown in Figs. 1(c) and 1(d). The average grain size in both alloys was found to be well over 500 μ m. The composition analyses from EPMA in Table 1 also show that the alloys are HH phase but with small degree of deviation towards Ni-rich composition, *i.e.*, 1.17 in the ZrNi_{1.1}Sn and 1.09 in the ZrNiSn (see the molar ratio in Table 1). The relatively higher degree of Ni concentration ratio in the ZrNi_{1.1}Sn was caused by the overlapping of the HH matrix and H precipitates. However, the ZrNiSn alloy did not exhibit H precipitation, despite its slightly rich Ni concentration ratio. This result can be seen in the XRD analysis in Fig. 1 and in the TEM observation [24]. The absence and presence of H-phases in the ZrNiSn and ZrNi_{1.1}Sn, respectively, indicate that the solid solubility limit for Ni in the HH phase of ZrNiSn must be below 37.5 at% for the ZrNiSn HH alloy, *i.e.*, ZrNi_{1+x}Ni with $x < 0.17$. The actual solubility limit of Ni in the HH phase of the ZrNiSn could be lower, with x possibly less than 0.09, if the HH matrix was observed at the nanoscale level using HRTEM. This analysis revealed that a high density of nanoscale bands (a few nm wide) containing H lattices were embedded within the HH matrix due to clustering of the excess Ni atoms in the ZrNiSn [24]. This result shows the almost lack of mutual solubility between HH and H phases and confirms the theoretical prediction by Kirievsky *et al.* [29].

146 3.2. Microstructure of Heusler nanoprecipitates in the $\text{ZrNi}_{1.1}\text{Sn}$

147 As mentioned earlier, although the H phase was identified in the XRD profile of the
148 $\text{ZrNi}_{1.1}\text{Sn}$, clear detection by SEM was rather difficult due to limited imaging resolution.
149 Nevertheless, a high density of precipitates embedded within HH matrix of the
150 $\text{ZrNi}_{1.1}\text{Sn}$ alloy was observed using STEM, as shown in the bright field STEM image in
151 Fig. 2(a). The precipitates were mostly platelet (denoted as P1_H , P2_H and P3_H) and disc
152 (denoted as D1_H , D2_H and D3_H) morphologies. The numbers correspond to the three
153 variants that are preferentially orientated within the HH cube orientations, *i.e.*,
154 $\text{P1}_\text{H}/(100)_\text{HH}$, $\text{P2}_\text{H}/(010)_\text{HH}$ and $\text{P3}_\text{H}/(001)_\text{HH}$, and $\text{D1}_\text{H}/(100)_\text{HH}$, $\text{D2}_\text{H}/(100)_\text{HH}$ and
155 $\text{D3}_\text{H}/(100)_\text{HH}$, as shown in Fig. 2(a). The subscripts HH and H refer to half-Heusler and
156 Heusler phases, respectively. The plate and disc morphologies, as well as the
157 preferential $\{001\}_\text{HH}$ cube orientations of the H-nanoprecipitates in the HH alloys, were
158 found to be closely related with the HH/H interfacial coherency and structural
159 anisotropy of the alloy [21]. Most of the platelets were semicoherent, whereas the discs
160 were coherent. Nevertheless, coherent platelets were occasionally observed, but mainly
161 in platelets with thicknesses less than 20 nm. All of the platelets and discs were
162 confirmed as being in the H phase with an average chemical composition determined as
163 $\text{Zr: Ni: Sn} = 28: 45: 27 (\pm 4 \text{ at } \%)$. The composition mapping in Figure 2(b) confirms
164 the relatively higher Ni concentration in contrast with the H-nanoprecipitates and their
165 surrounding HH matrix. Only the edges of the P3_H and D3_H variants exhibited relatively
166 stronger in Ni concentration contrast due to relatively less interference with the HH
167 matrix. The other two variants, P1_H , P2_H , D1_H and D2_H , which were inclined to the
168 beam direction, showed relatively weaker Ni concentration contrast due to the overlap
169 with the surrounding HH matrix. The plate and disc morphologies are common for
170 H-nanoprecipitates and are strongly influenced by the coherency misfit strain and
171 structural anisotropy of the alloy [21]. Most of the H-nanoprecipitates in the alloy were
172 platelets, having a volume fraction estimated to be approximately 10 %. The remaining
173 H-nanoprecipitates were discs that only accounted for approximately 1 % of the volume
174 fraction. The sizes of the platelets were considerably large, with an average size of 330
175 nm long, 20 nm thick and 100 nm wide, whereas the discs were relatively smaller, with
176 a size of ~ 110 nm in diameter and ~ 7 nm thick. For simplicity, the volume fraction and
177 size of the H-nanoprecipitates have been summarised in Table 2. The inter-precipitate
178 spacing of the H-nanoprecipitates was also estimated to be approximately 90 nm. The
179 spacing was comparatively smaller than the X-ray spatial resolution limit (a few μm) of
180 the EPMA, and overlapping of the X-ray interaction volumes between the HH matrix
181 and H-nanoprecipitates would be anticipated during compositional analysis. This result

may explain the relatively higher degree of the Ni concentration ratio in the HH matrix of the alloys (Table 1).

3.3. Electrical transport properties of the $\text{ZrNi}_{1.1}\text{Sn}$ and ZrNiSn

The temperature dependence of the electrical transport properties, *i.e.*, the Seebeck coefficient (S), electrical resistivity (ρ) and power factor (S^2/ρ), of the $\text{ZrNi}_{1.1}\text{Sn}$ in three consecutive heating cycles are shown in Fig. 3. For comparison, the electrical transport properties of the ZrNiSn [27] are also included in Fig. 3.

3.3.1. Seebeck coefficient

Figure 3(a) shows variations the S of the ZrNiSn and $\text{ZrNi}_{1.1}\text{Sn}$ with increasing temperature up to 1073K. The temperature dependence S of the $\text{ZrNi}_{1.1}\text{Sn}$ was shown in three heating cycles, *i.e.*, 1st, 2nd and 3rd. The minus sign of S indicates that the majority of the carriers in the alloys were electrons, *i.e.*, n-type. As revealed in the 1st heating cycle, the variation trend of S behaves noticeably different with increasing temperature, not only from the ZrNiSn but also from the subsequent two heating cycles (2nd and 3rd), despite using the same specimen. At room temperature, the S in the 1st heating cycle was measured to be -208 $\mu\text{V/K}$. The magnitude was greater than 20% higher than the S of the ZrNiSn , *i.e.*, -170 $\mu\text{V/K}$. This improvement was attributed to an energy filtering mechanism due to the metallic H-nanoprecipitates present within the HH matrix [25]. However, the magnitudes of the S in the 1st heating cycle began to gradually decrease with increasing temperature. Beyond 500 K, the decrement was even lower than that of the ZrNiSn . This result shows a gradual loss of effectiveness for the H-nanoprecipitates in the $\text{ZrNi}_{1.1}\text{Sn}$ to improve the S at elevated temperatures. After cooling the $\text{ZrNi}_{1.1}\text{Sn}$ from the 1st heating cycle, subsequent measurements revealed a complete loss of S improvement for the entire temperature range, as shown in the 2nd heating cycle in Fig. 3(a). A similar loss of S improvement was also observed in the 3rd heating cycle. We observed that the magnitudes of S and their variation trends were approximately the same in both the 2nd and 3rd heating cycles, suggesting that stabilisation of S occurred after the 1st heating-cooling cycle. At elevated temperatures, we observed that the magnitudes of the S in the 2nd and 3rd heating cycles were relatively smaller than those of the ZrNiSn . For instance, at 900 K, the S values of the 2nd and 3rd cycles were approximately -175 $\mu\text{V/K}$, which was nearly 10% less than that of the ZrNiSn , *i.e.*, ~190 $\mu\text{V/K}$. This result was surprising because the high-density platelets and discs of the H-nanoprecipitates within the HH matrix in the $\text{ZrNi}_{1.1}\text{Sn}$ (see Fig. 2) not only lost their capability to improve the S but also degraded the S of the alloy at elevated

218 temperature.

219

220 3.3.2. Electrical resistivity

221 The temperature dependence ρ of the ZrNiSn and ZrNi_{1.1}Sn in three heating cycles,
222 1st-3rd cycles, is shown in Fig. 3(b). Similarly to the ZrNiSn, the magnitudes of the ρ of
223 the three heating cycles decreased with increasing temperature, indicating
224 semiconducting behaviour. The ρ values of all three heating cycles were similar in
225 magnitudes and were comparatively smaller than the ρ of the ZrNiSn for the entire
226 temperature range. At room temperature, the ρ of the three heating cycles was
227 approximately 37% smaller than the ρ of the ZrNiSn, which was measured to be $42 \times$
228 $10^{-6} \Omega\text{m}$. At elevated temperatures, however, a relatively smaller ρ value in the three
229 cycles was observed (approximately 30% at 900 K). The relatively smaller magnitudes
230 of ρ in the ZrNi_{1.1}Sn were anticipated because of the high density of metallic
231 H-nanoprecipitates present in the alloy that would increase the carrier concentration (n)
232 and result in a reduction of ρ .

233

234 3.3.3. Power factor

235 Figure 3(c) reveals the temperature dependence of the power factor (S^2/ρ) of the
236 ZrNiSn and ZrNi_{1.1}Sn alloys. Clearly, the power factors of the ZrNi_{1.1}Sn in all three
237 heating cycles, 1st, 2nd and 3rd, were higher than that of the ZrNiSn despite their
238 relatively smaller magnitudes of S . The maximum power factors of the ZrNi_{1.1}Sn in the
239 1st, 2nd and 3rd heating cycles were measured to be 4.1, 4.0 and 3.9 mW/m² at 900K,
240 respectively. There was an approximately 20% improvement from that of the ZrNiSn
241 (*i.e.*, 3.3 mW/m²). Following the analyses shown in Figs. 3(a) and 3(b), the power factor
242 improvement in the ZrNi_{1.1}Sn was primarily caused by the reduction of ρ and not the
243 improvement of S .

244

245 3.4. Microstructure evolution of the H-nanoprecipitates and Seebeck coefficient

246 To elucidate the different variation trends of the S of the ZrNi_{1.1}Sn with increasing
247 temperature, as exhibited in the three heating cycles in Fig. 3(a), the phase constituents
248 and microstructure of the ZrNi_{1.1}Sn after undergoing the three heating-cooling cycles
249 was further investigated by XRD and STEM-EDS analyses. The XRD analysis of the
250 post heating-cooling cycled ZrNi_{1.1}Sn is shown in Fig. 4(a). It revealed that only two
251 phases, HH (matrix) and H (precipitates) were present in the alloy. No new appreciable
252 phase was introduced in the alloy during the cyclic heating-cooling process. However,
253 the XRD peaks associated with the H-phase was noticed to be relatively broader and

254 lower intensity in the post heating-cooling cycled alloy as compared to that in the pre
 255 heating-cooling cycled alloy, see Fig. 4(b). This suggests an increase of overall misfit
 256 coherency strain from the HH/H interface in the post heating-cooling cycled $\text{ZrNi}_{1.1}\text{Sn}$.
 257 As will be seen later, such an increase of coherency strain in the alloy has large effect its
 258 κ . Bright field STEM images in Figs. 5(a) and 5(b) correspond to the post
 259 heating-cooling cycled H-nanoprecipitate microstructure in the $\text{ZrNi}_{1.1}\text{Sn}$ at low and
 260 high magnifications, respectively. Note that Fig. 5(a) was taken at the same
 261 magnification as Fig. 2(a). Clearly, the size of the H-nanoprecipitates in Fig. 5(a) was
 262 much smaller compared with those prior to the heating-cooling cycles, as shown in Fig.
 263 2(a). The relatively large platelets and discs of the H-nanoprecipitates no longer remain
 264 throughout the microstructure of the alloy. Figure 5(b) reveals that most of these
 265 size-reduced H-nanoprecipitates were composed of disc-shaped (indicated as ND1_H ,
 266 ND2_H and ND3_H), ellipsoidal (indicated as E1_H , E2_H and E3_H) and spherical (indicated
 267 as S_H) morphologies. The average size of the discs was estimated to be approximately
 268 20 nm in diameter and 3 nm thick, whereas the ellipsoids and spheroids (S_H) were even
 269 smaller, with an average diameter of less than 5 nm. Similarly, the discs and ellipsoids
 270 of the H-nanoprecipitates were also found to be preferentially orientated parallel to the
 271 $\{001\}_\text{HH}$ cube orientation, which was comprised of three variants, *i.e.*, $\text{ND1}_\text{H}/(100)_\text{HH}$,
 272 $\text{ND2}_\text{H}/(010)_\text{HH}$ and $\text{ND3}_\text{H}/(001)_\text{HH}$ and $\text{E1}_\text{H}/(100)_\text{HH}$, $\text{E2}_\text{H}/(010)_\text{HH}$ and $\text{E3}_\text{H}/(001)_\text{HH}$.
 273 An estimation of the total volume fraction of the H-nanoprecipitates was $9 \pm 3 \%$, with
 274 the discs accounting for more than two thirds of the total volume fraction.

275 Much efforts on analysing possible variation of composition on the post
 276 heating-cooling cycled H-nanoprecipitates have been carried out and the result has not
 277 been satisfactory because of overlapping of the X-ray interaction volume between the
 278 extremely small H-nanoprecipitates and the surrounding HH matrix. For instance, only
 279 some of the relatively larger disc-shaped H-nanoprecipitates exhibit relatively stronger
 280 Ni concentration contrast and their average composition was determined to be Zr: Ni:
 281 Sn = 32: 39: 29 (± 4 at%), see arrows in Fig. 5(c). It is unsure the higher degree of
 282 composition deviation from the H-phase stoichiometric composition than that of the pre
 283 heating-cooling cycled platelet H-nanoprecipitates, *i.e.* Zr: Ni: Sn = 28: 45: 27 (at%), is
 284 due to the overlapping effect or actual composition variation. Nevertheless, the rather
 285 diffuse post heating-cooling H-nanoprecipitates as seen in Fig. 5(b) may also suggest
 286 their composition, at least adjacent to the HH/H interface, may be relatively leaner in Ni
 287 concentration than the ‘core’ of the precipitates.

288 For ease of comparison, the volume fractions and sizes of the disc, ellipsoid and
 289 sphere H-nanoprecipitates are summarised in Table 3. Despite the greatly reduced size,

the total volume fraction of the post heating-cooling cycled H-nanoprecipitates was slightly smaller than those prior to the heating-cooling cycles ($\sim 11 \pm 2\%$, Table 2). Consequently, the n in the post heating-cooling cycled $\text{ZrNi}_{1.1}\text{Sn}$, measured to $7.1 \times 10^{25} \text{ m}^{-3}$, was also less than that prior to the heating-cooling cycles, measured to $10.1 \times 10^{25} \text{ m}^{-3}$.

We observed that the changes of n before and after the heating-cooling cycles in the $\text{ZrNi}_{1.1}\text{Sn}$ might not be sufficient to describe the varying behaviour of S among the three heating cycles (Fig. 3(a)), although the n could be inversely related to S for heavily doped HH alloys as shown in the following equation (1) [30],

$$S = \frac{8\pi^2 k_B^2}{3qh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (1)$$

where k_B , T , q , h , m^* and n represent the Boltzman constant, absolute temperature, carrier charge, Plank constant, carrier effective mass and carrier concentration, respectively. For instance, at room temperature, the relatively higher n (*i.e.*, $10.1 \times 10^{25} \text{ m}^{-3}$) in the prior heating-cooling cycled $\text{ZrNi}_{1.1}\text{Sn}$ exhibits a large magnitude of S (*i.e.*, -208 V/K of the 1st heating cycle in Fig. 3(a)), whereas the relatively lower n (*i.e.*, $7.1 \times 10^{25} \text{ m}^{-3}$) in the post heating-cooling cycle of the same alloy results in a relatively smaller magnitude of S (*i.e.*, $\sim -175 \text{ } \mu\text{V/K}$ of the 2nd and 3rd heating cycles in Fig. 3(a)). As mentioned earlier, the unusually large improvement of the magnitude of the S of the $\text{ZrNi}_{1.1}\text{Sn}$ at room temperature, as seen in the 1st heating cycle (Fig. 3(a)), was attributed to the low energy carrier filtering mechanism [25]. The band bending potential (V_B) created at the interface between the semiconducting HH matrix and the metallic H-nanoprecipitates was envisaged to filter out those low energy carriers, thus resulting in an improvement of S . With increasing temperature, however, the gradual reduction of S in the 1st heating cycle indicated a gradual loss of the band bending potential at the HH/H interface that was consequently insufficient to filter the low energy carriers. The magnitude of V_B at the HH/H interface was predicted to depend on two factors: the size of the precipitates and the interfacial properties between the matrix and the precipitates [25]. In the former case, smaller precipitates favour a larger V_B that may result in an increased carrier filtering probability and a larger improvement in the magnitude of S [25]. However, such an improvement of S with precipitate size reduction was not observed in the present case because no improvement of S was observed in the 2nd and 3rd heating cycles despite a significant size reduction of the H-nanoprecipitates in the post heating-cooling cycled microstructure (Figs. 3(a) and 5). This disagreement may originate from a change in the interfacial characteristics between the HH matrix and the H-nanoprecipitates as a result of the heating-cooling cycles. We observed that the

microstructure of the H-nanoprecipitates prior to the heating-cooling cycles appeared to be relatively sharper (Fig. 2) than those after the heating-cooling cycles (Fig. 5). The sharp and diffuse H-nanoprecipitates were found to originate from different distributions of strain at the HH/H interface, as further revealed by HRTEM observation (Fig. 6).

330

3.4.1. Characteristics of the HH/H interface before and after the heating-cooling cycles

The HRTEM images in Figs. 6(a)-(c) and 6(d)-(f) reveal the lattice structure of the H-nanoprecipitates embedded within the HH matrix of the $\text{ZrNi}_{1.1}\text{Sn}$ before and after the heating-cooling cycles, respectively. They were observed along $[110]_{\text{HH}}$, as indicated by the fast Fourier transformed (FFT) patterns (insets in Figs. 6(a) and 6(d), respectively). Figure 6(a) shows the lattice structure of an edge-on platelet H-nanoprecipitate (P3_H) with a sharp HH/H interface. The P3_H in this case was coherent with its surrounding HH matrix, as shown in the inverse-FFT (IFFT) analyzed image in Fig. 6(b). For simplicity, the HH/H interface has been highlighted with broken lines in the figure. We observed that the coherency strain (dark contrast with a length scale of approximately 2.5 nm) was mainly concentrated along the HH/H interfaces. Little strain contrast was observed in the HH matrix adjacent to the HH/H interfaces. We observed that the coherency strain field at the HH/H interface was not evenly distributed but mainly confined within the P3_H H-nanoprecipitate, suggesting that the H-nanoprecipitates are relatively softer than the HH matrix. The sharp HH/H interface as seen in Figs. 6(a)-(c) is believed capable of inducing V_B along the interface and acting as a filter for the low energy charge carriers, eventually resulting in an improved S .

In contrast, the lattice structure of those H-nanoprecipitates with a diffuse HH/H interface is shown in Fig. 6(d). Similarly, the figure is viewed along $[110]_{\text{HH}}$ (inset of FFT pattern in Fig. 6(d)). Some of the diffuse H-nanoprecipitates, which appeared as discs (D1_H and D3_H), ellipsoidal (E1_H) and spherical (S_H), are indicated by arrows, and their approximated HH/H interfaces are highlighted with white broken lines. All of the H-nanoprecipitates in the figure were coherent, and a coherency strain can be seen encompassing all of the H-nanoprecipitates, as shown by the dark contrast (coherency strain contrast) surrounding the edge-on ND3_H in Fig. 6(d) and in the IFFT images in Figs. 6(e)-(f) that reveal a coherent HH/H interface. The coherency strain along the approximate HH/H interface, however, appeared to spread out with a length scale up to 5 nm across the interface (arrows in Fig. 6(f)). The diffuse HH/H interface result from remnants of the diffusion paths of Ni atoms away from or into the H-nanoprecipitates

during the heating-cooling cycles. During the heating of the $\text{ZrNi}_{1.1}\text{Sn}$ with a miscibility gap between the pseudo binary HH (ZrNiSn) and H (ZrNi_2Sn) phases, a sharp HH/H interface at room temperature was anticipated to transform into a diffuse HH/H interface as the temperature approached the dissolution temperature of the H phase within the HH matrix [31]. Some of the diffusiveness of the HH/H interface might have remained as the alloy was cooled to room temperature during the measurement. Hence, such a diffuse HH/H interface may result in a reduction or disappearance of V_B at the interfaces. Consequently, the interface is unable to filter the low energy charge carriers and fails to improve S , as exhibited by the gradual reduction of the magnitude of S in the 1st heating cycle with increasing temperature and by the complete loss of S improvement in the 2nd and 3rd heating cycles of the $\text{ZrNi}_{1.1}\text{Sn}$ (Fig. 3(a)).

Changing the interfacial characteristic between the HH and H phases upon the heating-cooling cycles may also result in variations of carrier mobility (μ_e) in the alloys. For instance, prior to the heating-cooling cycles, the μ_e of the alloy was measurement to be $1.99 \times 10^{-3} \text{ m}^2/\text{Vs}$, which increased to $2.28 \times 10^{-3} \text{ m}^2/\text{Vs}$ after two heating-cooling cycles. The increment of μ_e could be caused by changing the HH/H interface coherency from semicoherent platelets before the heating-cooling cycles (Fig. 2) into coherent discs, ellipsoids and spheroids after the 1st heating-cooling cycle (Fig. 5).

3.5. Stability of the H-nanoprecipitates and variations of the Seebeck coefficient

The drastic size reduction of the H-nanoprecipitate microstructures in the $\text{ZrNi}_{1.1}\text{Sn}$ after the 1st heating-cooling cycle (Figs. 2 and 5, respectively) indicates that phase dissolution must be occurring during heating to 1073 K. The phase stability of the H-nanoprecipitates was evaluated using DTA, as shown in Fig. 7. Variations of heat flow in the $\text{ZrNi}_{1.1}\text{Sn}$ with increasing temperature up to 1273 K are shown in three heating (solid lines) and cooling (broken lines) cycles. Upon heating, the 1st heating cycle exhibits a large upward heat flow curve that is considerably different from the 2nd and 3rd heating trends, possibly caused by simultaneous and/or continuous coarsening and dissolution of the H-nanoprecipitates. Nevertheless, small exothermic peaks with onset peaks were observed at approximately 1067 K in the 2nd and 3rd heating cycles (inset in Fig. 7). This temperature most likely corresponds to the H precipitate dissolution temperature because the remaining relatively large platelets and discs of H-nanoprecipitates (Fig. 2) were not observed in the alloy after the heating-cooling cycles. The large platelets and discs of H-nanoprecipitates should be dissolved around the 1067 K. All three cooling cycles of the $\text{ZrNi}_{1.1}\text{Sn}$ reveal similar trends of heat flow variations. In this case, however, much smaller peaks (endothermic) were observed and

their onset peak temperature was about 1062 K (inset in Fig. 7). This temperature most likely corresponds to the spinodal decomposition temperature where the single phase (HH-H) solid solution decomposes into two phases containing HH as matrix and H as precipitates.

In Fig. 7, the different behaviour of the heat flow in the 1st heating cycle is compared with that of the 2nd and 3rd. Although insignificant variations of heat flow upon cooling among the three cycles suggested stabilisation of the H-nanoprecipitate microstructure, this stabilisation must be established from the 1st heating-cooling cycle because the alloy was heated to beyond the precipitate dissolution temperature (*i.e.*, 1067 K in this case) and cooled to below the phase decomposition temperature (*i.e.*, ~1050 K). The stabilisation of the H-nanoprecipitate microstructure in the alloy upon the heating and cooling cycles must corresponded to a minimisation of free energy, *i.e.*, $\Sigma A_i \gamma_i + \Delta G_s = \text{minimum}$, in the alloy system [33]. The terms $\Sigma A_i \gamma_i$ and ΔG_s refer to the interfacial energy and the coherent elastic strain energy of the H-nanoprecipitates, respectively. The terms A and γ represent the interface area and the free energy per unit area of the H-nanoprecipitates, respectively. Such microstructure stabilisation of the H-nanoprecipitates within the HH matrix should correspond to and be consistent with the thermoelectric stabilisation, *i.e.*, the ρ , S and power factor stabilised after the 1st heating-cooling cycle (Fig. 3).

416

3.6. Thermal transport properties

The temperature dependence of the calculated κ of the ZrNiSn and ZrNi_{1.1}Sn alloys is shown in Fig. 8(a). Only two heating cycles, *i.e.*, the 1st and 2nd, are shown in the figure. Nevertheless, the κ in the 3rd cycle will be similar to that in the 2nd because the microstructure of the H-nanoprecipitates would be similar in the 2nd and 3rd heating-cooling cycles due to the microstructure stabilisation. Clearly, the magnitudes of κ of the ZrNi_{1.1}Sn in the 1st heating cycle did not decrease much from that of the ZrNiSn, although a high density of H-nanoprecipitate platelets and discs was present in the alloy (Fig. 2). In fact, the magnitudes of the κ values in the 1st heating cycle increased slightly higher than those of the ZrNiSn at elevated temperature. Namely, the κ value (1st cycle) ≈ 7 W/mK at 900K, compared to 6.5 W/mK for the ZrNiSn. However, a significant reduction of κ was observed in the subsequent 2nd heating cycle, *e.g.*, an approximately 17% reduction from 6.3 W/mK in the ZrNiSn to 5.7 W/mK in the ZrNi_{1.1}Sn at room temperature. An even larger percentage reduction was observed with increasing temperature, *e.g.*, 23% reduction from 6.4 W/mK in the ZrNiSn to 4.9 W/mK in the ZrNi_{1.1}Sn at 900 K. The reduction of κ of the ZrNi_{1.1}Sn in the 2nd heating cycle was

433 attributed to the significant density increase of the H-nanoprecipitates per unit volume.
 434 This density increase causes their size and inter-precipitate spacing to be greatly
 435 reduced due to the dissolution and spinodal decomposition processes during the
 436 heating-cooling cycles. As a result, enhanced phonon scattering and eventual reduction
 437 of the κ in the alloy were observed.

438 The very slight reduction of the κ of the ZrNi_{1.1}Sn in the 1st heating cycle and
 439 drastic reduction of the κ in the 2nd cycle were rather interesting because they indicated
 440 that not all H precipitates with nanosize features are capable of providing large phonon
 441 scattering enhancement that resulted in a reduction of κ . One must take into account the
 442 correlation between the phonon mean free path (l_{ph}) and the inter-precipitate spacing of
 443 the H-nanoprecipitates. As shown earlier in Tables 2 and 4, the average inter-precipitate
 444 spacing of the H-nanoprecipitate platelets and discs before the heating-cooling cycles
 445 was approximately 90 nm (Fig. 2), whereas it reduced to only ~10 nm after the
 446 heating-cooling cycles (Fig. 5). The l_{ph} of the ZrNi_{1.1}Sn was estimated using the
 447 classical kinetic theory [34],

$$448 \quad l_{ph} = \frac{3\kappa_l}{C_v v_s}, \quad (2)$$

449 where the κ_l , C_v and v_s represent the lattice component of κ , volumetric heat capacity
 450 and average velocity of sound, respectively. The C_v = density x C_p . The density was
 451 estimated as 7.58 g/cm³, and the C_p values at 300K for the 1st and 2nd heating cycles
 452 were 0.288 and 0.268 J/gK, respectively. The v_s was taken as equal to 3481 ms⁻¹ for the
 453 ZrNi_{1.05}Sn alloy [34]. Here, the temperature dependence of the magnitudes of κ_l have
 454 been deduced based on $\kappa_l = \kappa - \kappa_e$. The κ_e is the electronic component of κ and can be
 455 calculated following the Wiedemann-Franz law: $\kappa_e = (LT)/\rho$. The symbol L is the
 456 Lorentz number and was assumed to be 1.6 x10⁻⁸ W Ω K⁻² [35]. T is the absolute
 457 temperature and ρ is electrical resistivity (Fig. 3(b)). The calculated temperature
 458 dependence κ_l and κ_e of the ZrNi_{1.1}Sn and ZrNiSn alloys are shown in Fig. 8(b). We
 459 observed that κ was dominated by κ_l in both alloys. The magnitudes of κ_l of the
 460 ZrNi_{1.1}Sn in the 1st heating cycle was similar to that of the ZrNiSn in the entire
 461 temperature range but were relatively smaller in the 2nd heating cycle. Using the
 462 magnitudes of κ_l at room temperature in the 1st and 2nd heating cycles, 5.5 and 5.0
 463 W/mK, respectively, their corresponding l_{ph} values were calculated as equal to 2.2 and
 464 2.1 nm, respectively. The calculated l_{ph} was significantly smaller (~40 times smaller)
 465 than the inter-precipitate spacing (~90 nm) of the platelet and disc H-nanoprecipitates,
 466 as seen in Fig. 2. Because the coherency strain around the platelet and disc
 467 H-nanoprecipitates has a rather small length scale (~2.5 nm from the sharp HH/H

interface, Figs. 6(a)-(c)), relatively less phonon scattering was anticipated. Hence, no or less reduction of the κ was observed in the in the 1st heating cycle. On the other hand, the l_{ph} was much closer in magnitude to the inter-precipitate spacing (~10 nm) of those post heating-cooling cycled H-nanoprecipitates, as seen in Fig. 5. Together with a relatively larger coherency strain at the diffuse HH/H interface (length scale up to approximately 5 nm), the post heating-cooling cycled microstructure of the H-nanoprecipitates would be more likely to provide stronger phonon scattering. Therefore, a larger κ reduction was observed.

3.7. Dimensionless figure of merit, ZT .

The temperature dependence of the dimensionless figure of merit ZT of the $ZrNi_{1.1}Sn$ in the 1st and 2nd heating cycles and of the $ZrNiSn$ are shown in Fig. 9. The ZT of the $ZrNi_{1.1}Sn$ in the 1st cycle shows no visible improvement compared to that of the $ZrNiSn$. The maximum ZT of the $ZrNi_{1.1}Sn$ in the 1st cycle was 0.54 at 900K, compared to 0.53 for the $ZrNiSn$ at 800K. On the other hand, a significant improvement of ZT was observed in the 2nd heating cycle of the $ZrNi_{1.1}Sn$, particularly at elevated temperature, *i.e.*, 0.75 at 900K. This improvement was an approximately 40% increment compared with those of the 1st cycle and the $ZrNiSn$. This large improvement of ZT of the $ZrNi_{1.1}Sn$ in the 2nd cycle was mainly caused by both improvement of the power factor and reduction of the κ . To the authors' knowledge, a ZT up to 0.75 may be the highest value among ternary HH alloys, and it is comparable if not better than other quaternary and heavy element-added HH alloys [14,36-39]. This result shows that the introduction of H-nanoprecipitates into HH alloys is an effective approach to improve thermoelectric properties, in agreement with previous reports [21-23]. We also observed that a maximum of the ZT of the $ZrNi_{1.1}Sn$ in both the 1st and 2nd heating cycles occurs at 900 K, whereas it occurs at 800 K for the $ZrNiSn$. This result shows that the presence of the H-nanoprecipitates is also capable of shifting the maximum ZT to a relatively higher temperature in HH alloys. Nevertheless, the current study suggests that the introduction of H-nanoprecipitates into HH alloys is capable of improving the ZT of the alloys.

4. Conclusions

The microstructure and thermoelectric stability of a $ZrNi_{1.1}Sn$ HH alloy containing a high density of H-nanoprecipitates has been investigated in this study. Several important findings have been concluded as follows:

- 1) At room temperature, a large improvement of S (1st cycle) was observed in the $ZrNi_{1.1}Sn$ compared with the $ZrNiSn$. The improvement was attributed to the carrier

504 filtering mechanism at the sharp HH/H interface. However, the improvement
 505 reduced with increasing temperature.

506 2) A complete loss of S improvement and even degradation of the S of the alloy were
 507 observed in the subsequent 2nd and 3rd heating cycles. This result might be caused by
 508 a complete loss of the carrier filtering effect due to the formation of a diffuse HH/H
 509 interface.

510 3) The stabilisation of S in the $\text{ZrNi}_{1.1}\text{Sn}$ after the 1st heating-cooling cycle corresponded
 511 to the microstructure stabilisation of the H-nanoprecipitates upon heating beyond
 512 the dissolution temperature (1067 K) and cooling below the spinodal decomposition
 513 temperature ($\sim 1050\text{K}$).

514 4) The presence of the H-nanoprecipitates resulted in reduction of the ρ of the
 515 $\text{ZrNi}_{1.1}\text{Sn}$.

516 5) The power factor of the $\text{ZrNi}_{1.1}\text{Sn}$ containing H-nanoprecipitates improved to
 517 approximately 20% higher than that of the ZrNiSn without H-nanoprecipitates. The
 518 improvement was mainly caused by the reduction of ρ and not by the increment of
 519 S .

520 6) The large reduction of the κ of the $\text{ZrNi}_{1.1}\text{Sn}$ was found in the 2nd heating cycle due
 521 to a drastic reduction of the H precipitate size (<20 nm in diameter) and
 522 inter-precipitate spacing (~ 10 nm), as well as to the relatively larger length scale of
 523 the strain field around the diffuse HH/H interfaces (up to 5 nm) that provided
 524 relatively stronger enhancement for phonon scattering.

525 7) The ZT of the $\text{ZrNi}_{1.1}\text{Sn}$ (2nd cycle) was 0.75 at 900 K. This result was an
 526 approximately 40% improvement compared with the ZrNiSn containing no
 527 H-nanoprecipitates.

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612 the post heating-cooling cycled H-nanoprecipitates microstructure. See texts for details.

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Table 3: Size, volume fraction and inter-precipitate spacing of the H-nanoprecipitates in ZrNi_{1.1}Sn after undergoing three heating-cooling cycles

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 732 alloys.

Alloys	Lattice parameters (nm)		Chemical composition (at%)			Molar ratio
	a_{HH}	a_{H}	Zr	Ni	Sn	Zr : Ni : Sn
$\text{ZrNi}_{1.1}\text{Sn}$	0.6118	0.6270	30.5	37.5	32.0	0.95 : 1.17 : 1
ZrNiSn	0.6115	-	31.2	35.9	32.9	0.95 : 1.09 : 1

733

734

735 Table 2: Size, volume fraction, and inter-precipitate spacing of the H-nanoprecipitates in
 736 the $\text{ZrNi}_{1.1}\text{Sn}$ prior to heating-cooling cycles

Heusler nanoprecipitates	Volume fraction (%)	Average size (nm)			Inter-precipitate spacing (nm)
		l	t	w	
Platelets	$\sim 10 \pm 1$	326	19	96	89.6
Discs	$\sim 1 \pm 1$	112	7	-	

737 l , t and w denote length, thickness and width of the precipitates.

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740 Table 3: Size, volume fraction and inter-precipitate spacing of the H-nanoprecipitates in
 741 $\text{ZrNi}_{1.1}\text{Sn}$ after undergoing three heating-cooling cycles

Heusler nanoprecipitates	Volume fraction (%)	Average size (nm)		Inter-precipitate spacing (nm)
		l	t	
Discs	$\sim 7 \pm 2$	18	3	9.6
Ellipsoids/ spheres	$\sim 2 \pm 1$	4	-	

742 l and t denote length and thickness of the H-nanoprecipitates.

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