Preparation of ZrNiSn half-Heusler compounds with crystalline alignment by unidirectional solidification in short-duration microgravity and their thermoelectric properties

H Nagai1, R Muroi2 and T Okutnai2
1National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, 305-8565, Japan
2Graduate School of Environment and Information Sciences, Yokohama National University (YNU), 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
E-mail: hideaki-nagai@aist.go.jp

Abstract. A ZrNiSn half-Heusler compound was prepared by unidirectional solidification in short-duration microgravity. When a ZrNiSn half-Heusler pellet with Zr: Ni: Sn = 1:1:1 (in mole) was solidified in microgravity (m-g) by two different cooling systems, the sample solidified in m-g had a different crystallographic alignment of ZrNiSn phase along the cooling direction. However, both sample solidified in normal gravity (1-g) had no crystalline alignment. The solidified sample in m-g had higher electrical conductivity along the cooling direction than perpendicular to the cooling direction, although these samples did not exhibit Seebeck coefficient anisotropy. This electrical conductivity anisotropy was found to be affected by crystalline alignment of the sample. The thermal conductivity was also affected by the structural difference of the sample.

1. Introduction
Ternary intermetallic compounds of general formula MNiSn (M=Ti, Zr, Hf), referred to as the half-Heusler compounds, have semiconducting properties with a band structure and have been of interest due to their potential as thermoelectric materials [1, 2]. The half-Heusler compounds usually have been prepared by arc-melting and sintering the crushed arc-melting sample because it is difficult to prepare a sample with uniform composition and ordering of the crystal structure due to phase separation. Therefore the obtained samples had no crystallographic orientation, and the research focus has been to improve the thermoelectric properties of these samples by changing composition and annealing condition.

Previously, we succeeded in directly preparing the cubic crystal system samples with <111> crystalline alignment, such as TbFe2 and SmFe3, by unidirectional solidification in short-duration microgravity [3-5]. The samples with crystallographic alignment had higher magnetostrictive properties than those with random orientation. ZrNiSn half-Heusler compounds are cubic crystal systems, and it is possible to synthesize samples with crystallographic alignment by using this technique. In this study, we investigated the synthesis of ZrNiSn half-Heusler compounds with crystallographic alignment by unidirectional solidification in short-duration microgravity and measured the thermoelectric properties of the samples.
2. Experimental

Starting samples of ZrNiSn were prepared by arc-melting from the constituent elements (Zr:Ni:Sn=1:1:1[mole]). Zr and Ni ingots were supplied by Rare Metallic Co., Ltd. (Zr 99.9% and Ni 99.99% purity), and Sn ingots (99.999% purity) were supplied by Kishida Chemical Co., Ltd. Because it is difficult to melt the arc-melted samples completely due to the mixture of the components with high melting points (Zr-Sn alloys), the arc-melted samples were ground, and the pellets made from this powder were annealed at 1273 K in H₂ atmosphere to eliminate of those components by solid-state reaction. These pellets were set on 2 different unidirectional solidification systems. In system (1), the sample directly contacts the copper chill block; in system (2), the sample indirectly contacts the copper plate through a quartz glass tube (figure 1). The pellet was put in the quartz glass tube; the tube was then evacuated and filled with Ar gas up to a pressure of 0.1 MPa. The sample was heated in an infrared furnace at around 1673 K until it was completely melted. The sample was then unidirectionally solidified by contact with the copper block or plate. Microgravity experiments were performed using a 10m drop tower at AIST and a 2m drop tower at YNU (figure 2). The resultant samples were 8 to 10 mm in diameter and about 2mm thick.

The crystalline structures of the obtained samples were analyzed by X-ray diffraction (XRD; MAC Science, MXP3 or RIGAKU, RINT2500), and the microstructure and element distribution of the samples were analyzed by optical microscopy (OM; OLYMPUS, BX51M) and scanning electron microscopy with energy dispersive X-ray spectrometer (SEM; JEOL, JSM-5400 or JSM-6390LV). The thermoelectric properties of the samples were evaluated by electrical conductivity, Seebeck coefficient, and thermal conductivity. The electrical conductivity and Seebeck coefficient of the sample were measured by an electrical conductivity and Seebeck coefficient measurement system (Ozawa Science, RZ2001i); the thermal conductivities of the samples were measured by the laser-flash method (ULVAC—RIKO, TC-7000).

Figure 1. Schematic diagram of unidirectional solidification systems
3. Results and Discussion

Figure 3 depicts the element distribution of the arc-melted sample and typical samples unidirectionally solidified in 1-g (1-g sample) and m-g (m-g sample). The arc-melted samples had large Ni-poor regions, which XRD determined were mixtures of ZrNiSn and Zr-Sn alloys. The 1-g samples had more uniform composition distributions, and the m-g samples had almost uniform composition distributions.
Figure 4 presents typical contact surface and cross section photos of the 1-g sample and the m-g sample. Both samples contained many small bubbles. Analysis of the m-g sample revealed sheet-like structure grains aligned in the cooling direction. In contrast, the 1-g sample had random columnar and granular grain structures.

![Contact surface and cross section photos](image)

**Figure 4.** Microstructure of contact surface and cross section of the 1-g sample and m-g sample
(a-1): Contact surface of m-g sample, (a-2): Cross section of m-g sample
(b-1): Contact surface of 1-g sample, (b-2): Cross section of 1-g sample

Figure 5-(a) plots the XRD results of the contact surface of the 1-g sample and m-g sample acquired by using system (1). The 1-g sample had a pattern similar to that of the arc-melted sample and had no crystalline alignment along the cooling direction. The m-g sample had very strong (111) and (222) peaks. This result indicates that the m-g sample prepared using system (1) had a <111> crystallographic alignment of ZrNiSn phase along the cooling direction. Because Microgravity conditions produce a motionless and forceless melt and because the densest crystal plane in cubic system is [111], we obtained a sample with [111] alignment by using system (1). Neither sample had a crystalline alignment perpendicular to the cooling direction.

Figure 5-(b) plots the XRD results of the contact surface of the 1-g sample and m-g sample acquired by using system (2). The m-g sample had very strong (200) and (400) peaks, but the 1-g sample had no crystalline alignment along the cooling direction. This demonstrates that the m-g sample produced using system (2) had <100> crystallographic alignment along the cooling direction. When the sample was solidified using system (2), a ZrO$_2$ layer was formed on the contact surface of the sample with quartz glass. The obtained ZrO$_2$ layers had a monoclinic crystal structure, and that of the 1-g sample exhibited random alignment. However, that of the m-g sample exhibited strong (011), (022) and (033) peaks, suggesting that the ZrO$_2$ layer on the m-g sample had <011> crystallographic alignment. Because monoclinic ZrO$_2$ is transformed to high-temperature phase (tetragonal or cubic ZrO$_2$) when the sample melt solidifies, the aligned ZrO$_2$ layer of the high-temperature phase might be induced to produce a m-g sample with <100> crystallographic alignment along the cooling direction.
Figures 6 and 7 plot the electrical conductivity ($\sigma$) and Seebeck coefficient (S) of the 1-g and m-g sample. Parameters $\sigma$ and S of the m-g sample were measured along the cooling direction and perpendicular to the cooling direction, and those of the 1-g sample were only measured along the cooling direction because the 1-g sample had no crystalline alignment. Both m-g samples prepared by different systems had higher electrical conductivities along the cooling direction than perpendicular to the cooling direction, and those of the m-g sample along cooling direction were higher than those of the 1-g sample. The electrical conductivity anisotropy of the m-g sample obtained using system (2) exceeded that of the m-g sample obtained using system (1). These results suggested that this electrical conductivity anisotropy was affected by the crystalline alignment of the sample. In contrast, the sample’s Seebeck coefficient did not exhibit any clear anisotropy, although there were differences between the 1-g and the m-g sample and differences of the cooling direction.

Figure 5. XRD result of the contact surface of the 1-g and m-g sample produced by different systems
(a): Sample solidified by system (1), (b): Sample solidified by system (2)

Figure 6. Electrical conductivity of the 1-g and m-g sample solidified by different systems
(a): Sample solidified by system (1), (b): Sample solidified by system (2)
Figure 7. Seebeck coefficient of the 1-g and m-g sample solidified by different systems  
(a): Sample solidified by system (1),  
(b): Sample solidified by system (2)

Figure 8 plots the temperature dependence of the thermal conductivities and phonon thermal conductivities of the 1-g and m-g samples along the cooling direction solidified using system (2).

The thermal conductivity of the material, $\lambda$, is the sum of the electron and phonon contributions:

$$\lambda = \lambda_{\text{electron}} + \lambda_{\text{phonon}},$$

where $\lambda_{\text{electron}}$ is the electron thermal conductivity and $\lambda_{\text{phonon}}$ is the phonon thermal conductivity. The electron contribution to the thermal conductivity can be estimated by the Wiedemann-Franz law:

$$\lambda_{\text{electron}} = L \cdot \sigma \cdot T,$$

where $L$ is Lorenz number, which is $2.445 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ for a degenerate free-electron gas system, and $T$ is the absolute temperature. The thermal conductivity of the 1-g sample was less than those reported by Shen et al.[6] and Kawaharada et al.[7] because this sample contained many small bubbles, as indicated in figure 4. The m-g sample also contained many small bubbles, and the thermal conductivity was less than that of the 1-g sample. The m-g sample had a lower phonon contribution to the thermal conductivity than that of the 1-g sample. This lower phonon contribution of the m-g sample was considered due to phonon scattering by combination with bubbles and Ni site vacancies oriented by crystalline alignment.

Figure 8. Thermal conductivity and phonon thermal conductivity of the 1-g and m-g sample solidified by system (2)
Table 1 lists the dimensionless figure of merit $ZT = S^2 \sigma T / \lambda$ of the 1-g and m-g samples prepared using system (2). The $ZT$ values of the m-g sample were about twice those of the 1-g sample because of increased electrical conductivity and reduced thermal conductivity. The maximum $ZT$ of the m-g sample was 0.35 at 900 K. The $ZT$ values of the 1-g sample were lower than those reported by Shen et al.[6] and Kawaharada et al.[7] because of lower Power factor ($= S^2 \sigma$) of the 1-g sample. The $ZT$ values of the m-g sample at 900 and 1000 K were higher than the reference ones, although those of the m-g sample below 800 K were similar to those of the references.

| Temperature (K) | Sample | 1-g sample | m-g sample | Ref.[6] | Ref.[7] |
|-----------------|--------|------------|------------|--------|--------|
| 600             |        | 0.04       | 0.09       | 0.09   | 0.12   |
| 700             |        | 0.07       | 0.14       | 0.15   | 0.18   |
| 800             |        | 0.13       | 0.23       | 0.19   | 0.23   |
| 850             |        |            |            |        | 0.24   |
| 900             |        | 0.18       | 0.35       | 0.21   |        |
| 1000            |        | 0.12       | 0.32       | 0.21   |        |

4. Conclusion
A ZrNiSn half-Heusler sample with crystallographic alignment was prepared by unidirectional solidification in microgravity. The sample with crystallographic alignment exhibited the electrical conductivity anisotropy, and the thermal conductivity was affected by the structural difference of the sample. The $ZT$ of the sample with crystallographic alignment exceeded those of other samples, and the maximum $ZT$ was 0.35 at 900 K.

References
[1] Aliev F G, Kozyrkov V V, Moshchalkov V V, Scolozdra R V and Durczewski K 1990 Z. Phys. B 80 353
[2] Uher C, Yang J and Hu S 1999 Phys. Rev. B 59 8615
[3] Okutani T, Nakata Y and Nagai H 2004 Ann. N.Y. Acad. Sci. 1027 158
[4] Okutani T, Nakata Y and Nagai H 2005 Microgravity Sci. and Technol. 16 84
[5] Okutani T, Nagai H, Mamiya M, Shibuya M and Castillo M 2006 Ann. N.Y. Acad. Sci. 1077 146
[6] Shen L, Goto T, Hirai T, Yang J, Meisner G P and Uher C 2001 Appl. Phys. Lett. 79 4165
[7] Kawaharada Y, Uneda H, Muta H, Kurosaki K and Yamanaka S 2004 J. Alloys Comp. 364 59