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研究課題名（和文） Multiscale microstructure engineering and the development of high performance, environmental friendly, low cost and thermally stable half-Heusler thermoelectric materials

研究課題名（英文） Multiscale microstructure engineering and the development of high performance, environmental friendly, low cost and thermally stable half-Heusler thermoelectric materials

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研究成果の概要（和文）：本研究では、マルチスケール微細構造（アンチサイト点欠陥、ナノスケールおよびマイクロスケールのスピノーダル分解ハーフホイスラードメイン、ナノスケールホイスラーナノ析出物など）を含む一連の環境に優しいハーフホイスラー熱電合金の開発に成功した。この合金の熱電性能を向上させるためには、高温の繰り返し熱処理と適切な量のドーピングが有効であることがわかった。Nbをドープして熱処理したハーフホイスラー合金は、752KでZTが0.91と最も高くなりました。この改善の理由は、ドーピング効果、フルホイスラーナノ析出物の存在、高温サイクル熱処理によるマルチスケール微細構造の界面構造の改変と密接に関係している。

研究成果の学術的意義や社会的意義
Hence, this research aims at developing thermoelectric half-Heusler materials that can directly recycle waste heat energy from any high-temperature source. Most importantly, the energy generation is clean, involves no CO2 emission, environmentally friendly, low cost and stable at high temperature.

研究成果の概要（英文）：A series of environmentally friendly half-Heusler thermoelectric alloys containing multiscale microstructure (i.e., antisite point defects, the nanoscale and microscale spinodal-decomposed half-Heusler domains, the nanoscale full-Heusler nanoprecipitates of various sizes and morphologies) have ben successfully developed in this research. It was found that the high-temperature cyclic heat-treatment process and suitable amount of doping were two viable approaches to improve the overall thermoelectric performance of the alloys. The Nb-doped and cyclic-heat-treated half-Heusler alloy has shown the highest ZT to 0.91 at 752 K. The improvements are caused by the increment of power factor and the reduction of thermal conductivity. The former was due to the doping effects and the presence of the full-Heusler nanoprecipitates. The latter were closely associated with the diffuse interfacial structures among the multiscale microstructure upon the high-temperature cyclic heat-treatment process.

研究分野： Materials Science and Engineering

キーワード： half-Heusler alloys　microstructure　interfacial structure　defects　nanoprecipitates　crystallography　thermoeletric　phase transformation

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１．研究開始当初の背景

The worldwide appetite for fossil fuel and coals, and the non-stop increasing emission of greenhouse gasses demand our immediate attention to address the environmental consequences. The application of thermoelectric (TE) technology is one solution to diversify our energy sources to be cleaner, safer, and more sustainable. It is a green solid-state technology based on thermoelectric materials that can directly recycle waste heat energy from any high-temperature source (e.g., automobiles, aircraft engines, or even solar heat) into practical electricity. Most importantly, it involves no CO_2 emission, reliable and maintenance-free (no moving parts). Materials selection is probably the most critical aspect of fabricating high-performance TE devices to maximize the TE energy conversion performance. Owing to this, we proposed the development of high-performance half-Heusler thermoelectric materials that are non-toxic, environmentally friendly, low cost, and stable at elevated temperatures.

Half-Heusler thermoelectric materials, XYZ (X=Ti/Zr/Nb/Ta, Y=Ni/Co/Fe, Z=Sn), have been chosen in this research because of their apparent advantages over other conventional thermoelectric materials. For instance, (i) they often exhibit high thermopower ($S^2\sigma$) at high temperature (600-1000 K) that is ideal for high-temperature thermoelectric applications (e.g., automobiles and aircraft engines; (ii) they are environmentally friendly, sustainable, low cost and possible for large scale production because no toxic, no rare-earths and inexpensive elements are used in these materials, and (iii) competitive in power generation cost as the power generation based on half-Heusler materials has been estimated to be the cheapest (i.e., \$4.48/Watt, Quadrennial Technology Review 2015, Chapter 6: Technology Assessments, U.S. Department of Energy).

Despite the tremendous potential of the half-Heusler TE materials, their overall TE performance remains relatively less satisfactory, often with $ZT < 1$. Here, the ZT is referred to as Figure-of-merit, an indicator that characterizes the energy conversion efficiency of a TE material. Also, the $ZT = (S^2\sigma/\kappa)T$, is controlled by the material's parameters, such as the Seebeck coefficient (S), the electrical conductivity (σ), and the thermal conductivity (κ). T is temperature. For practical TE applications, many have tried exhaustively to develop TE materials with the benchmark, $ZT \geq 1$.

２．研究の目的

The ultimate goal of this research proposal was aimed at developing half-Heusler thermoelectric materials with high TE performance, environmentally friendly, low cost, and stable at high temperatures. Here, finding a viable approach to improve TE performance of the materials without sacrificing other properties is the most important and somewhat complex issue. Owing to this, the research has proposed the introduction of a multiscale microstructure, which might lead to a more effective reduction of thermal conductivity, and simultaneously improve the electrical properties ($S^2\sigma$) of the materials. Consequently, one anticipated a drastic improvement of the materials' TE performance, i.e., ZT. It is noted that various microstructure has been observed in half-Heusler materials, which includes (i) the atomic-scale point-defects of antisites, and (ii) the nanoscale full-Heusler precipitates of various morphologies, and (iii) the microscale Ti-rich and Zr-rich half-Heusler domains.

３．研究の方法

The development of the ‘performance-enhanced’ half-Heusler thermoelectric materials has been based on the five classical principles of Materials Science and Engineering.

➢ Materials designs.

Firstly, we have chosen several simple quaternary half-Heusler alloys with slightly off-stoichiometric compositions, i.e., $(Ti_x, Zr_{1-x})Ni_{1+y}Sn$, where x = 0.2 - 0.5, and y = 0-0.05, to investigate the multiscale microstructure formation. The fine compositional tuning is based on pseudo-ternary half-Heusler phase diagrams of TiNiSn and ZrNiSn. It is emphasized that those toxic, costly, and rare-earth elements are not considered in the initial stage. Next, a small amount of doping elements, such as V, Nb, and Ta, are added to the $(Ti_x, Zr_{1-x})Ni_{1+y}Sn$ alloys to further improve the electrical properties of the alloys.

➢ Materials fabrications and heat-treatment processes.

The materials were first fabricated by arc melting and followed by directional solidification. The latter has been shown to produce half-Heusler alloys with much fewer impurities, and a long-term heat-treatment process (e.g., two weeks at 1073 K) was unnecessary. The thermal and phase stability of the alloys were evaluated by differential thermal analysis (DTA). The high-temperature cyclic heat treatment process was also carried out between 1023 K - 1373 K to manipulate and control the multiscale microstructure.

➢ Characterization of the multiscale microstructure. The crystallography and microstructure were characterized by various techniques, such as XRD, SEM-EDS, TEM, HRTEM, STEM-EDS, and STEM-HAADF.

➢ Evaluation of thermoelectric properties.

The S and σ of the half-Heusler alloys were evaluated using the ULVAC ZEM-3 between 323 – 1073 K. The measurements were repeated for three consecutive heating cycles to study the thermoelectric stability of the alloys.　The carrier concentrations (n) and carrier mobility (μ_H) of the alloys were measured at room temperature using the Hall effect measurements with a DC four-probe van der Pauw subject to a 0.6 T magnetic field. The κ of the alloys 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 parameters d, α, and C_p were estimated based on the Archimedes principle, the laser flash method (ULVAC TC-1200RH), and differential scanning calorimetry (DSC8500, Perkin Elmer), respectively.

４．研究成果

A series of ternary, quaternary, and quinary half-Heusler alloys, i.e., ZrNiSn, (Ti_x, Zr_{1-x})NiSn, and ($Ti_{0.35}$, $Zr_{0.65})_{0.999}M_{0.001}$]$Ni_{1+y}$Sn (where M= V, Nb, Ta), have been fabricated in this research. Several significant findings have been discovered, as summarised below.

✓ Multiscale microstructure and the high-temperature cyclic heating process [i,ii].

Overall, the aforementioned multiscale microstructure was successfully introduced in the quaternary and quinary alloys, provided the composition ratio, x, associated with the Ti and Zr, was larger than 0.2, whereas y should be in the range between 0 to 0.1. Here, it is to emphasize that the idea of introducing the multiscale microstructure was intended to reduce the κ without sacrificing the electrical transport properties (i.e., $S^2\sigma$) of the alloys. Moreover, in addition to the relatively large microscale Ti-rich HH_1 and Ti-poor HH_2 domains (up to several hundred micrometers in size) that were formed during the solidification process, it was discovered that the half-Heusler phase-separated domains (i.e., HH_1 and HH_2) were actually formed nanoscale Ti-rich HH_1 and Ti-poor HH_2 phase-separated nano-clusters (up to several nm). These phase-separated nanoclusters, which appeared as a modulated structure under TEM, were likely formed via a so-called spinodal decomposition (i.e., HH' ➔ Ti-rich HH_1 + Ti-poor HH_2) during the cooling process.

These microscale and nanoscale half-Heusler domains provided additional phonon scattering enhancements at the HH1/HH2 interfaces and subsequently reduced κ the ($Ti_{0.5}$, $Zr_{0.5}$)NiSn half-Heusler alloy. Interestingly, it was noticed that the κ could be further reduced after it was subjected to the high temperature cyclic heating-cooling processes between 1223 – 1423 K (held for 10.8 ks for each cycle). The cyclic heat-treatment process modified the interfacial structure between the HH_1 and HH_2 domains to become more diffuse, further enhancing the phonon scattering. Here, it must be mentioned that other microstructures, such as the Ti- and Zr-atomic disorders, the nanosized Ni-rich clusters, and the full-Heusler nanoprecipitates, also played a role in the phonon scattering mechanism. The room temperature κ of the alloy was found to be 2.8 W/mK, which was more than a 50% reduction from that of the ternary ZrNiSn, i.e., about 6 W/mK. The highest *ZT* of the cyclic heat-treated the ($Ti_{0.5}$, $Zr_{0.5}$)NiSn half-Heusler alloy was found to be 0.85 at 800 K, which was about 20% increase as compared with those un-heat-treated alloy.

From these investigations, we have proposed a similar approach of using the cyclic heat treatment process to modify the microstructure of other TE materials possessing a miscibility gap in the alloy phase diagram and eventually improve their TE performance.

✓ Multiscale microstructure, high-temperature cyclic heating process, and the effect of doping[iii]

To further improve the overall TE performance, we have studied the impact of doping by V, Nb, and Ta in a series of quinary half-Heusler alloys, i.e., [($Ti_{0.35}$, $Zr_{0.65})_{0.999}M_{0.001}$]$Ni_{1.02}$Sn (where M= V, Nb, Ta) []. The idea of doping the half-Heusler alloys was intended to improve their electrical properties (i.e., power factor, $S^2\sigma$). Similarly, the alloys have been subjected to a high-temperature cyclic heat treatment process, i.e., between 1223 – 1373 K, and held for 10.8 ks for each cycle. As anticipated, all the alloys were found to contain the multiscale microstructure.

Overall, all three cyclic-heat-treated doped-half-Heusler alloys, V-, Nb- and Ta-doped, have shown an improvement in power factor, i.e., 3.9×10^{-3} W/mK^2 (at 753 K), 4.4×10^{-3} W/mK^2 (at 752 K), and 3.9×10^{-3} W/mK^2 (at 756 K), respectively. The respective improvements were about 15%, 29%, and 15%, as compared to the undoped $(Ti_{0.35}, Zr_{0.65})Ni_{1.05}Sn$ half-Heusler alloy, 3.4 $\times 10^{-3}$ W/mK^2 at 750 K.

In contrast, the cyclic-heat-treated doped-half-Heusler alloys did not reduce the κ, compared to the undoped alloy. For instance, their respective lowest κ was found to be 3.13 W/mK (at 561 K), 3.29 W/mK (at 562 K), and 3.29 W/mK (at 566 K), which were slightly higher than that of the undoped alloy, i.e., 3.08 W/mK (at 568 K). The initial microstructure investigations have suggested that the dopants might shift the phase stability of the alloys, and the conditions for the cyclic-heat-treatment process might be inadequate to the interfacial structures of the multiscale microstructure. A longer and higher temperature cyclic heat-treatment conditions may be necessary.

Nevertheless, we observed the dopants have still resulted in a slight improvement in the overall TE performance of the alloys. For instance, the highest ZT of the V-, Nb- and Ta-doped half-Heusler alloys was found to be 0.85 at 753 K, 0.91 at 752 K, and 0.82 at 756 K, respectively. These were about 8%, 15%, and 4%, improvements compared to the undoped alloy, i.e., ZT= 0.79 at 758 K.

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５．主な発表論文等

〔雑誌論文〕　計1件（うち査読付論文　0件／うち国際共著　1件／うちオープンアクセス　1件）

１．著者名 Chai, Yaw Wang; Kimura, Yoshisato	４．巻 2020
２．論文標題 Multiscale microstructure engineering and the development of high performance, environmental friendly, low cost and thermally stable half-Heusler thermoelectric materials	５．発行年 2020年
３．雑誌名 Impact	６．最初と最後の頁 65-67
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〔学会発表〕　計4件（うち招待講演　0件／うち国際学会　2件）

１．発表者名 Yaw Wang Chai, Yoshisato Kimura
２．発表標題 Effect of interfacial structure of Heusler nanoprecipitates on the thermoelectric properties of n-type half-Heusler alloys
３．学会等名 The 38th International Conference of Thermoelectrics & The 4th Asian Conference on Thermoelectrics（国際学会）
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１．発表者名
Yaw Wang Chai

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Effect of interfacial structure of Heusler nanoprecipitates on the thermoelectric properties of n-type half-Heusler alloys

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４．発表年
2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考
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〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

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