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P-type thermoelectric properties of half-Heusler alloys $TiNi_{1-x-y}Co_ySn$ ($0 \leq x \leq 0.1$, $0 \leq y \leq 0.05$) below 800 K

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Half-Heusler (hH) alloy TiNiSn is a thermoelectric material with high environmental compatibility, low cost, good mechanical properties, and chemical stability at high temperatures. There are many studies on the N-type thermoelectric properties of TiNiSn-based material, but few experimental reports on the P-type. Our research group reported the thermoelectric properties of $TiNi_{1-x-y}Co_ySn$ (x=0, $0 \leq y \leq 0.15$) [1]. However, the *ZT* of P-type is still lower than that of N-type TiNiSn-based materials, and the high electrical resistivity is found to be one of the reasons. In addition, it was found that Ni formed intrinsic defects in Co-substituted TiNiSn fabricated with stoichiometric composition. This defect acts as a donor impurity, emitting free electrons. Therefore, the present work aims to optimize the Ni composition ratio ($x \neq 0$) in order to reduce defects, leading to an increase in hole density. This is expected to decrease electrical resistivity and improve the *ZT* of Co-substituted TiNiSn.

The raw materials were weighed to obtain 15 g of $TiNi_{1-x-y}Co_ySn$ ($0 \leq x \leq 0.1$, $0 \leq y \leq 0.05$) and melted under an Ar atmosphere. The samples were cut to measurable scale by wire Electrical Discharge Machining, annealing in vacuum-sealed quartz tubes for homogenization, and heat treatment. All the samples were subjected to powder X-ray diffraction measurements, and the crystal phases were identified by Rietveld analysis using the obtained diffraction patterns. The sample composition was confirmed to be almost nominal compositions by using ICP-AES. ResiTest8300 (TOYO Corporation) was used for electrical resistivity and Seebeck coefficient measurements from 80 K to 395 K, and a home-made apparatus was used for measurements from 395 K to 800 K. Thermal conductivity measurements from 300 K to 800 K were used by PEM-2 (ADVANCE RIKO, Inc.), and *ZT* up to 800 K was evaluated.

From crystal structure analysis, all samples are mostly composed of the hH phase. In addition, the fraction of the impurity phase increases with increasing x. Above $x = 0.08$, the impurity phase increased to around 5%, suggesting a deterioration of thermoelectric properties. From measurements of thermoelectric properties, electrical resistivity decreases with increasing x. Interestingly, the absolute value of the Seebeck coefficient remains unchanged up to $x = 0.05$. Therefore, at 800 K, the power factor increases from 0.85 $mWm^{-1}K^{-2}$ to 1.7 $mWm^{-1}K^{-2}$ as x increases from 0 to 0.03 for $y = 0.05$. The thermal conductivity increases with increasing x, which can be attributed to the disappearance of the phonon scattering and the decrease in electrical resistivity. As for *ZT*, $x = 0.03$, $y = 0.05$ shows the largest *ZT* of 0.18 at 700 K in this study. This value is higher than a similar P-type hH alloy, e.g., $ZrNi_{0.98}Co_{0.02}Sn$ ($ZT \approx 0.1$) at 700 K [2]. This result indicates that the decrease in the Ni composition ratio is effective in increasing *ZT* for P-type TiNiSn-based materials.

References

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