## P-type thermoelectric properties of half-Heusler alloys TiNi<sub>1-x</sub>Co<sub>x</sub>Sn ( $0 \le x \le 0.15$ ) at high temperature( $\le 800$ K)

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TiNiSn, a thermoelectric material composed of elements with low environmental impact, exhibits n-type characteristics. TiNiSn also can be converted to p-type by effectively doping holes. For hole doping, elemental substitutions with elements having smaller valence electron numbers than either of the elements are effective [1]. Suppose a high dimensionless performance index ZT can be obtained even in p-type. In that case, it is possible to develop a conventional  $\Pi$ -type thermoelectric conversion device using TiNiSn as the matrix phase. Since TiNiSn has high thermal stability, it is expected to be used in thermoelectric modules at high temperatures. The purpose of this study is to prepare TiNi<sub>1-x</sub>Co<sub>x</sub>Sn ( $0 \le x \le$ 0.15) in which Co atoms with a smaller valence electron than Ni are substituted at the Ni site of TiNiSn to evaluate thermoelectric properties up to high temperature and to clarify the amount of Co substitution that shows the highest ZT. The samples were prepared by arc melting. The raw materials were weighed to obtain 15 g of stoichiometric composition and melted under an Ar atmosphere. The samples were cut to measurable scale by wire Electrical Discharge Machining (EDM), annealing in vacuum-sealed quartz tubes for homogenization, and heat-treated. 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. ResiTest8300 (TOYO Corporation) was used for electrical resistivity and Seebeck coefficient measurements from 80 to 395 K, and a home-made apparatus was used for measurements from 395 to 800 K. Thermal conductivity



**Fig. 1** Temperature dependence of Seebeck coefficiet (a) and p-type ZT (b) for TiNi<sub>1-x</sub>Co<sub>x</sub>Sn ( $0 \le x \le 0.15$ )

measurements from 300 to 800 K were used by PEM-2 (ADVANCE RIKO, Inc.), and *ZT* up to 800 K was evaluated. Fig. 1 shows the temperature dependence of the Seebeck coefficient and *ZT* of TiNi<sub>1-x</sub>Co<sub>x</sub>Sn ( $0 \le x \le 0.15$ ). The sign of the Seebeck coefficient changes in the temperature range for  $x \ge 0.03$ . This indicates that the Co substitution changed the majority of carriers to holes. The highest Seebeck coefficient was shown at x=0.05. In conclusion, the substitution of Co at the Ni site changes from n-type to p-type, with the p-type highest *ZT* shown at x=0.05.

## **References:**

 Romaka, V. A., Stadnyk, Y. V., Fruchart, D., Dominuk, T. I., Romaka, L. P., Rogl, P., Goryn, A. M. The Mechanism of Generation of the Donor and AcceptorType Defects in the n-TiNiSn Semiconductor Heavily Doped with Co Impurity. *Semiconductors*. 43 (9), 1124-1130 (2009)