Thermoelectric Properties of p-Type Cr Doped MnSi₂, Prepared by Liquid Quenching Technique

Swapnil Ghodke¹, A. Yamamoto², M. Omprakash², H. Ikuta¹ and T. Takeuchi²,³

¹Department of Crystalline Materials Science, Nagoya University, Nagoya 464–8603, Japan
²Toyota Technological Institute, Nagoya 468–8511, Japan
³Green Mobility Collaborative Research Center, Nagoya University, Nagoya 464–8603, Japan

In this work, higher manganese silicide (HMS) with partial substitution of Cr for Mn has been studied. The Cr substitution was used to tune the carrier concentration for obtaining optimized thermoelectric properties. In order to have a wide range of carrier concentration, we employed liquid quenching technique, because the rapid quenching increases the solubility of Cr in HMS. The maximum solubility of 11 at.% Cr at Mn site in HMS was achieved in this study. The hole concentration increases with increasing Cr concentration, with that minimum electrical resistivity of 1 mΩ cm was observed for Mn₂₅.₃Cr₁₁Si₆₃.₉. The power factor was decreased with increasing Cr concentration due to reduction in Seebeck coefficient, but further addition of Cr showed increasing tendency for power factor. The maximum power factor of 1.5 mW cm⁻² K⁻² with ZT of 0.4 was obtained at 700 K for Mn₂₅.₃Cr₁₁Si₆₃.₉. [doi:10.2320/matertrans.M2016246]

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1. Introduction

Thermoelectric devices with materials consisting solely of cheap and non-hazardous elements are being considered as the prospect of practical technology. Here, higher manganese silicide (HMS) known to possess chimney ladder structure is the one of the most plausible candidate because of its abundant, non-toxic constituent elements. Notably, HMS satisfies the conditions of electronic structure required for practical thermoelectric materials. The large band gap of ~0.8 eV, strong energy dependence of the density of states near band edge, and multiple bands within few k_BT energy range around chemical potential.

The good electronic structure gives a large Seebeck coefficient (200 μV K⁻¹), together with a low electrical resistivity, and a large power factor of 1 x 10⁻³ W m⁻¹ K⁻² at 700K. The thermal conductivity of 2 W m⁻¹ K⁻¹ presumably due to complex Nowotny Chimney ladder (NCL) structure, with this a moderate value of ZT = 0.4 can be obtained at 700 K. However, this ZT-value is not large enough to be used for commercial applications. Though, considering the good electronic structure, environmental friendly and cheap material, it was worth to make an attempt to improve the performance of this promising material.

It has been reported that the partial Cr substitution for Mn could be an effective method to improve the ZT of HMS. The report showed that the hole concentration increases with increasing Cr concentration, and the ZT-value was slightly increased from that of Cr-free sample. The improvement in ZT was limited by the amount of Cr substitution for Mn, as the maximum solubility was observed for the Mn₀.₈Cr₀.₂Si₁.₇₄ sample, which contained 7.3 at% Cr. This result suggested that if the solubility limit of Cr in HMS was increased, the ZT-value would be further increased.

Recently, by employing liquid quenching method, we succeeded in expanding the solubility limits of W, Fe and Re in HMS. Therefore, we expected that further increase in the amount of Cr substitution for Mn could be realized by liquid quenching method for wider tuning the carrier concentration, which would help us to obtain a higher ZT value.

2. Experimental Procedure

A series of higher manganese silicides Mn₃₆.₅–ₓCrₓSi₆₃.₅ with Cr concentration varying from x = 0 to x = 11% were synthesized. Manganese (99.99%), Chromium (99.99%), and Silicon (99.99%) powders in stoichiometric ratio were mixed using mortar and pestle. Pellets were prepared by hydraulic press at room temperature and then melted several times in an arc-melting furnace under the pressurized Argon atmosphere. All the ingots containing Cr were re-melted in a silica tube and injected on a copper wheel rotating at 4500 rpm in the pressurized Argon atmosphere. The quenched ribbon samples were crushed into powders again and sintered under the conditions of 1123 K, 60 MPa axial pressure, 50°C/min heating rate, and 5 min soaking.

The phases formed in the arc-melted, liquid quenched, and sintered samples were identified by conventional powder X-ray diffraction using BRUKER D8 Advance with Cu-Kα radiation. The microstructure by scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDX) was analyzed by JEOL JSM-6330F and JED-2140GS. The Seebeck coefficient was measured by using Micro-miniature refrigerator (MMR) technologies inc. in the temperature range of 300–700 K. The electrical resistivity and the thermal conductivity was measured in the temperature range of 300–700 K using a conventional four-probe method and Laser flash method (LFA457, NETZSCH), respectively. The density of sintered samples was measured by Archimedes method.

3. Results

The measured XRD patterns of Mn₃₆.₅–ₓCrₓSi₆₃.₅ were plot-
The XRD patterns of arc melted samples clearly showed the precipitation of the impurity CrSi$_2$ phase at $x \geq 7.3$, whereas this impurity phase disappeared by the rapid quenching (Fig. 1 (b)). However, there remained a small amount of MnSi impurity in all the samples and the intensity of impurity peaks increased with increasing Cr concentration. The precipitation of MnSi was confirmed also by the SEM-EDX analysis.

The lattice constants $a'$ and $c'$ of the sintered samples are plotted as a function of Cr concentration $x$ in Fig. 2 (a) and (b), respectively. The lattice constants for HMS were calculated by considering Mn$_3$Si$_7$ as a nominal crystal structure. Even after the sintering, the impurity phase CrSi$_2$ was not observed regardless of Cr concentrations as shown in Fig. 1 (c). This fact indicates that the thermal stability of supersaturated solid solution was good enough to keep the nearly single chimney-ladder phase at high temperatures at least up to 1123 K. The relative density for all the sintered samples was more than 91%, which is good enough to measure thermoelectric properties.

The SEM image of the liquid quenched ribbon shaped Mn$_{25.5}$Cr$_{11}$Si$_{63.5}$ was shown in Fig. 3 (top) and (bottom). We observed a very fine microstructure with an average grain size of $\sim$500 nm and 2000 nm, respectively. This significant reduction in grain size was related the enhanced nucleation in association with the rapid quenching process.
with Cr atoms in the rapid quenching process. Figure 4 shows the wider range SEM image of Mn$_{25.50}$Cr$_{11}$Si$_{63.5}$ sintered sample, where we observed the impurity phase together with the chimney ladder phase. The EDX mapping confirmed that the impurity phase has a composition of (Mn, Cr)$_2$Si and it was safely assigned to MnSi-phase. This result was very consistent with the XRD patterns.

The temperature dependence of Seebeck coefficients were plotted in Fig. 5 (a), and their values at 600 K were plotted in Fig. 5 (b) as a function of Cr concentration $x$. The Seebeck coefficient of Mn$_{36.5}$Si$_{63.5}$ at 600 K was 200 $\mu$VK$^{-1}$ which was the largest among the present samples, and the value of Seebeck coefficient was reduced with increasing Cr concentration up to 7 at.$\%$ and saturated at $\sim$130 $\mu$VK$^{-1}$ for the larger Cr concentration. A very small increase of Seebeck coefficient was also observable for $x > 7$. The reduction in Seebeck coefficient must be related to the increased carrier concentration because the number of valence electron in Cr is smaller than that of Mn.

The electrical resistivity shown in Figs. 5 (c) and (d) was reduced with Cr substitution. The reduction of electrical resistivity indicates that the hole-concentration was increased with Cr substitutions. It is also very important to note that very week temperature dependence, which is almost flat at high temperature was observable especially for the samples containing more than 7 at.$\%$ Cr. The less obvious temperature dependence of electrical resistivity means that the mean free path of carriers reached the minimum value known as Mott-Ioffe-Regel limit never to be further shortened.

The temperature dependence of power factor $PF$ was plotted in Fig. 5 (e), and the value of $PF$ at 600 K was also plotted in Fig. 5 (f) as a function of Cr concentration $x$. We observed a local minimum of $PF$ at around $x = 3.7$ in Fig. 5 (f). The increases of $PF$ at $x < 3.7$ and $x > 3.7$ were attributed to the increase of Seebeck coefficient and the decrease of electrical resistivity, respectively. The largest value of $PF$ at 600 K was 1.4 Wm$^{-1}$K$^{-2}$ and this value was realized both at $x = 0$ and 11.

The measured thermal conductivity was plotted as a function of temperature in Fig. 6 (a). Its values at 600 K were also plotted as a function of $x$ in Fig. 6 (b). We confirmed that the lattice thermal conductivity was hardly affected by Cr substitution presumably due to the similar atomic mass of Cr and Mn. The electrical thermal conductivity, on the other hand, increased with increasing Cr concentration because of the increased number of carrier concentration. The linear increase of $\kappa_{el}$ with increasing temperature was naturally brought about by the nearly temperature independent $\sigma$ and the Wiedemann-Franz law $\kappa_{el} = L_0\sigma T$ used to estimate the electron thermal conductivity.

The temperature dependence and composition dependence of $ZT$ were plotted in Fig. 6 (c) and (d), respectively. The behavior of $ZT$ was similar to the power factor. The highest value of $ZT$ was observed at $x = 0$, and the sample at 11 at.$\%$ Cr showed comparable value with that of $x = 0$. The minimum value of $ZT$ at 600 K was observed at $x = 3.7$.

4. Discussion

The present results of transport properties are definitely...
conflicting with the results reported by Kikuchi et al., who claimed the power factor and \( ZT \) increased with increasing Cr concentration, but our results showed the maximum values were obtained for the Cr free sample. We considered that the difference lied in the carrier concentration of Cr-free sample, which could be varied by different composition or different synthesis technique because of the high vapor pressure of Mn. The XRD patterns reported by Kikuchi et al. showed a small amount of silicon precipitation, while our samples showed the precipitation of MnSi. This means that the samples reported by Kikuchi et al. and our samples stayed in the same condition of smaller \( ZT \) composition, our sample showed the maximum values at 600 K, while Kikkushi et al. showed a smaller \( ZT \) at 700 K.

The increase of \( ZT \) at \( x > 7 \) is also very important. In the present study, we succeeded in increasing the solubility limit of Cr in HMS by employing the liquid quenching technique. However, near the solubility limit \( ZT \) showed increasing tendency with increasing Cr concentration. We strongly expect that the value of \( ZT \) would increase more if we could increase the solubility limit of Cr to \( x > 11 \). This could be realized when we employ a faster quenching technique, i.e., the much higher rotating speed or a larger diameter of Cu wheel in the liquid quenching apparatus.

Before closing discussion, we would like to briefly comment on the grain size of samples. We observed very fine grains in the liquid quenched, Cr-substituted HMS. We also considered that the reduction of grain size is attributed to the rapid quenching and the increased number of nucleation sites in association with Cr atoms. Recently, the energy filtering effect to increase Seebeck coefficient was reported for the different several compounds. Some of the reports attributed the source of energy filtering effect to the grain boundaries. If it is the case, the fine grain boundary realized in the present samples, would contribute to the increase of \( ZT \).

5. Conclusion

We succeeded in increasing the solubility limit of Cr in HMS up to 11 at.% from 7 at.% by employing liquid quenching technique. We also obtained a fine microstructure with average grain size of \( \sim 500 \) nm. As a result, the largest \( ZT \) of \( \sim 0.4 \) at 700 K was observed both at \( x = 0 \) and 11.

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