Journal of Ceramic Processing Research. Vol. 13, No. 6, pp. 816~819 (2012)

J O U R N A L O F
Ceramic Processing Research

Thermoelectric properties of Nowotny phase, higher manganese silicides synthesized by mechanical alloying process

Young-Geun Lee[a], Moon-Kwan Choi[a,b], Il-Ho Kim[a] and Soon-Chul Ur[a,*]

[a]*Department of Materials Science and Engineering / RIC-ReSEM, Korea National University of Transportation, 50 Daehangno, Chungju, Chungbuk 380-702, Korea*

[b]*Korea Institute of Limestone and Advanced Materials(KILAM), 63 Wooduck-Ri, Maepo-Eup, Danyang, Chungbuk 395-903, Korea*

Higher manganese slicides (HMS), $MnSi_{1.73}$, were synthesized by the mechanial alloying of stoichiometric elemental powder compositions, and the as-milled powders were consolidated by vacuum hot pressing. Phase transformation and microstructural evolution during mechanical alloying and hot consolidation were investigated using XRD and SEM, respectively. Thermoelectric properties as a function of temperature were evaluated in terms of Seebeek coefficient, electrical resistivity, thermal conductivity and the figure of merit. Transport properties were also evaluated and discussed with analogue studies. Mechanically alloyed HMS showed the figure of merit value of 0.5 at 823 K, and appeared to have a great potential as a thermoelectric material.

Key words: Higher manganese silicide, $MnSi_{1.73}$, Thermoelectric, Mechanical alloying.

Introduction

For the development of functional materials and devices including thermoelectric materials, many researchers have become to consider current emerging issues such as environmental friendliness, the abundance and the cost of its constituent materials over the performance. Recent researches on the thermoelectric materials with these trends discovered a new class of intermetallics, manganese silicides, as good candidates for higher performance thermoelectric conversion [1-3]. It was reported that manganese silicides with a composition of MnSi (monosilicide) show metallic behavior, while those with a composition near $MnSi_{1.7}$, so called higher manganese silicide (HMS), are of p-type semiconductors with narrow band gap energy of 0.4-0.7 eV [2-3]. HMS ($MnSi_{1.75-x}$, $0 \le x \le 0.04$) takes great attention as a potential thermoelectric material for high temperature application [1-3]. It was reported that HMS with tetragonal structure has five phases with slightly different stoichiometries of Mn_4Si_7, $Mn_{11}Si_{19}$, $Mn_{26}Si_{45}$, $Mn_{15}Si_{26}$ and $Mn_{27}Si_{47}$, which are characterized by an abnormally large C- axis as a function of composition [4, 5]. These members of the family are also referred as Nowotny phases [2, 4-5]. It is known that single phase HMS is inherently difficult to form due to its peritectical nature, and coexistence with residual MnSi phase is quite usual [1-2, 5]. HMS are generally prepared by melting [6], crystal growth [5, 7-8], chemical reaction method [9], powder metallurgy process [1-2], thin film process [3] and so forth. Among the composition range of $MnSi_{1.75-x}$ ($0 \le x \le 0.04$), $MnSi_{1.73}$ has been shown to have the highest thermoelectric properties [1-2, 6]. For the thermoelctric characteristics investigation, the figure of merit is defined as $ZT = \alpha^2 T/\rho\kappa$, where α is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity and T is the temperature in Kelvin. The maximum figure of merit value of HMS was reported 0.3-0.47 in undoped state with micro sized microstructure [1, 6] and 0.62 in nano sized microstructure [2]. In fact, reducing thermal conductivity via microstructure refinement was shown to be very effective in enhancing the thermoelectric property [10]. Numerous efforts have also been attempted to improve thermoelectric properties utilizing elemental or secondary phase doping in this composition [6, 11]. However, there seems not to be significant property enhancements yet. For producing HMS, conventional ingot technology needs long termed huge energy and frequently results in inhomogeneity. In order to address these problems, mechanical alloying with hot pressing or spark plasma sintering has been set up as an alternative processing route for the formation of these types of functional intermetallics [1-2, 9, 11]. Mechanical alloying (MA) process has been considered to be one of the optimal processing route [1, 9, 11], since it provides a ultra fine grain size leading to enhance thermoelectric efficiency by the reduction in lattice thermal conductivity [11]. In this work, $MnSi_{1.73}$ was synthesized by the mechanical alloying of stoichiometric elemental powder compositions, and then as-milled powders were consolidated by vacuum hot pressing.

*Corresponding author:
Tel : +82-43-841-5385
Fax: +82-43-841-5380
E-mail: scur@ut.ac.kr

Phase transformation and microstructure evolution during mechanical alloying and hot consolidation were investigated using XRD and SEM. Thermoelectric properties as a function of temperature in terms of Seebeck coefficient, thermal conductivity, electrical resistivity and ZT were evaluated for the hot pressed specimens. Transport properties were also evaluated in terms of Hall coefficient, carrier mobility and carrier density, and compared with analogue studies.

Experimental

Appropriate elemental powder mixtures of Mn (-250 mesh, 99.9%) and Si (-325 mesh, 99.99%) for stoichiometric $MnSi_{1.73}$ were prepared and mechanically alloyed in a Spex mill (8000D) up to for 24 hrs. The milling operation was carried out inside a dedicated glove box under an Ar atmosphere. For this milling, ball to powder ratio was 10:1 and the rotation speed was 1,750 rpm. As-milled powders were hot pressed in a cylindrical high strength graphite die at 1123K with a stress of 70 MPa for 2 hrs in vacuum. In order to investigate the phase transformation during synthesis, X-ray diffraction (XRD, Bruker AXS ADVANCE D-8) analyses using Cu K_α radiation were carried out for the powders as well as hot pressed samples. In order to observe microstructures, e-SEM (FEI, Quanta-400), and optical microscope (OM) were employed. Densities after hot consolidation were measured using a He pycnometer. Thermoelectric properties in terms of Seebeck coefficient, electrical resistivity and thermal conductivity were measured from 323 K to 823 K, and ZT was evaluated. Here, vacuum hot pressed (VHPed) specimens were cut into the size of $3 \times 3 \times 10\ mm^3$ for Seebeck coefficient and electrical resistivity measurements, and into $10\phi \times 1mm$ for thermal conductivity measurement. Seebeck coefficient and electrical resistivity was measured by the differential and 4-point probe methods (Ulvac-Riko ZEM2-M8). Thermal conductivity was evaluated from the measure-ments of thermal diffusivity, specific heat and density by the laser flash method (Ulvac-Riko TC7000). Transport properties in terms of Hall coefficient, carrier mobility and carrier concentration were examined. The measurement of the Hall effect (Keithley 7065) was carried out in a constant magnetic field (1 T) and electric current (50 mA) at 300 K.

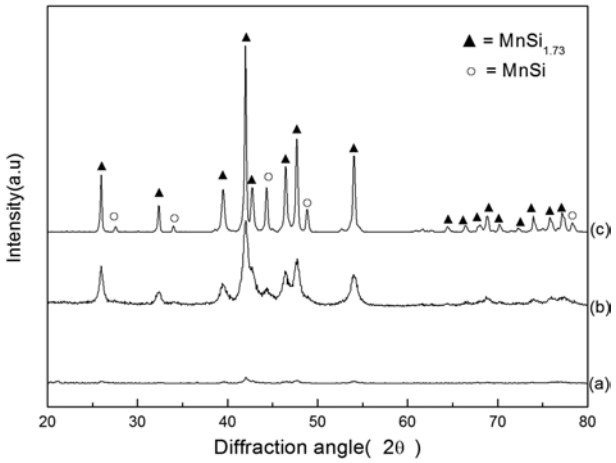

Fig. 1. XRD patterns of MA HMS powders and VHPed sample ; (a) MA for 12 hrs, (b) MA for 24 hrs, (c) VHPed at 1123 K for 2 hrs.

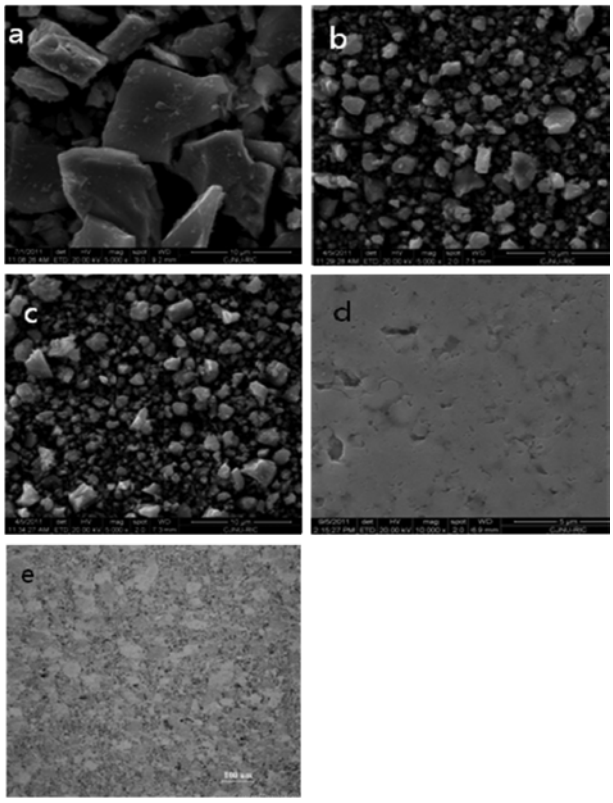

Fig. 2. SEM and OM micrographs of MA powders and VHPed sample; (a) as-mixed powders, (b) MA for 12 hrs, (c) MA for 24 hrs, (d) SEM of VHPed specimen, (e) OM of VHPed specimen.

Results and Discussion

XRD analysis during mechanical alloying (MA) revealed that alloy development of $MnSi_{1.73}$, Nowotny phase, appeared from 12 hrs and saturated after 24 hrs of milling as shown in Fig. 1. The elemental peaks disappeared after 12 hrs of milling, and the typical alloying development during MA showing the appearance of a superlattice line with decreasing elemental powder peaks during MA process [10] was observed in this process. No amorphous transition was observed during milling, but significant peak broadening was observed, possibly resulting from particle refinement and cold work. Particle size decreases as milling continues up to 24 hrs in Fig. 2. As-milled powder size after 24 hrs was typically less than 5 μm. Single phase of $MnSi_{1.73}$ seemed to be formed after 12 hrs of milling, but a trace of MnSi appeared after hot consolidation by VHP. It is recognized that single phase HMS is inherently difficult to form due to its peritectical nature, and coexistence

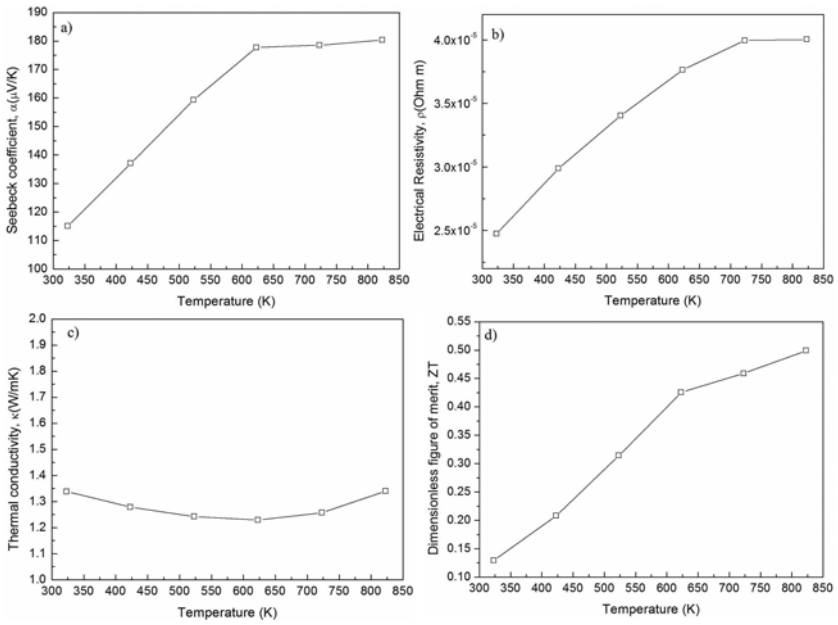

Fig. 3. Thermoelectric properties of VHPed MA HMS ; (a) Seebeck coefficient, (b) electrical resistivity, (c) thermal conductivity, (d) figure of merit, ZT.

with residual MnSi phase is quite usual [2, 5] in the synthesis of manganese silicides. MAed powders were also believed to be in a metastable state, which is normally transform to the designed phase during hot consolidation process or post annealing [10, 11]. However, as-milled powders of peritectoid or peritectic system might need extremely long term annealing to complete transformation, due to the inherently slow rate of phase transformation [2], such as in pritectiodal nature of MA $FeSi_2$ [12]. VHPed specimens showed average 90.2% of theoretical density in this process condition. Though the decomposition mechanism and the fraction of MnSi could not be rationalized in this study, the degree of alloying progress (f) can be briefly calculated using an equation, $f = I_{HMS}/(I_{HMS} + I_{MnSi})$, where I is the strongest peak intensity of each corresponding diffraction index [1]. The degree of alloying calculated in this study is 63.3%. This is less than that of an analogue study, for which MA plus pulse discharge sintering method was adopted, resulting in 49-87% depending on process condition [1]. It should also be considered that the melt spin process followed by pulverizing spark plasma sintering seemed to result in higher amount of HMS with nano size microstucucture comparison to those in this study, though the amount of HMS was not presented [2]. SEM and OM micrographs revealed no microcracks, but some voids were unavoidable, as shown in Fig. 2.

Thermoelectric properties were evaluated as a function of temperature. Seebeck coefficients at test range showed positive values, representing p-type conductivity, as presented in Fig. 3(a). Seebeck coefficients were shown to be compatible to, but a little bit less than analogue studies [1-2], possibly due to the higher amount of metallic MnSi phases. It is increased with increasing temperature up 623 K and saturated. Fig. 3(b) shows the temperature dependence of electrical resistivity of HMS. Electrical resistivity showed very similar values to the analogue studies [1-2] and increased with increasing temperature, representing a degenerating semi-conductor behavior. Thermal conductivity of MA HMS as a function of temperature was presented in Fig. 3(c). Thermal conductivity in this study (1.25-1.35 W/mK) was shown to be significantly lower than those of analogue studies (3-4.8 W/mK) [1] and even lower to those of the HMS with nano sized microstructure (2.1-2.4 W/mK) [2]. From the point of view, reducing thermal conductivity shall be the priority issue in enhancing thermoelectric performance, and inducing phonon scattering via grain refinement or introducing second phases/atoms at appropriate sites are most recognized methods [10, 12]. For this reason, lowered thermal conductivity in this process might be attributed to the induced phonon scattering by grain refinement which is typically (50 nm-100 nm) in MA process [12]. From the values of ρ, α and κ obtained above, ZT values were able to be calculated, as presented in Fig. 3(d). The maximum value was found to be 0.5 at 823 K. It can be considered that this value is relatively higher than that of analogue study, though the fraction of MnSi phase contained is relatively higher than those in analogue study [1]. This could be attributed to the reduced thermal conductivity cause by grain refinement in this study. It should also be speculated that ZT value in this study was relatively lower than those of another analogue case ($ZT = 0.62$ at 800 K) [2] which was believed to have similar microscopic scheme to our study. This is believed due to the relatively lower Seebeck coefficient value caused by relatively lower fraction of HMS phase in this study. It can be

Table 1. Transport properties of MA HMS at 300 K with comparison references [1-2].

Materials	Degree of HMS phase	Hall coefficient (cm^3/C)	Mobility ($cm^2/Vsec$)	Carrier concentration ($/cm^3$)
MA HMS	66.3%	0.00987	45.3	9.47×10^{19}
Ref.1	87%	positive	200.0	2.20×10^{19}
	49%	positive	130.0	1.30×10^{19}
Rer.2	n/a	positive	n/a	2.14×10^{19}

considered that if an appropriate attempt could be introduced to promote the degree of HMS phases into this system along with producing an ultra fine microstructure by MA process, it would be an effective, alternative process for the high performance manganese silicide thermoelectric materials and devices.

Transport properties in terms of Hall coefficient, carrier mobility and carrier concentration were examined as shown in Table 1. Hall coefficient showed positive value, confirming p-type conductivity. Carrier concentration is in the similar order for degenerate semiconucting materials. Carrier mobility seems to be lower than reference 1 cases, possibly due to the grain refinement by MA in this study.

Summary

Nowotny phase HMS ($MnSi_{1.73}$) thermoelectric materials have been successfully synthesized by mechanical alloying of elemental powders, followed by VHP. Single phase of $MnSi_{1.73}$ seemed to be formed after 24 hrs of milling, but a trace of MnSi appeared after hot consolidation by VHP. The degree of alloying calculated is 63.3% which is less than analogue studies. Seebeck coefficients at test range and Hall coefficient value showed positive values, representing p-type conductivity. Seebeck coefficients were shown to be compatible to, but a little bit less than analogue studies, possibly due to the higher amount of metallic MnSi phases. Electrical resistivity showed very similar values to the analogue studies, showing a degenerate semiconductor behavior. Thermal conductivity (1.25-1.35 W/mK) was shown to be significantly lower than those of analogue studies, possibly due to the induced phonon scattering by grain refinement in this MA work. The maximum value of ZT obtained is 0.5 at 823 K, which is relatively higher than or compatible to that of analogue studies, though the fraction of MnSi phase contained is relatively higher. This could be attributed to the reduced thermal conductivity caused by grain refinement in this study. Transport properties were also examined. Carrier concentration is in the similar order for degerate semiconucting materials. Carrier mobility seems to be little lower than analogue studies, possibly due to due to the grain refinement by MA in this study. It can be considered that if appropriate attempts will be incorporated into this system to promote the degree of HMS phases along with producing an ultra fine microstructure by MA process, it may be an effective, alternative process for the high performance manganese silicide thermoelectric materials and devices.

Acknowledgement

The research was supported by a grant from the Academic Research Program of Korea National University of Transportation in 2012, and by the Regional Innovation Center (RIC) Program which was conducted by the Ministry of Knowledge Economy of the Korean Government.

References

1. T. Itoh and M. Yamada, J. Elec. Mater. 38 [7] (2009) 925-929.
2. W. Luo, H. Li, Y. Yang, Z. Lin, X. Tang, Q. Zhang, and C. Uher, Intermetallics 19 (2011) 404-408.
3. Q.R. Hou, Z.M. Wang and Y.J. He, Appl. Phys. A 80 (2005) 1807-1811.
4. H.Q. Ye and S. Amelinckx, J. Solid State Chem. 61 (1986) 8-39.
5. U. Gottlieb, A. Aulpice, B. Lambert-Andronj and O. Laborde, J. Alloys Comp. 361 (2003) 13-18.
6. A.J. Zhou, X.B. Zhao, T.J. Zhu, S.H. Yang, T. Dasgupta, C. Stiewe, R. Hassdorf and E. Mueller, Mater. Chem. Phys. 124 (2010) 1001-1005.
7. M. Uemoto, Z.G. Liu, R. Omatsuzawa and K. Tsuchiya, Mater. Sci. Forum 343-346 (2000) 918-921.
8. S. Okada, T. Shishido, M. Ogawa, F. Matsukawa, Y. Ishizawa, K. Nakajima, T. Fukuda and T. Lundstroem, J. Cry. Growth 229 (2001) 532-536.
9. J. Hu, C. Zhang, W. Li, S. Guan and H. Tatsuoka, Phy. Procedia 11 (2011) 138-141.
10. S.-C. Ur, P. Nash and I.-H. Kim, J. of Alloys and Comp. 361 (2003) 84-91.
11. Q.R. Hou, W. Zhao, Y.B. Chen, and Y.J. He, Mater. Chem. Phy. 121 (2010) 103-108.
12. S.-C. Ur and I.-H. Kim, Met. Mater. Inter. 11[4] (2005) 301-308.