**The effect of a fourth element (Co, Cu, Fe, Pd) on the standard enthalpy of formation of the
Heusler compound Ni_2MnSn**

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Abstract

The standard enthalpies of formation of quaternary Heusler compounds $(\text{X}, \text{Ni})_2\text{MnSn}$ ($\text{X} = \text{Co}, \text{Cu}, \text{Fe}, \text{Pd}$) were investigated experimentally using high temperature direct reaction calorimetry. Lattice parameters of these compounds were determined using X-ray diffraction analysis. Microstructures were identified using scanning electron microscopy and energy dispersive spectroscopy. The effect of an additional X element on the standard enthalpy of formation of the Heusler compound Ni_2MnSn is discussed.

Keywords: Heusler compound; Standard enthalpy of formation; Calorimetry

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1. Introduction

Heusler compounds (prototype Cu_2MnAl , Pearson symbol cF16, space group $\text{Fm}\bar{3}\text{m}$) with the general formula X_2YZ are a class of very promising materials [1] with wide potential applications. What makes the Heusler alloys more fascinating is their tunable characteristics through either preparing off-stoichiometric alloys or adding a fourth or even a fifth element. Ni_2MnSn ($T_c = 344 \text{ K}$) [2] is of special interest due to its magnetic shape memory effect [3] as well as the inverse magneto-caloric effect [4]. Yin *et al.* [5] measured the standard enthalpy of formation of several off-stoichiometric Ni-Mn-Sn Heusler alloys and observed a linear dependence on the substitution of Ni by Mn. Han *et al.* [6] found that doping a small amount of Co to Ni-Mn-Sn Heusler alloy will rapidly increase the temperature of the martensitic transformation and magnetic transition, favoring a high magneto-caloric effect. Bose *et al.* [7] investigated the electronic and magnetic properties of the quaternary Heusler alloys $(\text{Ni}, \text{T})_2\text{MnSn}$ ($\text{T} = \text{Cu}, \text{Pd}$) by means of *ab initio* calculations and observed that while the magnetic moments were only weakly dependent on the alloy composition, the Curie temperatures exhibited strongly nonlinear behavior with respect to Cu doping in contrast with an almost linear concentration dependence in the case of Pd doping.

To have a better understanding of the tuning effect, a good knowledge of phase equilibria and thermodynamics of the quaternary systems is required. There are only a limited number of transition elements that can be substituted for Nickel in this compound on the same crystallographic sites. In order to investigate the effects of substitution we selected elements close to Nickel in the 3d transition series, so that they have similar atomic size, Fe, Co and Cu and one element in the 4d transition series, Pd in the same column as Nickel so that it has the same number of d electrons. In this work, we make a contribution to the thermodynamic understanding of the $(\text{X}, \text{Ni})_2\text{MnSn}$ ($\text{X} = \text{Co}, \text{Cu}, \text{Fe}, \text{Pd}$) quaternary systems through experimental measurements of the standard enthalpies of formation ($\Delta_f H^\circ$), lattice parameters (a) and related phase.

2. Materials and methods

All elemental materials were purchased from Alfa Aesar[®]. Purity and size of the powders are listed in Table 1. Co, Fe and Ni powders were heat treated at 873 K for an hour in flowing hydrogen to remove oxides on the surface. The reduced powders were then ground and sieved ($< 44 \mu\text{m}$) immediately prior to sample preparation.

The experimental procedure for measuring standard enthalpy of formation using the high temperature direct reaction calorimeter (also known as the Kleppa calorimeter) was described previously [8, 9]. Elemental powders of the desired ratio ($\text{X}_n\text{Ni}_{2-n}\text{MnSn}$, $n = 0, 0.25, 0.5, \dots, 1.75, 2$) were mixed using a spoon and compressed together with a load of around 20 MPa. The compressed pellets generally had dimensions of $\phi 4 \times 1.5 \text{ mm} \times \text{mm}$ with a weight of 100 mg. The temperature of the calorimeter was maintained at $1373 \pm 2 \text{ K}$ for Co, Pd and the first three Fe containing alloys and $1273 \pm 2 \text{ K}$ for $\text{Cu}_x\text{Ni}_{2-x}\text{MnSn}$ alloys and the last three Fe-rich alloys, FeNiMnSn , $\text{Fe}_{1.25}\text{Ni}_{0.75}\text{MnSn}$ and $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{MnSn}$. The change of temperature was to accommodate other experiments and did not affect the result in the present work as long as the elements fully reacted with each other. Boron Nitride (BN) crucibles and an argon atmosphere purified with a Ti getter were used. Samples were dropped into the calorimeter individually to measure the heat of reaction ($\Delta_r H$) over an interval of 20 min each to reach thermal equilibrium ($T = 1373 \text{ K}$ or 1273 K). The reacted samples were taken out and dropped into the calorimeter again to measure the heat content ($H_T - H_{298}$) at the corresponding temperature ($T = 1373$ or 1273 K). The standard enthalpy of formation ($\Delta_f H^\circ$) is obtained using the heat of reaction minus the heat content. The determined uncertainty is from the calculated standard deviation of multiple measurements. The calorimeter calibration was performed using the NIST SRM 720 sapphire. The weight loss for each sample was less than 1 wt. %. The reacted samples were removed from the calorimeter for characterization using XRD (Thermo ARL, X'TRA; Bruker, D2 PHASER) and SEM (JEOL, JSM-5900LV) with an energy dispersive spectrometer (Oxford Instruments, 80 mm^2 X-Man^N Silicon Drift Detector) after appropriate

preparation (samples crushed to powders with a size less than 44 μm for XRD analysis and standard metallographic preparation for SEM examination).

It is relatively easy to obtain the lattice parameters (a) of cubic structured Heusler phases since they are related to the interplanar d-spacing (d) and the atomic plane index (h k l) in a simple form,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

The interplanar d-spacing can be obtained using the Bragg's Law

$$\lambda = 2d \sin \theta$$

in which λ is the wave length of the generated X-ray (for Cu target, λ ($K\alpha$) = 0.15418 nm, λ ($K\alpha_1$) = 0.15406 nm, λ ($K\alpha_2$) = 0.15444 nm).

The calculated lattice parameters of each peak are linearly extrapolated to $\frac{1}{2} \left(\frac{\cos^2 \theta}{\sin^2 \theta} + \frac{\cos^2 \theta}{\theta} \right)$ to remedy the error caused by absorption and divergence [10].

Considering that the "Fe₂MnSn" composition is not a stable Heusler compound according to previous work [11], an alloy with the composition Fe_{1.5}Ni_{0.5}MnSn was prepared through arc melting followed by long term annealing (1173 K for 14 days) in an evacuated quartz tube to determine the maximum equilibrium solubility of Fe in Ni₂MnSn. The Cu_{1.75}Ni_{0.25}MnSn alloy was investigated in the same manner.

3. Results

All of the studied alloys have the L2₁ Heusler structure. The measured lattice parameters (a) and compositions of the reacted samples from the Kleppa calorimeter before the heat content measurement are compiled in Table 2, together with the data of ternary compounds from previous work [5, 11, 12].

The measured standard enthalpies of formation ($\Delta_f H^\circ$) are listed in Table 3, as well as the heats of reaction ($\Delta_r H$) and heat contents ($H_T - H_{298}$).

4. Discussion

The data in Table 2 show that the determined compositions are close to the nominal ones. The content of Mn shows the largest variations in general and the reasons could be the oxide (MnO) introduced from the commercially purchased Mn powders, the relatively high vapor pressure, the lost of elemental powders during sample preparation and the error from the EDS instrument. The amount of the additional phases is small in most cases and those beyond 5 vol. % are marked out and the corresponding measured values are indicative rather than precise.

It is obvious from Table 3 that different X elements have a different effect on the standard enthalpy of formation of the Heusler compound Ni_2MnSn .

4.1. $(\text{Co}, \text{Ni})_2\text{MnSn}$

All alloys crystallize in an L2_1 structure and three XRD patterns are shown in Fig. 1 as examples together with the simulated pattern of the equiatomic composition CoNiMnSn . A very limited amount of additional phases (MnO from the elemental material and Ni_3Sn_2) were observed in some alloys. Helmholdt and Buschow [13] observed no substitution of atoms in the Ni_2MnSn alloy by neutron diffraction. Thus, it is reasonable to assume that there is no substitution between (Co, Ni) and Mn or Sn element in this work. Plus, the X-ray scattering amplitude of Co and Ni are very close based on their atomic weight, making it reasonable that the relative intensities do not change much with the variation of the content of Co as shown in Fig. 1.

With the increase of the content of Co (x) in the $\text{Co}_x\text{Ni}_{2-x}\text{MnSn}$ alloys, the lattice parameter (a) decreases and this can be fitted using a second order polynomial $a = -0.0008x^2 - 0.0014x + 0.6044$ (nm)

as shown in Fig. 2. A positive deviation from the Vegard's law [14], though very slight, is observed indicating an increasing interatomic distance and thus a less stable crystal structure than the perfect substitution between Co and Ni. The fact that substitution of Ni by Co atoms decreases the lattice parameter is consistent with the fact that the lattice parameter of the stoichiometric binary B2 structured compound CoAl (0.28628 nm) is smaller than that of NiAl (0.28863 nm) [15] and is consistent with values from the *ab initio* calculations from the Open Quantum Materials Database (OQMD) [1].

The melting points (T_m) of $\text{Co}_{0.5}\text{Ni}_{1.5}\text{MnSn}$ (1373 ± 5 K) and CoNiMnSn (1355 ± 5 K) alloys were determined using a Setsys 1700 DSC with a heating rate of 10 K/min in argon under atmospheric pressure. The results are consistent with the phenomena observed in the reacted samples that Ni_2MnSn , $\text{Co}_{0.25}\text{Ni}_{1.75}\text{MnSn}$ and $\text{Co}_{0.5}\text{Ni}_{1.5}\text{MnSn}$ alloys did not melt in the calorimeter at 1373 K.

The standard enthalpy of formation is best fit using a third order polynomial in Fig. 3, $\Delta_f H^\circ = 16.1x^3 - 50.4x^2 + 42.4x - 28.8$ (kJ/mole of atoms), even though the difference between the two end members is small. The wave shape variation of standard enthalpy of formation was also observed by Su *et al.* [9] in the Al-Ni-Ru system which was used to explain the miscibility gap in the alloy system. However, in the Co-Ni-Mn-Sn system, a miscibility gap was not observed in the backscattered electron image and no corresponding peaks were found in the XRD pattern. Further investigation is required to establish the reason for this behavior.

4.2. $(\text{Cu}, \text{Ni})_2\text{MnSn}$

The reacted alloys of the composition $\text{Cu}_x\text{Ni}_{2-x}\text{MnSn}$ ($x = 0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75$) were close to a single L_{21} Heusler phase, as well as the as cast $\text{Cu}_{1.75}\text{Ni}_{0.25}\text{MnSn}$ alloy. However, after annealing the as cast alloy at 1173 K for 14 days, Cu_4MnSn phase ($\text{Cu}_{65}\text{Mn}_{17}\text{Sn}_{18}$, prototype Cu_4MgSn , Pearson symbol cF24, space group $F\bar{4}3m$) was observed at the grain boundaries and

$\text{Cu}_{10}\text{Sn}_3$ phase ($\text{Cu}_{64}\text{Ni}_3\text{Mn}_7\text{Sn}_{26}$, prototype $\text{Cu}_{10}\text{Sn}_3$, Pearson symbol hP26, space group P6_3) was found precipitating out with a needle shape in the L2_1 structured matrix ($\text{Cu}_{40}\text{Ni}_9\text{Mn}_{24}\text{Sn}_{27}$) as shown in Fig. 4 (a). The same phases were observed in the reacted ternary $\text{Cu}_{50}\text{Mn}_{25}\text{Sn}_{25}$ alloy from the calorimeter as shown in Fig. 4 (b). XRD analysis provides evidence consistent with this conclusion as shown in Fig. 5. The Cu-Mn-Sn ternary phase diagram has not been established completely due to the complexity of the Cu-Sn binary system. However, the equilibrium between the Cu_4MnSn phase and the Cu_3Sn phase of a D0_3 structure, which is a disordered structure of the L2_1 Heusler structure, is well established [17]. Therefore, it is concluded that Heusler structured “ Cu_2MnSn ” is a metastable phase at the stoichiometric composition, which can be stabilized through introducing around 9 at. % of Ni at 1173 K. Also, the OQMD predicts a positive enthalpy of formation (5.8 kJ/mole of atoms at 0 K) for the Heusler structured Cu_2MnSn , while the extrapolated experimental data indicate an enthalpy of formation of around -27 kJ/mole of atoms at 298 K. This is a substantial difference between the two values that cannot be simply ascribed to experimental error and the difference in temperature for the two results.

The variation of the lattice parameter with the content of Cu in $\text{Cu}_x\text{Ni}_{2-x}\text{MnSn}$ alloys can be fit using a straight line, $a = 0.0054x + 0.6039$ (nm) in Fig. 6, indicating an ideal mixing between the two end members, “ Cu_2MnSn ” and Ni_2MnSn . While the standard enthalpy of formation remains almost constant (the averaged value is -26.9 kJ/mole of atoms which is shown as a horizontal) considering the similarity between Cu and Ni in Fig. 7.

4.3. $(\text{Fe}, \text{Ni})_2\text{MnSn}$

Alloys of the composition $\text{Fe}_{0.25}\text{Ni}_{1.75}\text{MnSn}$, $\text{Fe}_{0.5}\text{Ni}_{1.5}\text{MnSn}$ and $\text{Fe}_{0.75}\text{Ni}_{1.25}\text{MnSn}$ were single phase while a minor amount of fcc Fe solid solution ($\text{Fe}_{78}\text{Ni}_6\text{Mn}_{14}\text{Sn}_2$) and Ni_3Sn_2 ($\text{Fe}_{17}\text{Ni}_{20}\text{Mn}_{26}\text{Sn}_{37}$, prototype $\text{Co}_{1.75}\text{Ge}$, space group $\text{P6}_3/\text{mmc}$, Pearson symbol hP6, note that Fe_5Sn_3 , Mn_2Sn , and Ni_3Sn_2 have the same crystal structure) were found in the FeNiMnSn and $\text{Fe}_{1.25}\text{Ni}_{0.75}\text{MnSn}$ alloys.

In the reacted $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{MnSn}$ sample, a large amount of primary phase Fe solid solution ($\text{Fe}_{79}\text{Ni}_4\text{Mn}_{14}\text{Sn}_3$) was found in contact with the peritectically formed Heusler phase ($\text{Fe}_{33}\text{Sn}_{16}\text{Mn}_{25}\text{Sn}_{26}$) in the matrix phase Ni_3Sn_2 ($\text{Fe}_{15}\text{Ni}_{22}\text{Mn}_{26}\text{Sn}_{37}$), as well as a small amount of remaining Ni_3Sn_4 ($\text{Fe}_1\text{Ni}_{37}\text{Mn}_4\text{Sn}_{58}$), as shown in Fig. 8(a). While in the as cast sample in Fig. 8(b), the primary phase Fe solid solution ($\text{Fe}_{76}\text{Ni}_4\text{Mn}_{16}\text{Sn}_4$) was surrounded by the peritectic Heusler phase ($\text{Fe}_{35}\text{Ni}_{14}\text{Mn}_{26}\text{Sn}_{25}$) in the matrix phase Ni_3Sn_2 ($\text{Fe}_{24}\text{Ni}_{27}\text{Mn}_{13}\text{Sn}_{36}$). After annealing at 1173 K for 14 days, the equilibrium between the Heusler phase ($\text{Fe}_{37}\text{Ni}_{14}\text{Mn}_{24}\text{Sn}_{25}$) and Ni_3Sn_2 ($\text{Fe}_{29}\text{Ni}_{11}\text{Mn}_{24}\text{Sn}_{36}$) was observed in Fig. 8(c). Therefore, the conclusion could be drawn that substitution of 14 at. % of Fe with Ni atoms would stabilize the “ Fe_2MnSn ” Heusler phase at 1173 K, which is formed through the peritectic reaction of fcc Fe solid solution and liquid phase.

The variation of the lattice parameter of $\text{Fe}_x\text{Ni}_{2-x}\text{MnSn}$ alloys with the increase of Fe content is shown in Fig. 9. A second order polynomial, $a = 0.0011x^2 - 0.0028x + 0.6041$ (nm) is used to fit the Ni-rich side. A negative deviation from the Vegard's law is observed, indicating the two end members “ Fe_2MnSn ” and Ni_2MnSn prefer to mix with each other. With the further increase of Fe, the composition enters into a two-phase region as shown in Fig. 8(c). Therefore, the lattice parameter remains constant within the instrumental error (± 0.0002 nm).

The variation of the standard enthalpy of formation with the content of Fe in $\text{Fe}_x\text{Ni}_{2-x}\text{MnSn}$ alloys up to $x = 1$ can be fitted reasonably well ($R^2 = 0.9115$) with a linear function, $\Delta_f H^\circ = 18.7x - 30.8$ (kJ/mole of atoms). The extrapolation to “ Fe_2MnSn ” gives a value of 6.8 kJ/mole of atoms which is close to the *ab initio* value of 10.1 kJ/mole of atoms [17]. Both results support the conclusion that “ Fe_2MnSn ” with a Heusler structure is not stable.

4.4. $(\text{Pd}, \text{Ni})_2\text{MnSn}$

A small amount (< 5 vol. %) of $(\text{Ni}, \text{Pd})_3\text{Sn}_2$ (prototype $\text{Co}_{1.75}\text{Ge}$, space group $\text{P6}_3/\text{mmc}$, Pearson

symbol hP6) was observed in some of the alloys, as well as a negligible amount of MnO from the elemental powders.

The variation of the lattice parameter (a) with the content of Ni can be fitted using a second order polynomial, $a = -0.002x^2 - 0.0132x + 0.6389$ (nm), deviating slightly positively from the Vegard's law, $a = -0.0173x + 0.6386$ (nm), as shown in Fig. 11.

The variation of the standard enthalpy of formation ($\Delta_f H^\circ$) with the content of Ni is shown in Fig. 12. It has a linear dependence with composition, $\Delta_f H^\circ = 19.0x - 55.9$ (kJ/mole of atoms) from Pd_2MnSn to $\text{Ni}_{1.25}\text{Pd}_{0.75}\text{MnSn}$ and then reaches a plateau with further increase of Ni. Only alloys of composition $\text{Ni}_{1.5}\text{Pd}_{0.5}\text{MnSn}$, $\text{Ni}_{1.75}\text{Pd}_{0.25}\text{MnSn}$ and Ni_2MnSn were found to be ferromagnetic at room temperature which is in agreement with the experimental result found by Uhl *et al.* [18] that the alloy composition with a Curie temperature at 298 K is $\text{Ni}_{1.48}\text{Pd}_{0.52}\text{MnSn}$. Therefore, the conclusion can be drawn that the additional stability, *i. e.*, the extra negative standard enthalpy of formation relative to the dashed extrapolated line in Fig. 12, is mainly from the magnetic contribution in those Ni-rich samples.

5. Conclusions

Four series of quaternary Heusler type compositions were investigated, $(\text{X}, \text{Ni})_2\text{MnSn}$ ($\text{X} = \text{Co}, \text{Cu}, \text{Fe}, \text{Pd}$). Standard enthalpies of formation were measured using high temperature direct reaction calorimetry and lattice parameters of 29 alloy compositions were determined. Introduction of different X elements have different effects on the standard enthalpy of formation of Ni_2MnSn due to the nature of the bonding. Through adding a certain amount of a fourth element, unstable Heusler compounds such as “ Cu_2MnSn ” and “ Fe_2MnSn ” can be stabilized. It has been shown that the addition of a fourth element to Ni_2MnSn changes the enthalpy of formation and therefore can be used to “tune” other properties of the compound.

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Table 1. Purity and particle size of the elemental powders used in this work.

Element	Purity, (wt. %)	Particle size, (μm)
Co	99.8	1.6
Cu	99.999	149
Fe	99.9+	10
Mn	99.95	44
Ni	99.9+	< 30
Pd	99.9	< 1
Sn	99.999	44

Table 2. Overall composition and lattice parameter (*a*) of each Heusler alloy, as well as the amount of additional phases.

Compound ^a	Overall composition, (at. %)	<i>a</i> /nm	Additional phases ^b
Ni ₂ MnSn [•]	Ni _{48.0} Mn _{24.6} Sn _{27.4}	0.6041	0.05 Ni ₃ Sn ₂
Co _{0.25} Ni _{1.75} MnSn	Co _{6.3} Ni _{43.3} Mn _{24.0} Sn _{26.4}	0.6047	0.01 Ni ₃ Sn ₂ , 0.01 MnO
Co _{0.5} Ni _{1.5} MnSn	Co _{11.8} Ni _{37.6} Mn _{25.0} Sn _{25.6}	0.6031	0.02 Ni ₃ Sn ₂
Co _{0.75} Ni _{1.25} MnSn	Co _{18.5} Ni _{31.2} Mn _{23.8} Sn _{26.5}	0.6030	Single phase
CoNiMnSn	Co _{24.7} Ni _{24.7} Mn _{23.9} Sn _{26.7}	0.6023	Single phase
Co _{1.25} Ni _{0.75} MnSn	Co _{31.2} Ni _{18.6} Mn _{24.0} Sn _{26.1}	0.6013	Single phase
Co _{1.5} Ni _{0.5} MnSn	Co _{37.2} Ni _{12.4} Mn _{23.8} Sn _{26.6}	0.6006	Single phase
Co _{1.75} Ni _{0.25} MnSn	Co _{43.4} Ni _{6.4} Mn _{23.7} Sn _{26.5}	0.5994	Single phase
Co ₂ MnSn [•]	Co _{49.0} Mn _{24.0} Sn _{27.0}	0.5985	0.01 CoSn ₂
Cu _{0.25} Ni _{1.75} MnSn	Cu _{6.5} Ni _{42.7} Mn _{25.2} Sn _{25.5}	0.6055	0.01 Ni ₃ Sn ₂ , 0.01 MnO
Cu _{0.5} Ni _{1.5} MnSn	Cu _{11.3} Ni _{37.6} Mn _{25.5} Sn _{25.6}	0.6063	0.02 Ni ₃ Sn ₂ , 0.01 MnO
Cu _{0.75} Ni _{1.25} MnSn	Cu _{18.5} Ni _{30.8} Mn _{24.6} Sn _{26.0}	0.6076	0.01 MnO
CuNiMnSn	Cu _{25.5} Ni _{25.1} Mn _{22.8} Sn _{26.7}	0.6093	Single phase
Cu _{1.25} Ni _{0.75} MnSn	Cu _{32.1} Ni _{19.1} Mn _{22.5} Sn _{26.3}	0.6111	Single phase
Cu _{1.5} Ni _{0.5} MnSn	Cu _{38.2} Ni _{12.8} Mn _{22.5} Sn _{26.5}	0.6123	Single phase
Cu _{1.75} Ni _{0.25} MnSn	Cu _{44.5} Ni _{6.4} Mn _{22.2} Sn _{26.8}	0.6133	0.05 Cu ₄ MnSn, 0.05 Cu ₁₀ Sn ₃
Fe _{0.25} Ni _{1.75} MnSn	Fe _{6.0} Ni _{44.0} Mn _{23.5} Sn _{26.5}	0.6034	< 0.01 Ni ₃ Sn ₂
Fe _{0.5} Ni _{1.5} MnSn	Fe _{12.5} Ni _{37.4} Mn _{23.4} Sn _{26.7}	0.6030	< 0.01 Ni ₃ Sn ₂
Fe _{0.75} Ni _{1.25} MnSn	Fe _{19.3} Ni _{31.0} Mn _{23.2} Sn _{26.6}	0.6026	0.01 Ni ₃ Sn ₂
FeNiMnSn	Fe _{23.9} Ni _{24.0} Mn _{25.1} Sn _{27.0}	0.6024	0.02 fcc Fe, 0.04 Ni ₃ Sn ₂ , < 0.01 FeSn ₂
Fe _{1.25} Ni _{0.75} MnSn [*]	Fe _{31.9} Ni _{17.1} Mn _{27.7} Sn _{23.3}	0.6029	0.05 fcc Fe, 0.05 Ni ₃ Sn ₂ , 0.01 FeSn ₂
Pd ₂ MnSn [•]	Pd _{51.2} Mn _{22.3} Sn _{26.5}	0.6386	0.02 PdSn
Ni _{0.25} Pd _{1.75} MnSn	Ni _{6.9} Pd _{45.8} Mn _{20.1} Sn _{27.2}	0.6361	0.03 Pd ₃ Sn ₂ , 0.01 MnO
Ni _{0.5} Pd _{1.5} MnSn	Ni _{12.8} Pd _{38.8} Mn _{21.6} Sn _{26.8}	0.6314	0.02 Pd ₃ Sn ₂ , 0.01 MnO
Ni _{0.75} Pd _{1.25} MnSn	Ni _{19.5} Pd _{32.1} Mn _{21.1} Sn _{27.2}	0.6281	Single phase
NiPdMnSn	Ni _{24.2} Pd _{25.4} Mn _{24.6} Sn _{25.7}	0.6235	0.03 Ni ₃ Sn ₂
Ni _{1.25} Pd _{0.75} MnSn	Ni _{29.3} Pd _{18.2} Mn _{27.8} Sn _{24.7}	0.6192	0.02 Ni ₃ Sn ₂ , 0.01 MnO
Ni _{1.5} Pd _{0.5} MnSn	Ni _{36.8} Pd _{16.9} Mn _{24.4} Sn _{25.9}	0.6139	0.02 Ni ₃ Sn ₂
Ni _{1.75} Pd _{0.25} MnSn	Ni _{43.4} Pd _{6.7} Mn _{23.2} Sn _{26.7}	0.6097	0.03 Ni ₃ Sn ₂

a [•] indicates the data are from References [5, 11, 12]; ^{*} indicates the measured lattice parameter

does not correspond to the nominal composition due to the presence of large amounts of additional phases;

b The amount of the additional phases are presented in volume fraction.

Table 3. Measured standard enthalpy of formation ($\Delta_f H^\circ$), heat of reaction ($\Delta_r H$) and heat content ($H_T - H_{298}$) of each alloy.

Compound ^a	$\Delta_f H^\circ$	$\Delta_r H$	$H_T - H_{298}$ ^b
Ni ₂ MnSn [°]	-29.7 ± 2.9	3.8 ± 0.4	33.5 ± 2.4
Co _{0.25} Ni _{1.75} MnSn	-19.0 ± 1.7	12.1 ± 0.8	31.2 ± 1.5
Co _{0.5} Ni _{1.5} MnSn	-17.9 ± 1.2	15.8 ± 0.4	33.7 ± 1.1
Co _{0.75} Ni _{1.25} MnSn	-21.8 ± 4.0	16.3 ± 1.5	38.1 ± 3.7 [▲]
CoNiMnSn	-20.2 ± 3.3	31.2 ± 1.0	51.4 ± 3.1 [▲]
Co _{1.25} Ni _{0.75} MnSn	-21.2 ± 2.6	35.4 ± 1.9	56.6 ± 1.8 [▲]
Co _{1.5} Ni _{0.5} MnSn	-23.0 ± 2.3	39.8 ± 1.3	62.8 ± 1.9 [▲]
Co _{1.75} Ni _{0.25} MnSn	-24.9 ± 3.1	38.2 ± 2.3	63.1 ± 2.1 [▲]
Co ₂ MnSn [°]	-15.6 ± 2.8	29.9 ± 1.4	45.5 ± 2.5 [▲]
Cu _{0.25} Ni _{1.75} MnSn [•]	-25.0 ± 2.1	4.2 ± 1.3	29.2 ± 1.7
Cu _{0.5} Ni _{1.5} MnSn [•]	-27.8 ± 2.6	8.0 ± 0.1	35.9 ± 2.6
Cu _{0.75} Ni _{1.25} MnSn [•]	-26.5 ± 1.9	18.2 ± 0.7	44.7 ± 1.8 [▲]
CuNiMnSn [•]	-25.4 ± 2.0	23.9 ± 1.4	49.3 ± 1.5 [▲]
Cu _{1.25} Ni _{0.75} MnSn [•]	-27.8 ± 2.3	22.0 ± 1.1	49.8 ± 2.0 [▲]
Cu _{1.5} Ni _{0.5} MnSn [•]	-26.5 ± 3.6	20.4 ± 2.4	46.9 ± 2.7 [▲]
Cu _{1.75} Ni _{0.25} MnSn [•]	-26.6 ± 2.2	20.6 ± 1.5	47.2 ± 1.6 [▲]
Fe _{0.25} Ni _{1.75} MnSn	-25.2 ± 3.4	16.6 ± 0.7	41.8 ± 3.4
Fe _{0.5} Ni _{1.5} MnSn	-26.6 ± 2.5	24.9 ± 1.6	51.5 ± 1.9 [▲]
Fe _{0.75} Ni _{1.25} MnSn	-17.5 ± 3.0	38.4 ± 2.2	55.9 ± 2.1 [▲]
FeNiMnSn ^{•*}	-10.2 ± 2.4	26.5 ± 0.5	36.7 ± 2.3
Fe _{1.25} Ni _{0.75} MnSn ^{•*}	-14.3 ± 2.5	30.8 ± 1.2	45.2 ± 2.2 [▲]
Pd ₂ MnSn [°]	-54.6 ± 3.1	-20.6 ± 1.6	33.9 ± 2.7
Ni _{0.25} Pd _{1.75} MnSn [*]	-51.8 ± 3.7	-21.0 ± 1.1	30.7 ± 3.5
Ni _{0.5} Pd _{1.5} MnSn	-47.0 ± 1.1	-13.5 ± 1.9	33.5 ± 0.5
Ni _{0.75} Pd _{1.25} MnSn	-42.4 ± 2.5	-14.2 ± 1.4	28.2 ± 2.1
NiPdMnSn	-37.5 ± 1.0	-5.0 ± 0.5	32.4 ± 0.8
Ni _{1.25} Pd _{0.75} MnSn	-30.8 ± 2.2	0.5 ± 0.1	31.2 ± 2.2
Ni _{1.5} Pd _{0.5} MnSn	-28.8 ± 1.4	1.5 ± 0.5	30.2 ± 1.3
Ni _{1.75} Pd _{0.25} MnSn	-28.8 ± 2.6	4.4 ± 0.5	33.2 ± 2.5

Data are in kJ/mole of atoms.

a [°] indicates the value is from Reference [5, 11, 12]; [•] indicates the alloy was investigated at 1273 K;

* indicates the measured data are indicative due to the presence of large amounts of additional phases.

b [▲] indicates the sample melts at the corresponding temperature.

Figure Captions

Fig. 1. XRD patterns of (a) $\text{Co}_{0.5}\text{Ni}_{1.5}\text{MnSn}$; (b) CoNiMnSn ; (c) $\text{Co}_{1.25}\text{Ni}_{0.75}\text{MnSn}$; (d) simulated CoNiMnSn alloys in relative intensity ($10^2 I/I_{\max}$).

Fig. 2. Variation of the lattice parameter (a) with the content of Co (x) in the $\text{Co}_x\text{Ni}_{2-x}\text{MnSn}$ Heusler alloys.

Fig. 3. Variation of the standard enthalpy of formation ($\Delta_f H^\circ$) with the content of Co (x) in the $\text{Co}_x\text{Ni}_{2-x}\text{MnSn}$ Heusler alloys.

Fig. 4. Backscattered electron micrograph of (a) annealed $\text{Cu}_{1.75}\text{Ni}_{0.25}\text{MnSn}$ alloy and (b) reacted “ Cu_2MnSn ” alloy.

Fig. 5. Experimental XRD patterns of $\text{Cu}_{1.75}\text{Ni}_{0.25}\text{MnSn}$ of (a) the reacted, (b) the as cast, (c) the annealed sample in relative intensity ($10^2 I/I_{\max}$) and the simulated patterns of $\text{Cu}_{1.75}\text{Ni}_{0.25}\text{MnSn}$ of an L2_1 structure, Cu_4MnSn and $\text{Cu}_{10}\text{Sn}_3$.

Fig. 6. Variation of the lattice parameter (a) of the $\text{Cu}_x\text{Ni}_{2-x}\text{MnSn}$ alloys with the increase of Cu content (x).

Fig. 7. Variation of the standard enthalpy of formation ($\Delta_f H^\circ$) of the $\text{Cu}_x\text{Ni}_{2-x}\text{MnSn}$ alloys with the increase of Cu content (x).

Fig. 8. Backscattered electron micrographs of $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{MnSn}$ alloys, (a) reacted sample from the calorimeter; (b) as cast sample from arc melting; (c) annealed sample at 1173 K for 14 days.

Fig. 9. Variation of the lattice parameter (a) of the $\text{Fe}_x\text{Ni}_{2-x}\text{MnSn}$ alloys with the increase of Fe content (x). Fe-rich compositions are in a two-phase field.

Fig. 10. Variation of the standard enthalpy of formation ($\Delta_f H^\circ$) of the $\text{Fe}_x\text{Ni}_{2-x}\text{MnSn}$ alloys with the increase of Fe content (x).

Fig. 11. Variation of the lattice parameter (a) of the $\text{Ni}_x\text{Pd}_{2-x}\text{MnSn}$ alloys with the increase of Ni content (x).

Fig. 12. Variation of the standard enthalpy of formation ($\Delta_f H^\circ$) of the $\text{Ni}_x\text{Pd}_{2-x}\text{MnSn}$ alloys with the increase of Ni content (x).

Fig. 1. XRD patterns of (a) $\text{Co}_{0.5}\text{Ni}_{1.5}\text{MnSn}$; (b) CoNiMnSn ; (c) $\text{Co}_{1.25}\text{Ni}_{0.75}\text{MnSn}$; (d) simulated CoNiMnSn alloys in relative intensity ($10^2 I/I_{\max}$).

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