Standard enthalpies of formation of selected Ni₂YZ Heusler compounds

Ming Yin ^{a*}, Philip Nash ^a, Wei Chen ^b, Song Chen ^a

^a Thermal Processing Technology Center, Illinois Institute of Technology (IIT),

10 West 32nd Street, Chicago, IL 60616, USA

^b Mechanical, Materials and Aerospace Department, Illinois Institute of Technology (IIT),

10 West 32nd Street, Chicago, IL 60616, USA

Abstract

The standard enthalpies of formation ($\Delta_f H^\circ$) of selected ternary Ni-based Heusler compounds Ni₂YZ (Y = Co, Cu, Fe, Hf, Mn, Ti, V; Z = Al, Ga, In, Si, Ge, Sn) were measured using high temperature direct reaction calorimetry. The measured standard enthalpies of formation (in kJ/mole of atoms) of the Heusler structured (L2₁, prototype Cu₂MnAl, Pearson symbol cF16, space group Fm $\bar{3}$ m) compounds are: Ni₂MnGa (-29.8 $\pm$ 3.9); Ni₂MnIn (-24.5 $\pm$ 2.0); Ni₂MnSn (-29.7 $\pm$ 2.9); Ni₂TiGa (-42.5 $\pm$ 2.2); Ni₂TiIn (-28.5 $\pm$ 1.1); Ni₂TiSn (-46.8 $\pm$ 2.0), for the B2 compound (prototype CsCl, Pearson cP2, space group Pm $\bar{3}$ m): Ni₂MnAl (-32.0 $\pm$ 2.8), for the inverse Heusler structured (i-L2₁, prototype Li₂AgSb, Pearson symbol cF16, space group F $\bar{4}$ 3m) compound: Ni₂CuSn (-12.5 $\pm$ 2.1), for the compounds of the L1₂ (prototype AuCu₃, Pearson symbol cP4, space group Pm $\bar{3}$ m) structure: Ni₂CuAl (-38.9 $\pm$ 3.1); Ni₂FeGe (-25.8 $\pm$ 3.0). Several off-stoichiometric alloys in the Ni-Mn-Sn system were also investigated: Ni_{0.55}Mn_{0.20}Sn_{0.25} (-26.6 $\pm$ 1.0); Ni_{0.45}Mn_{0.30}Sn_{0.25} (-27.5 $\pm$ 2.6); Ni_{0.40}Mn_{0.35}Sn_{0.25} (-26.6 $\pm$ 2.6); Ni_{0.25}Mn_{0.50}Sn_{0.25} (-20.9 $\pm$ 2.6); Ni_{0.50}Mn_{0.30}Sn_{0.20} (-21.0 $\pm$ 3.2); Ni_{0.50}Mn_{0.35}Sn_{0.15} (-20.1 $\pm$ 1.7). Values are compared with those from first principles calculations in published papers and the Open Quantum Materials Database (OQMD). Lattice parameters were determined using X-ray diffraction analysis. Microstructures were characterized using scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS). Differential scanning

calorimetry (DSC) was used to measure the melting points of the compounds.

Keywords: Heusler compound; Standard enthalpy of formation; Calorimetry

*Corresponding author:

Ming Yin

Phone: 1+(312) 567 3203

fax: 1+(312) 567 8875

e-mail: myin1@hawk.iit.edu

1. Introduction

Heusler compounds are ternary intermetallics with an $L2_1$ structure (prototype Cu_2MnAl , Pearson symbol cF16, space group $\text{Fm}\bar{3}\text{m}$) with the formula X_2YZ in which X and Y are different transition elements and Z is a group III to V element in the periodic table. Many of them are well known for the half-metallic property [1] with an energy gap between valence and conduction bands for electrons of one spin polarization (semiconducting minority-spin electrons) and continuous bands for the electrons of the other spin polarization (normal metallic majority-spin electrons). As a consequence, the conduction electrons at the Fermi level are 100% spin polarized, making them very promising for spintronics applications.

Besides the half-metallic property, some of the Ni-based Heusler alloys (e.g. Ni_2MnGa , Ni_2FeGa , Ni_2MnAl) exhibit interesting magneto-mechanical properties such as magnetic shape memory effect and magnetic field induced super-elasticity, which are very attractive for applications as sensors in magnetic micro-electro-mechanical systems for the recording and storage of information [2]. The superconductor Ni_2ZrGa exhibits a relatively high superconducting transition temperature ($T_c = 2.9$ K) [3].

As with many intermetallic compounds, utilization of their properties is often dependent on their phase relationships within the alloy system as well as the constitutional defect structures produced at off-stoichiometric compositions. For this reason it is important to develop an understanding of the whole alloy system incorporating the intermetallic compound. This requires both phase diagram and thermodynamic studies so that the CALPHAD method and first principles calculations may be used to predict phase equilibria and properties. Only limited data are available for the enthalpies of formation in many nickel containing ternary systems. Kubaschewski [4] and Hu *et al.* [5] measured the standard enthalpy of formation ($\Delta_f H^\circ$) of Ni_2TiAl using calorimetry. Hu *et al.* [6] reviewed the published data on experimental enthalpies of formation of compounds in a number of Al-Ni-X

systems and Hu *et al.* [7] also measured the enthalpies of formation of several Al-Ni-X B2 compounds. This work aims to investigate thermodynamic properties of Heusler compounds for further alloy design of these functional materials and to provide benchmark data for first principles calculations. The standard enthalpies of formation ($\Delta_f H^\circ$), lattice parameters (a) and related phase relationships of selected ternary Ni-based Heusler compounds Ni_2YZ ($\text{Y} = \text{Co}, \text{Cu}, \text{Fe}, \text{Hf}, \text{Mn}, \text{Ti}, \text{V}$; $\text{Z} = \text{Al}, \text{Ga}, \text{In}, \text{Si}, \text{Ge}, \text{Sn}$) are determined experimentally and reported in this paper.

2. Materials and methods

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

The experimental procedure for measuring the standard enthalpy of formation ($\Delta_f H^\circ$) using the high temperature direct reaction calorimeter, also known as the Kleppa calorimeter, was described previously [8, 9]. The temperature of the calorimeter was maintained at $1373 \pm 2 \text{ K}$ except for Ni_2TiGa and Ni_2TiIn which were measured at a lower temperature (1273 K) to avoid the reaction between the liquid solution containing Ti element and the Boron nitride (BN) crucible. A titanium “gettering” furnace operated at 1173 K was used to purify the argon atmosphere supplied to the calorimeter providing a partial pressure of oxygen of about $1.3 \times 10^{-28} \text{ Pa}$. Stoichiometric amounts of elemental powders were mixed using a spoon and compressed to make 7 pellets which were individually dropped into the BN crucible in the calorimeter at intervals of 20 minutes to measure the heat of reaction ($\Delta_r H$). The reacted alloys were cooled to room temperature and dropped into the calorimeter again to measure the heat content ($H_T - H_{298}$, $T = 1373$ or 1273 K). The standard enthalpy of formation ($\Delta_f H^\circ$) is obtained using the heat of reaction minus the heat content. Heat

effects were integrated individually and the measured average value was compared to those of NIST SRM 720 sapphire to calculate the corresponding enthalpy. The determined uncertainty is obtained from the calculated standard deviation of multiple measurements. Heat contents for each compound at the corresponding temperature were calculated using the empirical Neumann-Kopp rule [10] for comparison. The elemental data are from the compilation by Dinsdale [11].

Microstructures of the reacted samples from the calorimeter were examined optically and with a scanning electron microscope (Jeol, JSM-5900LV) equipped with an energy dispersive spectrometer (Oxford Instruments, 80 mm² X-Man^N Silicon Drift Detector) after standard metallographic preparation. XRD analysis (Thermo ARL, X'TRA and Bruker, D2 PHASER) was used to identify the structure of the phases, as well as to determine lattice parameters (a). Alloys were crushed to powders and sieved ($< 44\ \mu\text{m}$) before XRD analysis. Commercial software CrystalMaker[®] and CrystalDiffract[®] were used to simulate the XRD patterns and estimate the amount of impurity phases by comparing the experimental intensities of the strong diffraction peaks.

Melting points (T_m) were measured using a Setaram[®] Setsys 1700 DSC at a heating rate of 10 K/min in flowing argon at atmospheric pressure. NIST SRM 720 sapphire was used as the reference material.

3. Results

The measured lattice parameters (a) for the reacted samples from the Kleppa calorimeter are summarized in Table 2, together with data from the literature when available [12-25]. Chemical Abstracts Service (CAS) registry numbers for each compound are also listed.

The measured standard enthalpies of formation ($\Delta_f H^\circ$) are listed in Table 3. Data from first principles calculations [26, 27, 28] and the Open Quantum Materials Database (OQMD) [29], a

publicly accessible database of density functional theory calculated thermodynamic and structural properties, are included for comparison. All calculated values correspond to the L2₁ Heusler structure. The experimentally identified structure and relative amount of additional phases are also given.

Table 4 summarizes the measured heats of reaction ($\Delta_r H$) and heat contents ($H_T - H_{298}$) (from 298 K to 1273 or 1373 K), together with the values calculated using the Neumann-Kopp rule. The melting points determined in this work are also included.

4. Discussion

4.1. Microstructures and phase equilibria

In the following text, the observed microstructures and phase equilibria are discussed. The estimated amount of additional phases is presented in volume percent and the phase compositions in atomic percent measured using EDS, are given in parentheses.

4.1.1. Ni₂CoZ

Ni₂CoZ (Z = Al, Ga, Sn) compounds were investigated. In the reacted samples from the calorimeter, fcc (Co, Ni) solid solution (Ni₆₉Co₂₇Al₄, Ni₄₄Co₃₅Ga₂₁) was found with a martensite phase of the AuCu structure (Ni₄₂Co₂₆Al₃₂, Ni₄₆Co₂₀Ga₃₀, Pearson symbol tP2, space group P4/mmm) in the Ni₅₀Co₂₅Al₂₅ and Ni₅₀Co₂₅Ga₂₅ alloys respectively. Considering that an “Ni₂CoGa” Heusler structure was reported experimentally in the book written by Webster and Ziebeck [30], a 10 g sample was prepared through arc melting for further investigation. The as-cast structure consisted of two phases, (Co, Ni) fcc solid solution (Ni₅₅Co₂₈Ga₁₇) and a B2 phase (Ni₅₈Co₁₈Ga₂₄) in a dendritic structure in agreement with the high temperature phase diagram provided by Ducher *et al.* [31]. After annealing at 1173 K for 3 days, the morphology changed but the constituents did not, as

shown in Fig. 1, *i. e.*, the Heusler phase was not observed. The first-principles calculations from the OQMD shows the Heusler structured Ni_2CoGa compound is 13.1 kJ/mole of atoms above the convex hull, which indicates the L_{21} Heusler structure is energetically preferred to decompose to a mixture of more stable phases.

No Heusler phase was observed in the $\text{Ni}_{50}\text{Co}_{25}\text{Sn}_{25}$ alloy. Instead, primary phase Ni_3Sn_2 ($\text{Ni}_{60}\text{Co}_4\text{Sn}_{36}$) and (Co, Ni) fcc solid solution ($\text{Ni}_{49}\text{Co}_{44}\text{Sn}_7$) were observed with a eutectic structure of composition $\text{Ni}_{52}\text{Co}_{26}\text{Sn}_{23}$, consistent with the predictions from the OQMD.

4.1.2. Ni_2CuZ

Compositions of the type Ni_2CuZ ($Z = \text{Al, In, Si, Ge, Sn}$) were investigated. The Ni_2CuAl alloy crystallized in the AlNi_3 structure (prototype AuCu_3 , space group $\text{Pm}\bar{3}\text{m}$, Pearson symbol cP4) while Ni_2CuIn ($\text{Ni}_{54}\text{Cu}_{20}\text{In}_{26}$) crystallized in the InNi_3 structure (prototype CdMg_3 , space group $\text{P6}_3/\text{mmc}$, Pearson symbol hP8) together with 10 % InNi ($\text{Ni}_{44}\text{Cu}_{25}\text{In}_{31}$). The $\text{Ni}_{31}\text{Si}_{12}$ phase ($\text{Ni}_{62}\text{Cu}_{10}\text{Si}_{28}$) coexisted with Cu solid solution ($\text{Ni}_7\text{Cu}_{86}\text{Si}_7$) in the $\text{Ni}_{50}\text{Cu}_{25}\text{Si}_{25}$ alloy. Ni_3Ge ($\text{Ni}_{63}\text{Cu}_{11}\text{Ge}_{26}$, space group $\text{Pm}\bar{3}\text{m}$, Pearson symbol cP4) and $\text{Ni}_{3.3}\text{Cu}_{1.7}\text{Ge}_2$ ($\text{Ni}_{52}\text{Cu}_{20}\text{Ge}_{28}$, space group $\text{P6}_3\text{cm}$, Pearson symbol hP42) were found together in the $\text{Ni}_{50}\text{Cu}_{25}\text{Ge}_{25}$ alloy. Ni_2CuSn is almost a single phase microstructure with less than 1 % of (Ni, Cu) solid solution ($\text{Ni}_{28}\text{Cu}_{65}\text{Sn}_7$). The measured relative intensities of (111) and (200) peaks compared to (220) peak are 13.2 % and 3.8 % respectively, while the simulated peaks for the Heusler structure are 6.3 % and 4.4 %, those of the D0_3 structure are 6.9 % and 3.6 % and those of the inverse Heusler structure are 7.3 % and 3.2 %, making it impossible to determine the crystal structure unambiguously using XRD analysis. Liu *et al.* [32] suggested that the inverse-Heusler structure (i-L_{21} , prototype CuHg_2Ti , Pearson symbol cF16, space group $\text{F}\bar{4}3\text{m}$) was preferred when the X element (Ni) has fewer valence electrons than the Y element (Cu) which indicates that the structure in this case is likely to be the

inverse-Heusler structure.

4.1.3. Ni_2FeZ

Alloys of the composition Ni_2FeZ ($Z = \text{Ga}, \text{In}, \text{Ge}$) were studied. The reacted Ni_2FeGa alloy was composed of an AuCu structured martensite phase with 14 % of (Fe, Ni) fcc solid solution, while the structure observed in the annealed arc melted sample was (Fe, Ni) fcc solid solution dendrites ($\text{Ni}_{55}\text{Fe}_{32}\text{Ga}_{13}$) with B2 phase ($\text{Ni}_{58}\text{Fe}_{21}\text{Ga}_{21}$). Liu *et al.* [13] reported successfully preparing Ni_2FeGa Heusler structured compound using the melt spinning technique, indicating that the phase may be metastable and require non-equilibrium processing to exist. In the $\text{Ni}_{50}\text{Fe}_{25}\text{Ge}_{25}$ alloys, Ni_3Ge ($\text{Ni}_{50}\text{Fe}_{23}\text{Ge}_{27}$, space group $\text{Pm}\bar{3}\text{m}$, Pearson symbol cP4) was in equilibrium with 2 % GeNi_2 ($\text{Ni}_{50}\text{Fe}_{13}\text{Ge}_{36}$) at the grain boundary. InNi ($\text{Ni}_{48}\text{Fe}_4\text{In}_{48}$), (Fe, Ni) fcc solid solution ($\text{Ni}_{50}\text{Fe}_{49}\text{In}_1$) and a minor amount of InNi₂ were found in the $\text{Ni}_{50}\text{Fe}_{25}\text{In}_{25}$ alloy which is in agreement with the slight positive enthalpy of formation of the Heusler structure (0.4 kJ/mole of atoms) from the OQMD.

4.1.4. Ni_2HfZ

Ni_2HfZ ($Z = \text{Ga}, \text{In}$) compositions were prepared. 14 % of GaHfNi and 20 % of GaNi were observed with the Heusler compound Ni_2HfGa in the reacted sample. The as cast sample after arc melting also had a large amount of GaHfNi and GaNi with the Heusler phase Ni_2HfGa . After annealing at 1173 K for 21 days, the amount of impurities was substantially reduced, as shown in Fig. 2. The annealed samples were used for the subsequent heat content measurement.

20 % of HfNi₅ was found coexisting with the L2₁ structured Ni_2HfIn compound in the $\text{Ni}_{50}\text{Hf}_{25}\text{In}_{25}$ alloy obtained from the calorimeter. The reason for the presence of a large amount of additional phases with the Heusler phase is probably due to phase separation during solidification.

4.1.5. Ni_2MnZ

Alloys of the composition Ni_2MnZ ($Z = \text{Al, Ga, In, Si, Ge, Sn}$) were investigated, as well as several off-stoichiometric compositions in the Ni-Mn-Sn system as a case study, $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ ($x = 20, 30, 35, 50$) and $\text{Ni}_{50}\text{Mn}_x\text{Sn}_{50-x}$ ($x = 30, 35$) alloys. The reasons for choosing the Ni-Mn-Sn system are its extensive Ni_2MnSn phase field and due to its magnetic shape memory effect [33], the inverse magneto-caloric effect [34] and the readiness to complete reaction at the calorimeter temperature (1373 K). The Ni_2MnAl alloy has a B2 structure while Ni_2MnGa and Ni_2MnIn compounds were single phase Heusler compounds. $\text{Ni}_{50}\text{Mn}_{25}\text{Si}_{25}$ alloy was composed of $\text{Mn}_6\text{Ni}_{16}\text{Si}_7$ ($\text{Ni}_{50}\text{Mn}_{22}\text{Si}_{28}$, space group Fm-3m, Pearson symbol cF116) and $\text{Mn}_3\text{Ni}_3\text{Si}_2$ ($\text{Ni}_{41}\text{Mn}_{33}\text{Si}_{26}$) which is consistent with the Mn-Ni-Si ternary phase diagram provided by Hu *et al.* [35]. $\text{Ge}_7\text{Mn}_6\text{Ni}_{16}$ ($\text{Ni}_{56}\text{Mn}_{21}\text{Ge}_{23}$, space group Fm $\bar{3}$ m, Pearson symbol cF116) and $\text{Ge}_3\text{Mn}_4\text{Ni}_5$ ($\text{Ni}_{50}\text{Mn}_{29}\text{Ge}_{21}$) were observed in the reacted $\text{Ni}_{50}\text{Mn}_{25}\text{Ge}_{25}$ alloys and the same microstructure was found in the arc melted and annealed samples. Even though Heusler compound Ni_2MnGe has been reported by several authors [14, 36, 37], the first principles calculations by Zayak *et al.* [38] indicated the presence of incommensurate phonon instability suggesting that the Heusler structure is mechanically unstable, which is consistent with the present work. Also, the enthalpy of formation of the Heusler structure (-22.8 kJ/mole of atoms) from the OQMD is less negative than that of the combination of the phases in the three-phase region (-24.0 kJ/mole of atoms).

5 % of Ni_3Sn_2 ($\text{Ni}_{48}\text{Mn}_{10}\text{Sn}_{42}$) was observed in the Ni_2MnSn alloys which had a Heusler structure. Less than 1 % of MnNi_3 ($\text{Ni}_{66}\text{Mn}_{23}\text{Sn}_{11}$) was observed at the grain boundary in $\text{Ni}_{55}\text{Mn}_{20}\text{Sn}_{25}$ alloys while $\text{Ni}_{45}\text{Mn}_{30}\text{Sn}_{25}$, $\text{Ni}_{40}\text{Mn}_{35}\text{Sn}_{25}$ and $\text{Ni}_{25}\text{Mn}_{50}\text{Sn}_{25}$ had a single Heusler-type phase. Without further advanced examination, it is impossible to determine the occupation of elements on each site. The neutron diffraction performed by Helmholtz *et al.* [39] indicated an inverse Heusler structure in $\text{Ni}_{25}\text{Mn}_{50}\text{Sn}_{25}$ with 37 % disorder between Ni and Mn atoms. The lattice parameter increases with increasing amount of the element Mn since the atomic radius of Mn is larger than Ni, as shown in

Fig. 3 where the diffraction peaks shift towards the smaller diffraction angles.

In $\text{Ni}_{50}\text{Mn}_{30}\text{Sn}_{20}$ alloys, 5 % of MnNi ($\text{Ni}_{53}\text{Mn}_{37}\text{Sn}_{10}$, space group $\text{Pm}\bar{3}\text{m}$, Pearson symbol cP2) was observed at the grain boundaries while in the $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$ alloy, an inhomogeneous microstructure with a small content of Sn at the grain boundary was observed, as shown in Fig. 4.

4.1.6. Ni_2TiZ

Alloys of the type Ni_2TiZ ($Z = \text{Ga, In, Si, Ge, Sn}$) were investigated. A single Heusler phase was observed in the Ni_2TiGa alloy while around 20 % of additional phases Ni_2In_3 ($\text{Ni}_{40}\text{In}_{60}$) and Ni_3Ti ($\text{Ni}_{75}\text{Ti}_{25}$) were observed in the reacted alloys of Ni_2TiIn . After annealing at 1173 K for 7 days, only 3 % Ni_3Ti coexisting with the Heusler phase was observed in the Ni_2TiIn alloy and these samples were used for the subsequent heat content measurement. Three ternary phases were observed in the $\text{Ni}_{50}\text{Ti}_{25}\text{Si}_{25}$ alloy, $\text{Ni}_{16}\text{Si}_7\text{Ti}_6$ ($\text{Ni}_{60}\text{Si}_{23}\text{Ti}_{17}$), NiSiTi ($\text{Ni}_{33}\text{Si}_{30}\text{Ti}_{37}$) and a small amount of $\text{Ni}_{40}\text{Si}_{31}\text{Ti}_{13}$ ($\text{Ni}_{49}\text{Si}_{28}\text{Ti}_{23}$) which agrees with the Ni-Si-Ti phase diagram optimized by Du *et al.* [40]. GeNiTi ($\text{Ge}_{35}\text{Ni}_{33}\text{Ti}_{31}$, space group Pnma , Pearson symbol oP12) was found with $\text{Ge}_7\text{Ni}_{16}\text{Ti}_6$ ($\text{Ni}_{50}\text{Ti}_{27}\text{Ge}_{23}$, space group $\text{Fm}\bar{3}\text{m}$, Pearson symbol cF116) and a similar microstructure was found in the as cast samples which did not change after annealing at 1073 K for 28 days. A Heusler phase was found in the Ni_2TiSn alloy together with 3 % of Ni_3Sn_2 ($\text{Ni}_{62}\text{Sn}_{38}$).

4.1.7. Ni_2VZ

Ni_2VZ ($Z = \text{Al, Ga, In, Sn}$) compositions were investigated. A small amount of AlNi_3 and V were found together with Ni_2VAl with a B2 structure. 20 % of σ phase ($\text{Ni}_{29}\text{V}_{50}\text{Ga}_{21}$, space group $\text{P4}_2/\text{mmn}$, Pearson symbol tP30) was observed in the as reacted Ni_2VGa alloy which had an L2_1 structure while 8 % of σ phase was observed in the annealed sample. Ni_2V and In_3Ni_2 coexisted with a small amount of In in the $\text{Ni}_{50}\text{V}_{25}\text{In}_{25}$ alloys. No Heusler structured compound was observed in the as reacted Ni_2VSn samples after the measurement of heat of reaction. Instead, primary phase

Ni_3Sn_2 ($\text{Ni}_{63}\text{V}_2\text{Sn}_{35}$) was found with V and σ phase ($\text{Ni}_{32}\text{V}_{65}\text{Sn}_3$) at the boundary, as shown in Fig. 5(a). However, in the sample which was arc melted and further annealed at 673 K for 35 days, Heusler compound Ni_2VSn ($\text{Ni}_{48}\text{V}_{28}\text{Sn}_{24}$) was observed with 10 % Ni_3Sn_2 ($\text{Ni}_{54}\text{V}_8\text{Sn}_{38}$) as shown in Fig. 5(b), and this was used for the subsequent heat content measurement. The same microstructure formed after the measurement of heat of reaction, *i.e.* Ni_3Sn_2 , V and σ phase was observed after the heat content measurement. The reason for the presence of a different microstructure suggests that Ni_2VSn decomposes at high temperature. However, no peak was observed in the DSC result besides the melting point (1373 K). It is reasonable to assume that either the enthalpy of phase transformation is small or the decomposition temperature is very close to the melting point.

4.2. Standard enthalpy of formation

It can be seen from Table 2 that the measured and the nominal compositions of the alloys are in good agreement. The Cu content tends to be slightly lower than intended due to the relatively large size of the powder which is easily lost during mixing and the reason for the low content of Ga is its high vapor pressure at high temperature and with a low melting point it extrudes easily during the compression when preparing the calorimeter samples. The loss of Mn is caused by the presence of oxide from the elemental material and its high vapor pressure. The lattice parameters determined in this work are consistent with those from published papers.

First principles calculations from different sources [26, 27, 28, 29] have very similar results. Comparison of the predictions from the OQMD [29] with the experimentally determined standard enthalpies of formation in Fig. 6 shows reasonable agreement in most cases. In some cases where there is a significant difference between experimental and computed enthalpies of formation which can be attributed to the formation of a different structure in the experiment. It is quite reasonable for the experimental values for these compounds to have a more negative formation energy than the ones calculated for a Heusler structure at that composition. For example values corresponding to the

Heusler structure from the OQMD, for Ni_2CuAl (-36.1 kJ/mole of atoms), Ni_2CuIn (-6.1 kJ/mole of atoms) and Ni_2FeGe (-14.1 kJ/mole of atoms), are less negative than the experimental values for these compounds. Since the first principles values are for a different structure they should not be compared to the experimental values other than to observe that the predicted values should be smaller than the experimental data since the Heusler structure is not the stable phase. For some of the compounds, such as Ni_2MnGa and Ni_2TiSn , the predictions from first principles calculations are quite precise. But for the others, the difference can be more than 10 kJ/mole of atoms, such as Ni_2MnIn and Ni_2TiGa alloys which were single phase Heusler structure and so have high experimental accuracy. The reason could be that the complex magnetic ordering is not adequately accounted for in calculations or site substitutional effects are occurring in the reacted compounds. For some of the other alloys, the contribution from additional phases should be considered as increasing the measurement error in the experiments. Also, it should be pointed out that in some cases, such as Ni_2HfGa and Ni_2MnIn , even though Heusler phases were synthesized experimentally, the calculated enthalpy of formation from the OQMD are less negative than the hull energy, suggesting Heusler structure is not the ground state phase for these systems. The reason for this discrepancy could be that the calculated enthalpy of formation is at 0 K and the value might be different at a higher temperature. It should be noted that in these cases the difference between the calculated enthalpy of formation and the hull energy is generally very small within the calculation error (0.5 kJ/mole of atoms). It is also observed that the predicted value for Ni_2YIn and Ni_2YSn are often less negative than the measured data while data of the other elements are more scattered.

The measured standard enthalpies of formation of Ni_2MnZ ($Z = \text{Al, Ga, In, Sn}$) and Ni_2TiZ ($Z = \text{Al, Ga, In, Sn}$) compounds are shown in Fig. 7 and Fig. 8 respectively. Two trends can be observed in the standard enthalpy of formation for these Heusler compounds, similar to our previous findings [41, 42]. First, for the same Z element, the standard enthalpies of formation for Ni_2MnZ are generally less negative than those for Ni_2TiZ . This trend is probably related to the d-band filling of

the Y elements. Since the d-band of Mn is half filled, it is usually more stable against forming compounds than elements towards the beginning of the series such as Ti. Second, for both Ni_2MnZ and Ni_2TiZ , the standard enthalpies of formation become less negative when the Z element moves down the Group III column from Al to In, but gets more negative when the Z element changes from In to Sn, *i.e.* from Group III to Group IV. This trend in standard enthalpies of formation correlates well with the atomic radii of the Z elements [43, 44]. It is important to note that the experimental and DFT computed lattice parameters for these Heusler compounds show the same trend, increasing on going down the column, as shown by the atomic radii of the Z elements. Within the same row moving from a Group III to a Group IV element, the atomic radius decreases and the enthalpy of formation becomes more negative. Therefore, in Heusler compounds, smaller lattice parameters indicate shorter bond length, which generally corresponds to higher bond energy, *i.e.*, more negative enthalpy of formation. The fact that Ni_2YZ (Y = Mn, Ti; Z = Si, Ge) Heusler compounds are not observed is because of the formation of another more stable ternary compound $\text{Ni}_{16}\text{Y}_6\text{Z}_7$ (space group $\text{Fm}\bar{3}\text{m}$, Pearson symbol cF116; Y = Mn, Ti; Z = Si, Ge).

The Neumann-Kopp rule also has limitations, especially for the alloys that have a lower melting point than the temperature (1373 K) of the calorimeter, since the latent heat of melting of the compound is not considered. Alloys containing Ti or Hf generally have a lower value of the heat content than the predicted one. This implies a lower specific heat than expected but the reason is not clear.

The standard enthalpies of formation of the $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloys are presented in Fig. 9 in which the enthalpy value of Ni_3Sn with D0_3 structure was determined by Vassilev *et al.* [45]. It can be seen from the graph that the stoichiometric composition has the most negative value indicating the highest thermodynamic stability. The enthalpy values are generally linear with the change of composition. The linear fit result is

$$\Delta_f H^\circ = \begin{cases} 34.6x - 38.3 & \text{when } x > 0.25 \\ -62.0x - 14.2 & \text{when } x < 0.25 \end{cases} \text{ (kJ/mole of atoms) in which } x \text{ is the atomic}$$

fraction of Mn. The difference in slope indicates differences in constitutional defect structure on either side of stoichiometry.

5. Conclusions

A series of Ni-based Heusler type compositions were investigated. The standard enthalpies of formation of 27 Ni₂YZ Heusler compositions and 6 off-stoichiometric compositions were measured using high temperature direct reaction calorimetry. Phase compositions were verified using EDS analysis, and crystal structure and lattice parameters were determined using XRD. The Heusler structure was identified in Ni₂HfGa, Ni₂HfIn, Ni₂MnGa, Ni₂MnIn, Ni₂MnSn, Ni₂TiGa, Ni₂TiIn, Ni₂TiSn, Ni₂VGa and Ni₂VSn compounds. Ni₂FeGa, Ni₂MnAl and Ni₂VAl compounds had a B2 structure and Ni₂CuSn compound had an inverse Heusler structure. Ni₅₀Cu₂₅Al₂₅ crystallized in the AlNi₃ structure while Ni₅₀Cu₂₅In₂₅ crystallized in the InNi₃ structure. No Heusler structure was observed in Ni₅₀Co₂₅Al₂₅, Ni₅₀Co₂₅Ga₂₅, Ni₅₀Co₂₅Sn₂₅, Ni₅₀Cu₂₅Ge₂₅, Ni₅₀Fe₂₅Ge₂₅, Ni₅₀Fe₂₅In₂₅, Ni₅₀Mn₂₅Si₂₅, Ni₅₀Mn₂₅Ge₂₅, Ni₅₀Ti₂₅Si₂₅, Ni₅₀Ti₂₅Ge₂₅ and Ni₅₀V₂₅In₂₅ alloys.

Acknowledgements

The authors would like to thank Prof. Carlo U. Segre for his help with the XRD measurement. This research is supported by NSF Grant #DMR1307631.

References

- [1] R. A. de Groot, F. M. Müller, P. G. van Engen, K. H. J. Buschow, New class of materials: half-metallic ferromagnets, Phys. Rev. Lett. 50 (1983) 2024-2027.
- [2] T. Graf, C. Felser, S. S. P. Parkin, Simple rules for the understanding of Heusler compounds, Prog. Solid State Ch. 39 (2011) 1-50.
- [3] J. Winterlik, G. H. Fecher, C. Felser, M. Jourdan, K. Grube, F. Hardy, H. von Löhneysen, K. L.

- Holman, R. J. Cava, Ni-based superconductor: Heusler compound ZrNi_2Ga , *Phys. Rev. B* 78 (2008) 184506/1-184506/9.
- [4] O. Kubaschewski, The heats of formation in the system Aluminum + Nickel + Titanium, *Trans. Faraday Soc.* 54 (1958) 814-820.
- [5] R. Hu, P. Nash, Q. Chen, Enthalpy of formation in the Al-Ni-Ti system, *J. Phase Equilib. Diff.* 30 (2009) 559-563.
- [6] R. Hu, P. Nash, Review: Experimental enthalpies of formation of compounds in Al-Ni-X systems, *J. Mater. Sci.* 41 (2006) 631-641.
- [7] R. Hu, H. Su, P. Nash, Enthalpies of formation and lattice parameters of B2 phases in Al-Ni-X systems, *Pure Appl. Chem.* 79 (2007) 1653-1673.
- [8] O. J. Kleppa, L. Topor, A new calorimeter for temperatures above 1400 K, *Thermochim. Acta* 139 (1989) 291-297.
- [9] H. Su, P. Nash, Enthalpies of formation in the Al-Ni-Ru system by direct reaction synthesis calorimetry, *J. Alloys Compd.* 403 (2005) 217-222.
- [10] H. Kopp, Investigation of the specific heat of solid bodies, *Phil. Trans. R. Soc. Lond.* 155 (1865) 71-202.
- [11] A. T. Dinsdale, SGTE data for pure elements, *Calphad* 15 (1991) 317-425.
- [12] M. M. Diviš, Ab-initio study of structural stability and magnetism of Ni_2CuSn , *Intermetallics* 4 (1996) 335-338.
- [13] Z. H. Liu, M. Zhang, Y. T. Cui, Y. Q. Zhou, W. H. Wang, Martensitic transformation and shape memory effect in ferromagnetic Heusler alloy Ni_2FeGa , *Appl. Phys. Lett.* 82 (2003) 424-426.
- [14] R. Marazza, G. Rambaldi, R. Ferro, Ternary intermetallic phases of the cesium chloride or aluminum-copper-manganese (AlCu_2Mn) structure type have related 1:1:2 stoichiometries, *Atti della Accademia Nazioale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti*, 55 (1974) 518-521.
- [15] J. H. Wernick, G. W. Hull, T. H. Gerballe, J. E. Bernardini, J. V. Waszczak, Superconductivity

in ternary heusler intermetallic compounds, Mater. Lett. 2 (1983) 90-92.

[16] V. P. Dubenskiy, V. I. Zaremba, Ya. M. Kalychaka, L. D. Gulay, D. Kaczorowski, J. Stepien-Damm, M. Woclyrz, Crystal structure, magnetic and electrical properties of $M'M_2\text{In}$ ($M' = \text{Ti, Hf}$; $M = \text{Ni, Cu}$), J. Alloys. Compd. 306 (2000) 21-25.

[17] K. R. A. Ziebeck, P. J. Webster, Helical magnetic order in Ni_2MnAl , J. Phys. F: Met. Phys. 5 (1975) 1756-1766.

[18] V. D. Buchelnikov, V. V. Sokolovskiy, Magnetocaloric effect in Ni-Mn-X ($X = \text{Ga, In, Sn, Sb}$) Heusler alloys, The Physics of Metals and Metallography. 112 (2011) 633-665.

[19] T. Kanomata, T. Yasuda, S. Sasaki, H. Nishihara, R. Kainuma, W. Ito, K. Oikawa, K. Ishida, K.-U. Neumann, K. R. A. Zeibek, Magnetic properties on shape memory alloys $\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$, J. Magn. Magn. Mater. 321 (2009) 773-776.

[20] H. Luo, G. Liu, Z. Feng, Y. Li, L. Ma, G. Wu, X. Zhu, C. Jiang, H. Xu, Effect of the main-group elements on the electronic structures and magnetic properties of Heusler alloys Mn_2NiZ ($Z = \text{In, Sn, Sb}$), J. Magn. Magn. Mater. 321 (2009) 4063-4066.

[21] E. I. Gladyshevskii, V. Y. Markiv, Y. B. Kuz'ma, E. E. Cherkashi, Crystal structure of some ternary intermetallic Titanium compounds, Titan i Ego Splavy 10 (1963) 71-73.

[22] P. G. van Engen, K. H. J. Buschow, Magnetic properties and magneto-optical spectroscopy of Heusler alloys based on transition metals and Sn, J. Magn. Magn. Mater. 30 (1983) 374-382.

[23] F. S. da Rocha, G. L. F. Fraga, D. E. Brandao, C. M. da Silva, A. A. Gomes, Specific heat and electronic structure of Heusler compounds Ni_2TAl ($T = \text{Ti, Zr, Hf, V, Nb, Ta}$), Physica B 269 (1999) 154-162.

[24] X. Liu, J. Lin, Y. Liu, Y. Jin, First-principles study on the electronic structures, magnetism and half-metallicity of full-Heusler X_2YGa ($X = \text{Co, Fe, Ni}$; $Y = \text{V, Cr, Mn}$) alloys, Acta Phys. Sin. 60 (2011) 107104/1-107104/10.

[25] C. C. M. Campbell, C. V. Stager, Magnetization studies of the Heusler alloys, $\text{Ni}_2\text{Mn}_x\text{Ti}_{1-x}\text{Sn}$, $\text{Ni}_2\text{Mn}_x\text{V}_{1-x}\text{Sn}$ and $\text{Ni}_2\text{Mn}_x\text{Cr}_{1-x}\text{Sn}$, Can. J. Phys. 54 (1976) 2197-2203.

- [26] M. Gilleßen, PhD thesis, RWTH Aachen University, Aachen, Germany (2009).
- [27] J. Kübler, A. R. Williams, C. B. Sommers, Formation and coupling of magnetic moments in Heusler alloys, *Phys. Rev. B* 28 (1983) 1745-1755.
- [28] R. E. Watson, M. Weinert, M. Alatono, Ternary transition-metal aluminide alloy formation: The BiF₃ structure, *Phys. Rev. B* 57 (1998) 12134-12139.
- [29] J. E. Saal, S. Kirklin, M. Aykol, B. Meredig, C. Wolverton, Materials design and discovery with high-throughput density functional theory: the Open Quantum Materials Database (OQMD) *JOM* 65 (2013) 1501-1509.
- [30] P. J. Webster, K. R. A. Ziebeck, Alloys and compounds of d-elements with main group elements, Part 2, edited by H. R. J. Wijn, Landolt-Bornstein, New Series, Group III, Vol. 19/c (Springer, Berlin, 1998, 2001), 75-184.
- [31] R. Ducher, R. Kainuma, K. Ishida, Phase equilibria in the Ni-Co-Ga alloy system, *J. Alloys Compd.* 466 (2008) 208-213.
- [32] G. D. Liu, X. F. Dai, S. Y. Yu, Z. Y. Zhu, J. L. Chen, G. H. Wu, Physical and electronic structure and magnetism of Mn₂NiGa: experiment and density-functional theory calculations, *Phys. Rev. B* 74 (2006) 054435/1-054435/8.
- [33] S. Chatterjee, S. Giri, S. K. De, S. Majumda, Ferromagnetic antiferromagnetic exchange coupling in Ni₂MnSn-derived magnetic shape memory alloys, *J. Phys. Conf. Ser.* 200 (2010) 032011/1-032011/4.
- [34] T. Krenke, E. Duman, M. Acet, E. f. Wassermann, X. Moya, L. Manosa, A. Planes, Inverse magnetocaloric effect in ferromagnetic Ni-Mn-Sn alloys, *Nat. Mater.* 4 (2005) 450-454.
- [35] B. Hu, H. Xu, S. Liu, Y. Du, C. He, C. Sha, D. Zhao, Experimental investigation and thermodynamic modeling of the Mn-Ni-Si system, *CALPHAD* 35 (2011) 346-354.
- [36] E. E. Cherkashyn, E. I. Gladyshevskii, Y. B. Kuz'ma, X-ray structural study of some systems of the transition metals, *Zh Neorg Khim.* 3 (1958) 650-653.
- [37] Y. P. Lee, R. J. Kim, Y. J. Yoo, K. W. Kim, Y. V. Kudryavtsev, Spin-photonic, photonic and

other relevant properties of Ni_2MnGe and other Heusler alloys, J. Korean Phys. Soc. 49 (2006) 2080-2083.

[38] A. T. Zayak, P. Entel, A critical discussion of calculated modulated structures, Fermi surface nesting and phonon softening in magnetic shape memory alloys $\text{Ni}_2\text{Mn}(\text{Ga}, \text{Ge}, \text{Al})$ and $\text{Co}_2\text{Mn}(\text{Ga}, \text{Ge})$, J. Magn. Magn. Mater. 290-291 (2005) 874-877.

[39] R. B. Helmholtz, K. H. J. Buschow, Crystallographic and magnetic structure of Ni_2MnSn and NiMn_2Sn , J. Less. Common Met. 128 (1987) 167-171.

[40] Y. Du, C. He, J. C. Schuster, S. Liu, H. Xu, Thermodynamic description of the Ni-Si-Ti ternary system, Inter. J. Mat. Res. 97 (2006) 543-555.

[41] M. Yin, S. Chen, P. Nash, Enthalpies of formation of selected Co_2YZ Heusler compounds, J. Alloys Compd. 577 (2013) 49-56.

[42] M. Yin, P. Nash, Enthalpies of formation of selected Pd_2YZ Heusler compounds, Intermetallics. 58 (2015) 15-19.

[43] J. C. Slater, Atomic Radii in Crystals, J. Chem. Phys. 41 (1964) 3199-3204.

[44] R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and halcogenides, Acta Cryst. A32 (1976) 751-767.

[45] G. P. Vassilev, K. I. Lilova, J. C. Gachon, Enthalpies of formation of Ni-Sn compounds, Thermochim. Acta 447 (2006) 106-108.

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

Element	Purity, (wt. %)	Particle size, (μm)
Al	99.97	44
Co	99.8	1.6
Cu	99.999	149
Fe	99.9+	10
Ga	99.99	Filed from an ingot
Ge	99.995	149
Hf	99.6	44
In	99.999	44
Mn	99.95	44
Ni	99.9+	< 30
Sn	99.999	44
Ti	99.9	149
V	99.5	44

Table 2. Measured alloy compositions and lattice parameters (a) of the reacted samples of Ni_2YZ compounds.

Compound	CAS No.	Structure ^a	Composition, (at. %)	a/nm	
				This work	Literature
Ni_2CuAl	37322-33-1	cP4	$\text{Ni}_{50.8}\text{Cu}_{21.5}\text{Al}_{27.7}$	0.3584 a 0.5319, c 0.4314	-
Ni_2CuIn	-	hP8	$\text{Ni}_{52.4}\text{Cu}_{20.7}\text{In}_{26.9}$	0.5926	-
Ni_2CuSn	132027-64-6	i-L2 ₁	$\text{Ni}_{54.9}\text{Cu}_{22.1}\text{Sn}_{23.0}$	0.5988 [12]	0.5988 [12]
Ni_2FeGa	110446-06-5	B2	$\text{Ni}_{55.0}\text{Fe}_{23.5}\text{Ga}_{21.5}$	0.2886	0.57405 [13]
Ni_2FeGe	1211543-37-1	cP4	$\text{Ni}_{49.0}\text{Fe}_{24.0}\text{Ge}_{27.0}$	0.3609	-
Ni_2HfGa	60996-58-9	L2 ₁	$\text{Ni}_{49.9}\text{Hf}_{25.9}\text{Ga}_{24.3}$	0.5973	0.5945 [14], 0.6045 [15]
Ni_2HfIn	55964-06-2	L2 ₁	$\text{Ni}_{54.1}\text{Hf}_{23.2}\text{In}_{22.2}$	0.6253	0.62545 [16]
Ni_2MnAl	57572-06-2	B2	$\text{Ni}_{50.1}\text{Mn}_{24.3}\text{Al}_{25.6}$	0.2913	0.5822 [17]
Ni_2MnGa	53851-52-8	L2 ₁	$\text{Ni}_{54.3}\text{Mn}_{23.9}\text{Ga}_{21.8}$	0.5820	0.5825 [18]
Ni_2MnIn	51913-19-0	L2 ₁	$\text{Ni}_{49.9}\text{Mn}_{23.5}\text{In}_{26.6}$	0.6060	0.6073 [19]
$\text{Ni}_{0.50}\text{Mn}_{0.25}\text{Sn}_{0.25}$	12209-31-3	L2 ₁	$\text{Ni}_{48.0}\text{Mn}_{24.6}\text{Sn}_{27.4}$	0.6041	0.6048 [14]
$\text{Ni}_{0.55}\text{Mn}_{0.2}\text{Sn}_{0.25}$	-	L2 ₁	$\text{Ni}_{54.7}\text{Mn}_{19.1}\text{Sn}_{26.2}$	0.6024	-
$\text{Ni}_{0.45}\text{Mn}_{0.3}\text{Sn}_{0.25}$	-	L2 ₁	$\text{Ni}_{50.2}\text{Mn}_{26.4}\text{Sn}_{23.4}$	0.6043	-
$\text{Ni}_{0.4}\text{Mn}_{0.35}\text{Sn}_{0.25}$	-	L2 ₁	$\text{Ni}_{44.7}\text{Mn}_{30.4}\text{Sn}_{24.9}$	0.6060	-
$\text{Ni}_{0.25}\text{Mn}_{0.50}\text{Sn}_{0.25}$	-	L2 ₁	$\text{Ni}_{25.8}\text{Mn}_{47.3}\text{Sn}_{26.9}$	0.6100	0.602 [20]
$\text{Ni}_{0.50}\text{Mn}_{0.30}\text{Sn}_{0.20}$	-	L2 ₁	$\text{Ni}_{50.6}\text{Mn}_{29.6}\text{Sn}_{19.8}$	0.6042	-
$\text{Ni}_{0.50}\text{Mn}_{0.35}\text{Sn}_{0.15}$	-	L2 ₁	$\text{Ni}_{49.7}\text{Mn}_{34.4}\text{Sn}_{15.9}$	0.6011	-
Ni_2TiGa	12186-71-9	L2 ₁	$\text{Ni}_{51.3}\text{Ti}_{26.3}\text{Ga}_{22.4}$	0.5881	0.5880 [21]
Ni_2TiIn	100729-03-1	L2 ₁	$\text{Ni}_{50.1}\text{Ti}_{24.6}\text{In}_{25.3}$	0.6100	0.6099 [21]
Ni_2TiSn	12534-06-4	L2 ₁	$\text{Ni}_{53.0}\text{Ti}_{22.9}\text{Sn}_{24.1}$	0.6091	0.6096 [22]
Ni_2VAl	57594-79-3	B2	$\text{Ni}_{49.6}\text{V}_{22.8}\text{Al}_{27.6}$	0.2904	0.58031 [23]
Ni_2VGa	99786-77-3	L2 ₁	$\text{Ni}_{52.5}\text{V}_{21.4}\text{Ga}_{26.1}$	0.5809	0.5797 [24]
Ni_2VSn	12794-80-8	L2 ₁	$\text{Ni}_{48.5}\text{V}_{25.6}\text{Sn}_{25.9}$	0.6028	0.6037 [25]

^a Strukturbericht symbols were used to present the crystal structure when available or the Pearson symbols were used. The i-L2₁ structure is short for the inverse-Heusler structure.

Table 3. Measured standard enthalpies of formation ($\Delta_f H^\circ$) of the Heusler compounds compared with data from first principles calculations and the amount of additional phases.

Compound ^a	Structure	$\Delta_f H^\circ / (\text{kJ} \cdot \text{mole of atoms}^{-1})$ ^b			Comments ^c
		This work	First principles	OQMD	
Ni ₂ CuAl	cP4	-38.9 ± 3.1			Single phase
Ni ₂ CuIn [▲]	hP8	-21.6 ± 2.4			10 % InNi
Ni ₂ CuSn	i-L2 ₁	-12.5 ± 2.1	-14.5 [26]	-16.8	< 1 % (Cu, Ni)
Ni ₂ FeGa	B2	-24.8 ± 2.1	-20.5 [26]	-20.6	2 % GeNi ₂
Ni ₂ FeGe	cP4	-25.8 ± 3.0			2 % GeNi ₂
Ni ₂ HfGa [•]	L2 ₁	-69.3 ± 3.0		-54.7	1 % GaHfNi
Ni ₂ HfIn [▲]	L2 ₁	-51.7 ± 4.2		-41.5	20 % HfNi ₅
Ni ₂ MnAl	B2	-32.0 ± 2.8	-39.0 [26]	-39.5	Single phase
Ni ₂ MnGa	L2 ₁	-29.8 ± 3.9	-28.0 [26]	-29.1	Single phase
Ni ₂ MnIn	L2 ₁	-24.5 ± 2.0	-9.0 [26]	-10.3	Single phase
Ni _{0.55} Mn _{0.2} Sn _{0.25}	L2 ₁	-26.6 ± 1.0			1 % Ni ₃ Sn ₂
Ni _{0.50} Mn _{0.25} Sn _{0.25}	L2 ₁	-29.7 ± 2.9	-17.1 [26], -22.4 [27]	-20.2	5 % Ni ₃ Sn ₂
Ni _{0.45} Mn _{0.3} Sn _{0.25}	L2 ₁	-27.5 ± 2.6			Single phase
Ni _{0.4} Mn _{0.35} Sn _{0.25}	L2 ₁	-26.6 ± 2.6			1 % MnO
Ni _{0.25} Mn _{0.50} Sn _{0.25}	L2 ₁	-20.9 ± 2.6			1 % Mn ₃ Sn
Ni _{0.50} Mn _{0.30} Sn _{0.20}	L2 ₁	-21.0 ± 3.2			5 % MnNi
Ni _{0.50} Mn _{0.35} Sn _{0.15}	L2 ₁	-20.1 ± 1.7			Single phase
Ni ₂ TiAl	L2 ₁	-55.8 ± 2.2	-60.4 [26]	-61.0	[5]
Ni ₂ TiGa	L2 ₁	-42.5 ± 2.2	-52.4 [26]	-53.3	Single phase
Ni ₂ TiIn [•]	L2 ₁	-28.5 ± 1.1	-32.8 [26]	-36.1	3 % Ni ₃ Ti
Ni ₂ TiSn	L2 ₁	-46.8 ± 2.0	-42.5 [26]	-45.5	3 % Ni ₃ Sn ₂
Ni ₂ VAl [▲]	B2	-39.7 ± 0.5	-37.5 [26], -39.6 [28]	-37.4	2 % V, 5 % AlNi ₃
Ni ₂ VGa ^{▲•}	L2 ₁	-21.5 ± 3.0	-28.8 [26]	-27.7	8 % Ni ₂ V ₃
Ni ₂ VSn [▲]	L2 ₁	-24.2 ± 1.0	-11.1 [26]	-13.7	10 % Ni ₃ Sn ₂

a [▲] indicates experimental values are only indicative of the standard enthalpy of formation of the

compound due to significant amounts of impurity phases; [•] indicates the phases present in the

samples after the heat of reaction measurement and the heat content measurement are different,

making the measured standard enthalpy of formation indicative rather than precise;

b The measured enthalpies of formation in this work correspond to the structure listed in the second column while the calculated values correspond to the L2₁ Heusler structure;

c the estimated amount of additional phases is in volume percentage which corresponds to the

samples used for heat content measurement.

Table 4. Measured heats of reaction ($\Delta_r H$) and heat contents ($H_T - H_{298}$) of Heusler compounds compared with values from the Neumann-Kopp rule.

Compound ^a	$\Delta_r H /$ (kJ·mole of atoms ⁻¹)	$(H_T - H_{298}) / (\text{kJ} \cdot \text{mole of atoms}^{-1})$		T_m / K
		This work	Neumann-Kopp	
Ni ₂ CuAl	0.8 ± 0.2	39.7 ± 3.1	36.3	1542
Ni ₂ CuIn	31.3 ± 1.6	52.9 ± 1.8	36.8	1126
Ni ₂ CuSn	31.7 ± 0.9	44.3 ± 1.8	37.9	1370
Ni ₂ FeGa	13.2 ± 0.9	38.0 ± 1.9	36.4	1462
Ni ₂ FeGe	22.0 ± 2.1	47.7 ± 2.2	42.9	1309
Ni ₂ HfGa	-45.1 ± 2.3	24.2 ± 2.0	33.7	>1550
Ni ₂ HfIn	-21.2 ± 3.4	30.5 ± 2.4	33.6	>1550
Ni ₂ MnAl	-4.0 ± 0.4	28.0 ± 2.0	36.0	>1500
Ni ₂ MnGa	3.2 ± 0.1	33.0 ± 3.5	36.5	1396
Ni ₂ MnIn	23.9 ± 1.3	48.4 ± 2.5	36.4	1256
Ni _{0.55} Mn _{0.20} Sn _{0.25}	7.9 ± 0.6	34.5 ± 0.8	37.2	-
Ni _{0.50} Mn _{0.25} Sn _{0.25}	3.8 ± 0.4	33.5 ± 2.4	37.6	1406
Ni _{0.45} Mn _{0.30} Sn _{0.25}	9.4 ± 2.0	36.9 ± 1.6	37.9	-
Ni _{0.40} Mn _{0.35} Sn _{0.25}	23.6 ± 1.4	50.2 ± 2.2	38.3	-
Ni _{0.25} Mn _{0.50} Sn _{0.25}	24.5 ± 1.9	45.4 ± 1.8	39.3	-
Ni _{0.50} Mn _{0.30} Sn _{0.20}	18.1 ± 3.0	39.1 ± 1.1	37.6	-
Ni _{0.50} Mn _{0.35} Sn _{0.15}	30.9 ± 1.2	51.0 ± 1.3	37.8	-
Ni ₂ TiGa [▲]	-17.2 ± 1.0	25.3 ± 2.0	29.0	1632
Ni ₂ TiIn [▲]	-4.7 ± 0.4	23.8 ± 1.0	28.9	1454
Ni ₂ TiSn	-16.0 ± 1.7	30.8 ± 0.9	33.1	1696
Ni ₂ VAl	-5.8 ± 0.4	33.9 ± 0.2	32.0	>1700
Ni ₂ VGa	8.0 ± 0.4	29.5 ± 3.0	34.1	1398
Ni ₂ VSn	20.1 ± 0.6	44.3 ± 0.7	36.5	1373

a [▲] indicates the calorimeter temperature was 1273 K.

Figure caption

Fig. 1. Backscattered electron micrograph of $\text{Ni}_{50}\text{Co}_{25}\text{Ga}_{25}$ alloy, (a) as cast structure; (b) annealed structure.

Fig. 2. Measured XRD patterns of Ni_2HfGa alloys, (a) the reacted sample from the calorimeter after the measurement of heat of reaction; (b) the as cast sample; (c) the annealed sample with almost a single Heusler phase.

Fig. 3. Experimental XRD patterns of (a) $\text{Ni}_{55}\text{Mn}_{20}\text{Sn}_{25}$; (b) $\text{Ni}_{50}\text{Mn}_{25}\text{Sn}_{25}$; (c) $\text{Ni}_{45}\text{Mn}_{30}\text{Sn}_{25}$; (d) $\text{Ni}_{40}\text{Mn}_{35}\text{Sn}_{25}$.

Fig. 4. Backscattered electron micrograph of the reacted (a) $\text{Ni}_{50}\text{Mn}_{30}\text{Sn}_{20}$ and (b) $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$ alloys.

Fig. 5. Backscattered electron micrograph of $\text{Ni}_{50}\text{V}_{25}\text{Sn}_{25}$ alloy, (a) reacted sample and (b) annealed sample.

Fig. 6. Comparison between the measured enthalpies of formation (crystal structures indicated in Table 3) and the calculated results for the Heusler structure from the OQMD. Dashed lines indicate the error of ± 10 kJ/mole of atoms.

Fig. 7. Enthalpy of formation ($\Delta_f H^\circ$) of Ni_2MnZ ($Z = \text{Al, Ga, In, Sn}$).

Fig. 8. Enthalpy of formation ($\Delta_f H^\circ$) of Ni_2TiZ ($Z = \text{Al, Ga, In, Sn}$).

Fig. 9. The relationship between the standard enthalpies of formation of the $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloys and the Mn content. The enthalpy value for the D0_3 structure is from Reference [43].

Fig. 1. Backscattered electron micrograph of $\text{Ni}_{50}\text{Co}_{25}\text{Ga}_{25}$ alloy, (a) as cast structure; (b) annealed structure.

Fig. 2. Measured XRD patterns of Ni_2HfGa alloys, (a) the reacted sample from the calorimeter after the measurement of heat of reaction; (b) the as cast sample; (c) the annealed sample with almost a single Heusler phase.

Fig. 3. Experimental XRD patterns of (a) $\text{Ni}_{55}\text{Mn}_{20}\text{Sn}_{25}$; (b) $\text{Ni}_{50}\text{Mn}_{25}\text{Sn}_{25}$; (c) $\text{Ni}_{45}\text{Mn}_{30}\text{Sn}_{25}$; (d) $\text{Ni}_{40}\text{Mn}_{35}\text{Sn}_{25}$.

Fig. 4. Backscattered electron micrograph of the reacted (a) $\text{Ni}_{50}\text{Mn}_{30}\text{Sn}_{20}$ and (b) $\text{Ni}_{50}\text{Mn}_{35}\text{Sn}_{15}$ alloys.

Fig. 5. Backscattered electron micrograph of $\text{Ni}_{50}\text{V}_{25}\text{Sn}_{25}$ alloy, (a) reacted sample and (b) annealed sample.

Fig. 6. Comparison between the measured enthalpies of formation (crystal structures indicated in Table 3) and the calculated results for the Heusler structure from the OQMD. Dashed lines indicate the error of ± 10 kJ/mole of atoms.

Fig. 7. Enthalpy of formation ($\Delta_f H^\circ$) of Ni_2MnZ ($Z = \text{Al, Ga, In, Sn}$).

Fig. 8. Enthalpy of formation ($\Delta_f H^\circ$) of Ni_2TiZ ($Z = \text{Al, Ga, In, Sn}$).

Fig. 9. The relationship between the standard enthalpies of formation ($\Delta_f H^\circ$) of the $\text{Ni}_{75-x}\text{Mn}_x\text{Sn}_{25}$ alloys and the Mn content. The enthalpy value for the $D0_3$ structure is from Reference [43].