Enthalpies of formation of selected Pd_2YZ Heusler compounds

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ABSTRACT

Standard enthalpies of formation of selected ternary Pd-based Heusler type compositions Pd_2YZ ($Y =$ Cu, Hf, Mn, Ti, Zr; $Z =$ Al, Ga, In, Ge, Sn) were measured using high temperature direct synthesis calorimetry. The measured enthalpies of formation (in kJ/mole of atoms) of the Heusler compounds are, Pd_2HfAl (-81.6 ± 2.4); Pd_2HfGa (-79.9 ± 2.9); Pd_2HfIn (-76.4 ± 1.4); Pd_2HfSn (-77.6 ± 1.6); Pd_2MnSn (-54.6 ± 3.1); Pd_2TiGa (-65.6 ± 3.6); Pd_2TiIn (-69.9 ± 2.1); Pd_2TiSn (-78.6 ± 2.4); Pd_2ZrAl (-85.3 ± 3.0); Pd_2ZrGa (-76.2 ± 1.9); Pd_2ZrIn (-85.1 ± 3.9); Pd_2ZrSn (-92.2 ± 3.1); for the B2 compounds, Pd_2MnAl (-87.1 ± 3.0); Pd_2MnGa (-54.5 ± 1.7); Pd_2MnIn (-41.0 ± 2.5); Pd_2TiAl (-81.4 ± 1.9); for the tetragonal compound Pd_2CuAl (-55.2 ± 3.0) and for the orthorhombic compound Pd_2CuSn (-43.1 ± 2.3). Values were compared with those from published first principles calculation and the Open Quantum Materials Database (OQMD). Lattice parameters of these compounds were determined by X-ray diffraction analysis (XRD). Microstructures were identified using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Selected alloys were annealed at various temperatures to investigate phase transformations and phase relationships.

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1. Introduction

Heusler compounds have been of scientific interest since 1903 when German engineer Heusler [1] first discovered that the ternary compound Cu_2MnAl was ferromagnetic while none of the constituent elements were. Heusler compounds have the general formula X_2YZ with an $L2_1$ structure, in which X and Y are commonly transition elements, and Z is usually a group III to V element.

Heusler compounds possess many fascinating properties such as magnetic shape memory effect and half-metallic property. Superconductivity is reported in several Pd-based Heusler alloys, Pd_2ZrAl, Pd_2ZrIn, Pd_2HfAl, Pd_2HfIn [2]. It is also interesting to compare the ordering phenomenon and stability of Pd-based Heusler compounds to that of Co-based and Fe-based ones both theoretically and experimentally. Since there are a large number of potential compounds of this type, there is a need for basic research to establish their existence and their properties. In this work, enthalpies of formation, lattice parameters and related phase relationships of Pd-based Heusler compounds Pd_2YZ ($Y =$ Co, Cu, Fe, Hf, Mn, Ni, Ti, V, Zr; $Z =$ Al, Ga, In, Si, Ge, Sn) were investigated to generate data that can be of use in alloy design and validation of first principles predictions of structural stability.

2. Materials and methods

All elemental materials were purchased from Johnson Matthey/Alfa Aesar and Aldrich Chemical Company. Purity and size of the powders are listed in Table 1. Ga and Zr powders were filed from an ingot and Zr powders were sieved (<149 μm). Co, Fe and Ni powders were reduced in hydrogen at 873 K for half an hour to remove the surface oxide and cooled in the furnace. Then the reduced powders were ground and sieved (<149 μm).

The detailed experimental procedure for measuring the standard enthalpy of formation using the Kleppa calorimeter was described previously [3]. Stoichiometric amounts of elemental powders were mixed together and compressed to make 7 pellets which were then individually dropped into a boron nitride crucible in the calorimeter to measure the heat of reaction. The reaction time was around 20 min for each sample to reach thermal equilibrium. The obtained samples were cooled to room temperature in purified argon and dropped into the calorimeter again to measure the heat content. Standard enthalpy of formation is obtained from the heat of reaction minus the heat content. The temperature of the calorimeter was maintained at 1373 K with a flowing argon atmosphere purified using a Titanium gettering furnace. NIST SRM 720 sapphire was used for enthalpy calibration. The weight loss for each sample was less than 1%. Since the compressed pellets of Pd_2MnGa and Pd_2TiGa reacted at room temperature, samples were kept in a refrigerator (277 K) before dropping into the calorimeter.

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Since the temperature difference is small, 277 K versus 298 K, compared with the reaction temperature (1373 K), the measured values are taken as the standard enthalpy of formation. If the reacted samples were not a single Heusler phase, they were sealed in quartz tubes under vacuum after flushing with argon and further annealed in a furnace to check if the Heusler phase would appear at a lower temperature. Microstructures of the reacted samples and annealed samples were examined using scanning electron microscopy (JEOL, JSM-5900LV) after standard metallographic preparation. XRD analysis (Bruker, D2 PHASER) was used to determine lattice parameters and identify additional phases as well as their relative amounts by comparing the intensities of the strong peaks to the simulated ones. For Pd_2MnAl, Pd_2MnGa, Pd_2TiSn and annealed Pd_2CuAl, the ground powders for XRD measurement were annealed at 873 K for 30 min to relieve the deformation strain and cooled in the furnace in argon.

Heat contents at 1373 K for each compound were calculated using the empirical Neumann-Kopp rule [4]. The elemental data are tabulated in Dinsdale [5].

3. Results

The measured lattice parameters of the calorimeter reacted samples are compiled in Table 2, together with data from the references [6–20]. Chemical Abstracts Service (CAS) registry numbers for each compound are provided as well.

The measured enthalpies of formation are listed in Table 3. Data from first principles calculation [19,21–23] and Open Quantum Materials Database (OQMD) [24] are included for comparison. The identified structure and relative amount of additional phases are also given.

Table 4 summarizes the measured heats of reaction and heat contents, together with the values calculated from the Neumann-Kopp rule.

4. Discussion

The measured compositions of the Pd-based Heusler compounds are a little bit off-stoichiometry. The cause could be the loss of elements during sample preparation or the inaccuracy of the EDS measurement. The measured lattice parameters are generally consistent with the literature values. Pd-based Heusler compounds typically have a similar type of order but more negative enthalpy of formation when compared with their Co-based analogues [25] as shown in Fig. 1.

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

Element	Purity, %	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 ingot
Ge	99.995	149
Hf	99.6	44
In	99.999	44
Mn	99.95	44
Ni	99.9+	30
Pd	99.9	<1
Si	99.5	44
Sn	99.999	44
Ti	99.9	149
V	99.5	44
Zr	99	Filed from ingot and sieved, <149

Table 2
Measured overall compositions and lattice parameters of the Kleppa samples of Pd_2YZ compounds.

Compound	CAS no.	Structure	Composition	Lattice parameter (nm) This work[a]	Lattice parameter (nm) Selected literature value[b]
Pd_2CuAl	37274-66-1	tP2	$Pd_{52.5}Cu_{23.6}Al_{23.8}$	a 0.2862; c 0.3316	
Pd_2CuSn	77681-59-5	oP16	$Pd_{56.0}Cu_{20.5}Sn_{23.5}$	▲ a 0.7885; b 0.7885; c 0.3042 [6]	
Pd_2HfAl	55964-68-6	$L2_1$	$Pd_{50.1}Hf_{24.0}Al_{26.0}$	0.6360	0.6373 [7], 0.6370 [8]
Pd_2HfGa	110463-71-3	$L2_1$	$Pd_{53.2}Hf_{25.6}Ga_{21.2}$	0.6354	0.634 [9]
Pd_2HfIn	55964-05-1	$L2_1$	$Pd_{52.7}Hf_{24.0}In_{23.3}$	0.6519	0.6534 [7], 0.3266 [10]
Pd_2HfSn	No	$L2_1$	$Pd_{49.8}Hf_{26.8}Sn_{23.4}$	0.6527	
Pd_2MnAl	53810-35-8	B2	$Pd_{52.1}Mn_{22.9}Al_{25.0}$	0.3081	0.3082 [11], 0.6295 [12]
Pd_2MnGa	110463-71-3	B2	$Pd_{54.1}Mn_{23.8}Ga_{22.1}$	0.3088	0.6180 [13]
Pd_2MnIn	12293-43-5	B2	$Pd_{48.0}Mn_{25.7}In_{26.3}$	0.3196	0.6373 [11], 0.637 [14]
Pd_2MnSn	12293-64-0	$L2_1$	$Pd_{51.2}Mn_{22.3}Sn_{26.5}$	0.6386	0.6380 [11], 0.6383 [15]
Pd_2TiAl	55964-67-5	B2	$Pd_{50.8}Ti_{24.0}Al_{25.2}$	0.3096	0.3107 [10]
Pd_2TiGa	110463-68-8	$L2_1$	$Pd_{51.2}Ti_{25.4}Ga_{23.3}$	0.6222	0.6340● [16]
Pd_2TiIn	55964-01-7	$L2_1$	$Pd_{51.5}Ti_{24.3}In_{24.2}$	0.6397	0.6406 [17], 0.3217 [10]
Pd_2TiSn	165461-31-4	$L2_1$	$Pd_{52.9}Ti_{22.4}Sn_{24.7}$	0.6340	0.638 [18]
Pd_2ZrAl	55964-66-4	$L2_1$	$Pd_{51.3}Zr_{24.9}Al_{23.7}$	0.6389	0.6394 [8], 0.640 [19]
Pd_2ZrGa	1431973-26-0	$L2_1$	$Pd_{51.2}Zr_{25.6}Ga_{22.8}$	0.6379	0.6375 [20]
Pd_2ZrIn	55964-00-6	$L2_1$	$Pd_{50.5}Zr_{24.6}In_{24.9}$	0.6544	0.6553 [8], 0.6555 [10]
Pd_2ZrSn	1204164-52-2	$L2_1$	$Pd_{50.0}Zr_{26.1}Sn_{23.9}$	0.6555	0.655 [9]

[a] ▲ indicates there is no detailed structure analysis in the literature to permit cell parameter calculation.
[b] ● indicates the lattice parameter is a calculated result.

Basically, they also follow the trend that enthalpy of formation becomes more negative as the number of valence electrons of the Y element decreases and more positive as the number of valence electrons of the Z element decreases. The first principles calculations data provided by OQMD agree with the general trend but not the exact values of the measured values. The Neumann-Kopp rule predicts the heat content of most compounds well. However, two exceptions are noticed, Pd_2TiGa and Pd_2ZrGa. Relatively small values of heat content were observed in Pd_2HfZ compounds (Z = Al, Ga, In, Sn) and Pd_2ZrGa. The reason for this is not known.

a) Pd_2CuZ

Pd_2CuZ (Z = Al, Sn) were investigated. A single phase with HgMn structure (space group P4/mmm, Pearson symbol tP2) was identified in the Pd_2CuAl samples cooled in the calorimeter. After annealing at 1173 K for 7 days, a strained B2 structure was observed in the measured XRD pattern after grinding. After being stress relieved in Ar at 873 K for half an hour, two compounds were observed, a tetragonal and a B2 phase. Pante et al. [26] studied this alloy and observed a polymorphous transformation from a hexagonal to a tetragonal structure (space group P4/mmm) at 608 K and to a B2 at 1098 K. The explanation for the difference is that the stress relieving process induces partial structure transformation from B2 to tetragonal and there is insufficient driving force for the compound to further transform to hexagonal at low temperature. Pd_2CuSn has an orthorhombic structure with a and b almost equal