Standard enthalpies of formation of selected Rh₂YZ Heusler compounds

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Abstract

The standard enthalpies of formation ($\Delta_f H^\circ$) of selected ternary Rh-based Rh₂YZ (Y = Cu, Fe, Mn, Ni, Ru, Ti, V; Z = Al, Ga, In, Si, Ge, Sn) compounds were measured using high temperature direct reaction calorimetry. The measured standard enthalpies of formation (in kJ/mole of atoms) are, for the Heusler compound Rh₂MnSn (-40.1 ± 3.6), for the B2-structured compounds: Rh₂FeAl (-48.5 ± 2.9); Rh₂MnAl (-72.4 ± 2.7); Rh₂MnGa (-55.3 ± 2.0); Rh₂MnIn (-35.3 ± 1.9), for the tetragonal compounds: Rh₂FeSn (-28.9 ± 1.3); Rh₂TiAl (-97.6 ± 2.2); Rh₂TiGa (-79.0 ± 1.8); Rh₂TiSn (-74.7 ± 3.1). Values are compared with those from first principles calculations in published papers and the Open Quantum Materials Database (OQMD). Lattice parameters of these compounds are determined using X-ray diffraction analysis (XRD). Microstructures were characterized using scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS).

Keywords: Heusler compound; Standard enthalpy of formation; Calorimetry

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1. Introduction

Heusler compounds [1] have been of great scientific interest since 1903 when German engineer F. Heusler [2] first discovered that the ternary compounds including Cu_2MnAl that were ferromagnetic while none of the constituent elements were. They belong to a group of ternary intermetallics with the stoichiometric composition X_2YZ with an L2_1 structure (prototype Cu_2MnAl , space group $\text{Fm-}3\text{m}$, Pearson symbol cF16), in which X and Y are transition elements, and Z is usually a group III to V element. Many potential applications are to be expected from the Heusler compounds. The magnetic shape memory effect originating from the large magnetic-field-induced strains in some Heusler alloys can be used for designing actuators where the material elongates in the presence of a magnetic field [3]. Another impressive property is the half-metallic property where with an energy gap at the Fermi level, the insulator character is presented in one spin sub-band, and the metallic character in the other, leading to 100% spin polarization.

Basic research to establish the stability and thermodynamic properties of the Heusler compounds will contribute to their development. In this work, standard enthalpies of formation ($\Delta_f H^\circ$), lattice parameters and related phase relationships of selected ternary Rh-based Heusler compounds Rh_2YZ ($\text{Y} = \text{Cu, Fe, Hf, Mn, Ni, Ru, Ti, V}$; $\text{Z} = \text{Al, Ga, In, Si, Ge, Sn}$) were experimentally determined.

2. Materials and methods

All elemental powders were purchased from Alfa Aesar[®], purity and size of which are listed in Table 1. Ga and Zr powders were filed from an ingot and Zr powders were sieved ($< 149 \mu\text{m}$). 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. The reduced powders were then ground and sieved ($< 149 \mu\text{m}$) prior to sample preparation.

The experimental procedure for measuring standard enthalpy of formation using the high

temperature direct reaction calorimeter which is well known as the Kleppa calorimeter, named after Norwegian-born physical chemist Ole J. Kleppa, was described previously [4-6]. Elemental powders of the desired composition were mixed using a stainless steel spoon for around 20 seconds and compressed at a load of around 20 MPa to make seven pellets generally with a weight of 100 mg each. The temperature of the calorimeter was maintained at 1373 ± 2 K and Boron Nitride crucibles and an argon atmosphere purified using a Ti gettering furnace were applied for protection. Samples were dropped into the calorimeter individually over an interval of 20 min to reach thermal equilibrium. The resulting thermal EMF measured using the Pt-Rh thermopile was integrated over time and calibrated using NIST SRM 720 sapphire to obtain the heat of reaction.

The reacted samples were cooled in flowing argon and taken out for characterization using XRD (Bruker, D2 PHASER) and SEM (JEOL, JSM-5900LV) after appropriate sample preparation (samples crushed to powders with a size of less than 149 μm for XRD analysis and standard metallographic preparation for SEM examination). Once a reasonable amount (> 90 vol. %) of the major phase is observed, the reacted samples would be dropped into the calorimeter again to measure the heat content.

The standard enthalpy of formation is obtained using the heat of reaction minus the heat content.

The determined uncertainty is from the calculated standard deviation of multiple measurements. If the reacted samples were a multiphase microstructure or no Heusler phase was observed, they would be sealed in a quartz tube and annealed before being examined again. The annealing temperature and time for each alloy was designed based on the experimental information from published papers. The weight loss for each sample was less than 1 wt. %.

A Setaram[®] Setsys 1700 DSC with a heating rate of 10 K/min and a high purity argon atmosphere

was used to measure the melting points of the compounds. NIST SRM 720 sapphire was used as the reference material. Heat contents at corresponding temperatures for each compound were calculated using the empirical Neumann-Kopp rule [7]. The thermodynamic data for the elements are obtained from the compilation by Dinsdale [8].

3. Results & discussion

The measured lattice parameters of the reacted samples from the Kleppa calorimeter are compiled in Table 2, together with data from the literature [9-17]. Chemical Abstracts Service (CAS) registry numbers, determined crystal structure and overall composition for each compound are provided as well.

All the Rh_2YZ samples had a high melting point beyond the limit of the DSC (1700 K) except for Rh_2CuSn (1694 K). Due to the electronic instability of the band of the Jahn-Teller type, Rh_2YSn ($\text{Y} = \text{Co}, \text{Fe}, \text{Ti}, \text{V}$) crystallize in tetragonal structures, in agreement with the results observed by Suits [9]. However, the structure labeled with space group $\text{P4}_2/\text{ncm}$ and Pearson symbol tP16 [8, 9] is actually not the unit cell, which should be of space group $\text{I4}/\text{mmm}$ and Pearson symbol tI8 as shown in Fig. 1 (a) and (b). The tI8 structure can be obtained from the tP16 structure when a Ti (or Sn) atom is chosen as the origin and the line connecting its nearest Ti (or Sn) atom as the x-axis. This also explains why the measured lattice parameter a in Reference [10, 11] is $\sqrt{2}$ times that reported in this work. The tI8 structure can also be viewed as an ordered structure of tP2 in Fig. 1 (c), which can be distinguished experimentally through comparing the relative intensity of XRD peaks considering that the superlattice peaks are small and overlap with other peaks, as shown in Fig. 2.

3.1. Microstructures of the samples after calorimetric measurement

3.1.1. Rh_2CuZ

Rh_2CuZ ($\text{Y} = \text{Al, Ga, In, Sn}$) compounds were investigated. Rh_2CuSn has an L2_1 structure with 6 % (Cu, Rh) fcc solid solution ($\text{Cu}_{68}\text{Rh}_{32}$) while a B2 phase was observed in Rh_2CuZ ($\text{Z} = \text{Al, Ga, In}$) ($\text{Rh}_{52}\text{Cu}_{11}\text{Al}_{37}$, $\text{Rh}_{50}\text{Cu}_{16}\text{Ga}_{34}$, $\text{Rh}_{51}\text{Cu}_9\text{In}_{40}$) with the fcc Rh-rich solid solution ($\text{Rh}_{91}\text{Cu}_7\text{Al}_2$, $\text{Rh}_{62}\text{Cu}_{31}\text{Ga}_7$, $\text{Rh}_{58}\text{Cu}_{33}\text{In}_9$) as shown in Fig. 3. The fcc Cu-rich solid solution ($\text{Rh}_{22}\text{Cu}_{78}$) was also observed in the $\text{Rh}_{50}\text{Cu}_{25}\text{Al}_{25}$ alloy.

3.1.2. Rh_2FeZ

Rh_2FeZ ($\text{Z} = \text{Al, Ga, Si, Sn}$) compounds were investigated. Rh_2FeAl and Rh_2FeGa crystallized in the B2 structure ($\text{Rh}_{53}\text{Fe}_{20}\text{Al}_{27}$, $\text{Rh}_{48}\text{Fe}_{21}\text{Ga}_{31}$) with a small amount of the fcc Rh-rich solid solution ($\text{Rh}_{75}\text{Fe}_{23}\text{Al}_2$, $\text{Rh}_{76}\text{Fe}_{21}\text{Ga}_3$) as shown in Fig. 4.

$\text{Rh}_{50}\text{Fe}_{25}\text{Si}_{25}$ was found to be composed of A2 phase ($\text{Rh}_{51}\text{Fe}_{26}\text{Si}_{23}$) and Rh_3Si_2 ($\text{Rh}_{56}\text{Fe}_{15}\text{Si}_{29}$) while 3 % of Rh_3Sn_2 ($\text{Rh}_{57}\text{Fe}_3\text{Sn}_{40}$, prototype $\text{Co}_{1.75}\text{Ge}$, space group $\text{P6}_3/\text{mmc}$, Pearson symbol hP6) was observed with Rh_2FeSn of a tI8 structure.

3.1.3. Rh_2MnZ

Compounds of the type Rh_2MnZ ($\text{Z} = \text{Al, Ga, In, Ge, Sn}$) were investigated. A small amount of the fcc Rh-rich solid solution ($\text{Rh}_{75}\text{Mn}_{22}\text{Al}_3$, $\text{Rh}_{82}\text{Mn}_{13}\text{Ga}_5$) was observed in Rh_2MnZ ($\text{Z} = \text{Al, Ga}$) with the B2 structure ($\text{Rh}_{53}\text{Mn}_{23}\text{Al}_{24}$, $\text{Rh}_{55}\text{Mn}_{21}\text{Ga}_{24}$) consistent with the OQMD calculations of phase equilibria. Rh_2MnIn was a single phase B2 structure as shown in Fig. 5. Masumoto and Watanabe [12] reported Rh_2MnAl with an L2_1 structure after annealing at 1173 K for 100 hours. Since B2 phase is found in this work after reaction at 1373 K, this suggests that Rh_2MnAl disorders from L2_1 to B2 between 1173 K and 1373 K. GeRh_2 ($\text{Rh}_{66}\text{Mn}_2\text{Ge}_{32}$) was found coexisting with an L2_1 structure Rh_2MnGe , consistent with the OQMD and 1 % Rh_3Sn_2 ($\text{Rh}_{65}\text{Mn}_1\text{Sn}_{34}$) was found with Rh_2MnSn , which is not consistent with the OQMD as Rh_3Sn_2 was not predicted to be a stable phase. Neither system has a published ternary phase diagram for comparison.

3.1.4. Rh_2NiZ

Rh₂NiZ (Z = Al, Si, Ge, Sn) alloys were studied. Rh₅₀Ni₂₅Al₂₅ alloy is composed of two phases, B2 phase (Rh₅₃Ni₁₁Al₃₆) and fcc Rh-rich solid solution (Rh₆₁Ni₃₃Al₆). Rh₂Si (Rh₅₈Ni₉Si₃₃) was found with fcc (Ni, Rh) solid solution (Rh₄₁Ni₄₈Si₁₁) at the grain boundary in the Rh₅₀Ni₂₅Si₂₅ alloy as shown in Fig. 6.

Heusler phase was found in Rh₂NiGe together with 10 % of GeRh₂ (Rh₆₉Ni₅Ge₂₆). Rh₂NiSn was composed of Rh₃Sn₂ and Ni₃Sn₂ and fcc (Ni, Rh) solid solution.

3.1.5. Rh₂TiZ

Alloys of the type Rh₂TiZ (Z = Al, Ga, Sn) were investigated. Rh₂TiAl was found to have a tP2 structure which can be viewed as the substituted solution of RhTi, consistent with the high temperature phase relationship determined by Kornienko and Khoruzha [20]. Rh₂TiGa was also found to have a tP2 structure together with a minor amount of unknown impurity (Rh₂₆Ti₃₅Ga₃₉). The simulated and measured XRD patterns are shown in Fig. 7. Rh₂TiSn was a single phase tI8 structure.

3.1.6. Rh₂VZ

Rh₂VAl and Rh₂VSn were investigated. Rh₂VAl was composed of two phases, B2 (Rh₄₈V₁₄Al₃₈) and RhV (Rh₃₉V₄₃Al₁₈, prototype AuCu, space group P4/mmm, Pearson symbol tP2). Rh₂VSn is a tI8 structure with the presence of 6 % of Rh₃Sn₂ (Rh₆₂V₆Sn₃₂) and 6 % RhV (Rh₅₆V₄₁Sn₃, prototype AuCu).

3.1.7. others

Rh₂CoSn, Rh₂RuAl, Rh₂RuSi and Rh₂ZrAl were also studied. Rh₂CoSn has a tI8 structure together with 14 % Rh₃Sn₂. B2 phase (Rh₅₂Ru₄Al₄₄) was found with fcc (Rh, Ru) solid solution (Rh₇₁Ru₂₆Al₃) and hcp (Rh, Ru) solid solution (Rh₃₇Ru₆₁Al₂) in Rh₅₀Ru₂₅Al₂₅. Rh₂Si (Rh₅₉Ru₈Si₃₃)

was found with hcp (Rh, Ru) solid solution ($\text{Rh}_{22}\text{Ru}_{72}\text{Al}_6$) in $\text{Rh}_{50}\text{Ru}_{25}\text{Si}_{25}$. The L2_1 phase ($\text{Rh}_{52}\text{Zr}_{31}\text{Al}_7$) was found with the B2 phase AlRh ($\text{Rh}_{52}\text{Zr}_{18}\text{Al}_{30}$) in Rh_2ZrAl .

3.2. Standard enthalpy of formation

The measured standard enthalpies of formation ($\Delta_f H^\circ$) are listed in Table 3. The fraction of additional phases present in the experimental samples is also given. When the amount of the additional phases is more than 15 vol. %, the measured enthalpies of formation are not reported, such as $\text{Rh}_{50}\text{Cu}_{25}\text{Al}_{25}$ and $\text{Rh}_{50}\text{Ni}_{25}\text{Sn}_{25}$ alloys. When the amount of the additional phases is less than 15 vol. % but more than 5 vol. %, the measured values are listed in Table 3 and marked as indicative, such as Rh_2CuSn and Rh_2MnGe . When the amount of the additional phases is less than 5 vol. %, such as Rh_2FeAl and Rh_2MnIn , the data are considered precise within the error of measurement.

The *ab initio* data from the thesis by Gilleßen [18] and the Open Quantum Materials Database (OQMD) [19] using density functional theory and the Vienna *ab initio* Simulation Package (VASP), including plane-waves basis sets and the projector-augmented wave (PAW) method are listed for comparison. It should be noted that the experimental data are the standard enthalpy of formation at 298 K while calculated values correspond to 0 K. Also, all *ab initio* results correspond to the L2_1 Heusler structure even though in many cases, the experimentally observed structures are the relatively less ordered B2 structure such as Rh_2FeAl or the tetragonal structure, such as Rh_2FeSn . The *ab initio* calculations generally have reasonable prediction of the enthalpy of formation although a difference of 10 kJ/mole of atoms is observed sometimes. The reason for this could be due to the presence of additional phases in the experimental samples as seen in Rh_2CuSn and Rh_2MnGe . In the case of Rh_2FeAl and Rh_2FeGa with a B2 structure, the difference is likely due to the different structure observed from that used in the *ab initio* calculations. It is also interesting to see that the predicted enthalpies of formation of the

Heusler structure are very close to the measured values of the tetragonal structure which is understandable since the tetragonal structure can be viewed as a slightly elongated Heusler structure in the c direction.

Table 4 summarizes the measured heats of reaction $\Delta_r H$ (1373 K) and heat contents $H_{1373} - H_{298}$, together with the values from the Neumann-Kopp rule which generally has a higher predicted value than that observed. The reason for this is not clear.

4. Conclusions

26 Rh-based Heusler type compositions were investigated. Standard enthalpies of formation measured using high temperature direct reaction calorimetry and lattice parameters of 13 compositions were determined. The Heusler structure was identified in Rh_2CuSn , Rh_2MnGe , Rh_2MnSn , Rh_2NiGe while Rh_2CoSn , Rh_2FeSn , Rh_2TiAl , Rh_2TiGa , Rh_2TiSn and Rh_2VSn were tetragonal. Rh_2FeAl , Rh_2FeGa , Rh_2MnAl , Rh_2MnGa and Rh_2MnIn had the B2 structure. Multiphase structures were observed in $\text{Rh}_{50}\text{Cu}_{25}\text{Al}_{25}$, $\text{Rh}_{50}\text{Cu}_{25}\text{Ga}_{25}$, $\text{Rh}_{50}\text{Cu}_{25}\text{In}_{25}$, $\text{Rh}_{50}\text{Fe}_{25}\text{Si}_{25}$, $\text{Rh}_{50}\text{Ni}_{25}\text{Al}_{25}$, $\text{Rh}_{50}\text{Ni}_{25}\text{Si}_{25}$, $\text{Rh}_{50}\text{Ni}_{25}\text{Sn}_{25}$, $\text{Rh}_{50}\text{V}_{25}\text{Sn}_{25}$, $\text{Rh}_{50}\text{Ru}_{25}\text{Al}_{25}$, $\text{Rh}_{50}\text{Ru}_{25}\text{Si}_{25}$ and $\text{Rh}_{50}\text{Zr}_{25}\text{Al}_{25}$ alloys.

Acknowledgements

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

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Figure captions

Fig. 1. Crystal structures of (a) Rh_2TiSn , tI8; (b) Rh_2TiSn , tP16; (c) RhTi , tP2.

Fig. 2. XRD patterns of Rh_2TiSn of (a) simulated tP2 structure; (b) simulated tI8 structure; (c) experimental result.

Fig.3. Backscattered electron micrographs of (a) $\text{Rh}_{50}\text{Cu}_{25}\text{Al}_{25}$ alloy of the B2 phase, Cu-rich fcc solid solution and Rh-rich fcc solid solution; (b) $\text{Rh}_{50}\text{Cu}_{25}\text{Ga}_{25}$ alloy of the B2 phase and Rh-rich fcc solid solution; (c) $\text{Rh}_{50}\text{Cu}_{25}\text{In}_{25}$ alloy of the B2 phase and Rh-rich fcc solid solution.

Fig. 4. Experimental XRD patterns of (a) Rh_2FeAl alloy of the B2 phase and Rh-rich fcc solid solution; (b) Rh_2FeGa alloy of the B2 phase and Rh-rich fcc solid solution.

Fig. 5. Experimental XRD patterns of (a) Rh_2MnAl alloy with B2 phase and Rh-rich fcc solid solution; (b) Rh_2MnGa alloy of the B2 phase and Rh-rich fcc solid solution; (c) Rh_2MnIn alloy with B2 single phase.

Fig. 6. Backscattered electron micrographs of as reacted (a) $\text{Rh}_{50}\text{Ni}_{25}\text{Al}_{25}$ alloy of the B2 phase and Rh-rich fcc solid solution and (b) $\text{Rh}_{50}\text{Ni}_{25}\text{Si}_{25}$ alloy of Rh_2Si phase and (Ni, Rh) fcc solid solution.

Fig. 7. Experimental XRD patterns of (a) experimental Rh_2TiAl result; (b) simulated Rh_2TiAl of the tP2 structure; (c) experimental Rh_2TiGa result; (d) simulated Rh_2TiGa of the tP2 structure.

Table 1. Purity and particle size of the elemental powder 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 an ingot
Ge	99.995	149
Hf	99.6	44
In	99.999	44
Mn	99.95	44
Ni	99.9+	<30
Rh	99.95	75
Ru	99.95	44
Sn	99.999	44
Ti	99.9	149
V	99.5	44
Zr	99	Filed from an ingot and sieved, <149

Table 2. Measured overall composition and lattice parameter of the calorimeter samples of the Rh₂YZ compounds.

Compound	CAS No.	Structure	Composition	Lattice parameter, (nm)	
				This work	Literature value ^b
Rh ₂ CuSn	58834-84-7	L2 ₁	Rh _{48.4} Cu _{25.3} Sn _{26.3}	0.6144	0.6146 [9]
Rh ₂ FeAl	-	B2	Rh _{50.8} Fe _{24.8} Al _{24.3}	0.2986	-
Rh ₂ FeGa	-	B2	Rh _{49.9} Fe _{26.5} Ga _{23.6}	0.2989	-
Rh ₂ FeSn	58319-36-1	tI8	Rh _{51.4} Fe _{23.9} Sn _{24.7}	0.4158, 0.6842	0.4150, 0.6912 [9], 0.585, 0.690 [10] a 0.5330 c 0.6913 [11]•
Rh ₂ MnAl	12703-62-7	B2	Rh _{51.2} Mn _{28.3} Al _{20.4}	0.3012	0.3002 [9], 0.6022 [11]
Rh ₂ MnGa	61419-90-7	B2	Rh _{55.4} Mn _{20.3} Ga _{24.3}	0.3015	0.3028 [9]
Rh ₂ MnIn	61419-95-2	B2	Rh _{52.2} Mn _{26.2} In _{21.7}	0.3127	0.3144 [9] 0.604 [13], 0.6044 [14] 0.624 [15], 0.62512 [16], 0.62525 [17]
Rh ₂ MnGe	12592-79-9	L2 ₁	Rh _{52.4} Mn _{24.8} Ge _{22.8}	0.6042	
Rh ₂ MnSn	58834-79-0	L2 ₁	Rh _{51.4} Mn _{25.3} Sn _{23.3}	0.6243 0.2943,	
Rh ₂ TiAl	-	tP2	Rh _{51.3} Ti _{27.6} Al _{21.2}	0.3234 0.2913,	-
Rh ₂ TiGa	-	tP2	Rh _{49.0} Ti _{25.8} Al _{25.3}	0.3292 0.4128,	-
Rh ₂ TiSn	-	tI8	Rh _{50.0} Ti _{25.7} Sn _{24.3}	0.7242 0.4060,	-
Rh ₂ VSn	58834-73-4	tI8	Rh _{50.0} V _{26.5} Sn _{23.6}	0.7296	0.4062, 0.7291 [9]

a • indicates the value is obtained from first principles calculations.

Table 3. Measured $\Delta_f H^\circ$ of Rh_2YZ compounds compared with data from first principles calculations and the amount of additional phases.

Compound ^a	Structure	$\Delta_f H^\circ/\text{kJ (mole of atoms)}^{-1}$			Additional phases ^b
		This work	First principles	OQMD	
$\text{Rh}_2\text{CuSn}^\Delta$	L2_1	-29.1 ± 1.9	-36.0 [19]	-37.6	0.06 (Cu, Rh)
Rh_2FeAl	B2	-48.5 ± 2.9		-58.2	0.05 (Fe, Rh)
$\text{Rh}_2\text{FeGa}^\Delta$	B2	-31.1 ± 2.3		-42.4	0.1 (Fe, Rh)
Rh_2FeSn	tI8	-28.9 ± 1.3		-28.4	0.03 Rh_3Sn_2
Rh_2MnAl	B2	-72.4 ± 2.7	-66.4 [19]	-66.8	0.03 (Mn, Rh)
Rh_2MnGa	B2	-55.3 ± 2.0		-51.9	0.05 (Mn, Rh)
Rh_2MnIn	B2	-35.3 ± 1.9	-33.2 [19]	-33.3	Single phase
$\text{Rh}_2\text{MnGe}^\Delta$	L2_1	-55.0 ± 2.4		-43.5	0.1 GeRh_2
Rh_2MnSn	L2_1	-40.1 ± 3.6	-42.6 [19]	-45.7	0.01 Rh_3Sn_2
Rh_2TiAl	tP2	-97.6 ± 2.2		-95.8	Single phase
					Unknown impurity
Rh_2TiGa	tP2	-79.0 ± 1.8		-82.5	($\text{Rh}_{26}\text{Ti}_{35}\text{Ga}_{39}$)
Rh_2TiSn	tI8	-74.7 ± 3.1		-66.5	Single phase
$\text{Rh}_2\text{VSn}^\Delta$	tI8	-44.8 ± 2.2		-42.2	0.06 Rh_3Sn_2 , 0.06 RhV

a $^\Delta$ indicates experimental values are indicative of enthalpy of formation of the compound due to

significant amounts of impurity phases;

b the amount of other phases present in volume fraction.

Table 4. Measured heats of reaction $\Delta_r H$ (1373 K) and heat contents $H_{1373}-H_{298}$ compared to data from the Neumann-Kopp rule.

Compound	$\Delta_r H$ (1373 K)/ kJ (mole of atoms) ⁻¹	$H_{1373}-H_{298}$ /kJ (mole of atoms) ⁻¹	
		This work	Neumann-Kopp
Rh ₂ CuSn	-5.5 ± 1.8	25.7 ± 1.3	36.9
Rh ₂ FeAl	-20.5 ± 1.9	28.0 ± 2.2	34.9
Rh ₂ FeGa	-4.3 ± 0.6	26.8 ± 2.2	35.4
Rh ₂ FeSn	2.4 ± 0.6	31.3 ± 1.2	36.5
Rh ₂ MnAl	-44.4 ± 1.9	28.0 ± 2.0	35.0
Rh ₂ MnGa	-26.9 ± 1.0	28.4 ± 1.8	35.5
Rh ₂ MnIn	-5.3 ± 1.4	30.0 ± 1.3	35.4
Rh ₂ MnGe	-22.8 ± 1.7	32.2 ± 1.7	41.9
Rh ₂ MnSn	-6.9 ± 2.6	33.1 ± 2.6	36.7
Rh ₂ TiAl	-67.1 ± 1.9	30.5 ± 1.2	30.5
Rh ₂ TiGa	-54.9 ± 1.6	24.2 ± 0.8	31.0
Rh ₂ TiSn	-46.1 ± 1.5	28.6 ± 2.7	32.1
Rh ₂ VSn	-10.0 ± 0.7	34.8 ± 2.1	34.2

(a) Rh_2TiSn , tI8

(b) Rh_2TiSn , tP16

(c) RhTi , tP2

● Rh

● Ti

● Sn

Fig. 1. Crystal structures of (a) Rh_2TiSn , tI8; (b) Rh_2TiSn , tP16; (c) RhTi , tP2.

Fig. 2. XRD patterns of Rh_2TiSn of (a) simulated tP2 structure; (b) simulated tI8 structure; (c) experimental result.

Fig.3. Backscattered electron micrographs of (a) $\text{Rh}_{50}\text{Cu}_{25}\text{Al}_{25}$ alloy of the B2 phase, Cu-rich fcc solid solution and Rh-rich fcc solid solution; (b) $\text{Rh}_{50}\text{Cu}_{25}\text{Ga}_{25}$ alloy of the B2 phase and Rh-rich fcc solid solution; (c) $\text{Rh}_{50}\text{Cu}_{25}\text{In}_{25}$ alloy of the B2 phase and Rh-rich fcc solid solution.

Fig. 4. Experimental XRD patterns of (a) Rh₂FeAl alloy of the B2 phase and Rh-rich fcc solid solution; (b) Rh₂FeGa alloy of the B2 phase and Rh-rich fcc solid solution.

Fig. 5. Experimental XRD patterns of (a) Rh₂MnAl alloy with B2 phase and Rh-rich fcc solid solution; (b) Rh₂MnGa alloy of the B2 phase and Rh-rich fcc solid solution; (c) Rh₂MnIn alloy with B2 single phase.

Fig. 6. Backscattered electron micrographs of as reacted (a) $\text{Rh}_{50}\text{Ni}_{25}\text{Al}_{25}$ alloy of the B2 phase and Rh-rich fcc solid solution and (b) $\text{Rh}_{50}\text{Ni}_{25}\text{Si}_{25}$ alloy of Rh_2Si phase and (Ni, Rh) fcc solid solution.

Fig. 7. Experimental XRD patterns of (a) experimental Rh_2TiAl result; (b) simulated Rh_2TiAl of the tP2 structure; (c) experimental Rh_2TiGa result; (d) simulated Rh_2TiGa of the tP2 structure.

Graphical Abstract

$$\Delta_f H^0 = \Delta_r H - (H_{1373} - H_{298})$$