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Enthalpies of formation of compounds in Al-Ni-Y system ①

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[Abstract] The enthalpies of formation of the ternary compounds Al_4NiY, Al_2NiY, $Al_2Ni_6Y_3$, $Al_{16}Ni_3Y$, $AlNiY$, Al_3Ni_2Y, $AlNi_8Y_3$, $Al_7Ni_3Y_2$, and of the binary compounds Al_2Y containing nickel and Ni_5Y containing aluminum have been determined by high temperature reaction calorimetry. The enthalpy values measured are compared to previously published results where available as well as extended Miedema model predictions. The melting points of the compounds were determined by DTA and X-ray diffraction was used to confirm the crystal structures of the compounds. The enthalpies of formation of the ternary compounds show a maximum along the 50% Al (mole fraction) section. The ternary compounds appear along lines of constant yttrium content consistent with binary compound solubility extensions.

[Key words] enthalpy of formation; compound; Al-Ni-Y system
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1 INTRODUCTION

Alloys involving Ni, Al and other elements are of interest for applications such as high temperature structural materials. Alloy development of such materials requires a thorough knowledge of the phase equilibria in the binary, ternary and higher order alloy systems. To establish this knowledge experimentally requires a substantial amount of time and effort. Thermodynamic modeling of phase diagrams provides an opportunity to approach the phase equilibria aspects of alloy development in a more efficient manner than experimentally determining the phase equilibria in large numbers of alloys at many temperatures. A number of computer programs exist for the calculation of multi-component phase equilibria based on the Calphad method[1]. The basic approach is to develop a thermodynamic description for the free energy of each phase as a function of composition and temperature and then to compute the minimum in free energy for a particular composition at a given temperature. In this way the phase diagram can be mapped in a matter of minutes or hours rather than the months involved with experimental methods of phase diagram determination. Of course, the accuracy of the computed diagram is dependent on the accuracy of the thermodynamic data used in the free energy descriptions of the phases. Such data are often not available resulting from estimations being used. The authors have embarked on a project to experimentally determine enthalpies of formation for alloys in the Ni-Al-X alloy systems, where X is a transition element, for use in thermodynamic modeling and validation of first principles calculations. In this initial publication the authors have determined enthalpies of formation of intermetallic compounds in the Ni-Al-Y system as well as the binary compounds with significant solubility. The Ni-Al rich portion of the phase diagram of the Ni-Al-Y system was determined by Rykhal et al[2] and is shown in Fig. 1. The Al-rich region was recently re-investigated[3] and several additional compounds have been reported[4, 5]. Table 1 lists the standard crystallographic designations of the compounds in this system together with the mole fraction designations which are more convenient for thermodynamic considerations.

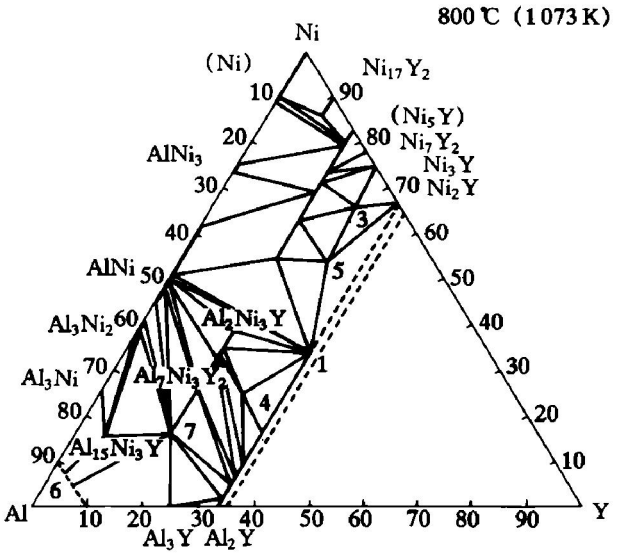

Fig. 1 Partial isothermal section of Al-Ni-Y system[2]
1—AlNiY; 2—AlNiY; 3—$AlNi_8Y_3$; 4—Al_2NiY; 5—$Al_2Ni_6Y_3$; 6—Al_3Ni_2Y; 7—Al_4NiY;

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Table 1 Compound designations

Crystallographic compound designation	Mole fraction
Al_4NiY	$Al_{0.67}Ni_{0.17}Y_{0.16}$
Al_2NiY	$Al_{0.50}Ni_{0.25}Y_{0.25}$
$Al_2Ni_6Y_3$	$Al_{0.18}Ni_{0.55}Y_{0.27}$
$Al_{16}Ni_3Y$	$Al_{0.80}Ni_{0.15}Y_{0.05}$
$Al_{2-x}Ni_xY$	$Al_{0.60}Ni_{0.07}Y_{0.33}$
$Al_{2-x}Ni_xY$	$Al_{0.53}Ni_{0.14}Y_{0.33}$
$AlNiY$	$Al_{0.33}Ni_{0.33}Y_{0.33}$
Al_3Ni_2Y	$Al_{0.50}Ni_{0.33}Y_{0.17}$
$Al_xNi_{5-x}Y$	$Al_{0.25}Ni_{0.58}Y_{0.17}$
$Al_xNi_{5-x}Y$	$Al_{0.15}Ni_{0.68}Y_{0.17}$
$Al_xNi_{5-x}Y$	$Al_{0.05}Ni_{0.78}Y_{0.17}$
$AlNi_8Y_3$	$Al_{0.08}Ni_{0.67}Y_{0.25}$
$Al_7Ni_3Y_2$	$Al_{0.58}Ni_{0.25}Y_{0.17}$
$Al_{23}Ni_6Y4$	$Al_{0.70}Ni_{0.18}Y_{0.12}$
Al_9Ni_3Y	$Al_{0.69}Ni_{0.23}Y_{0.08}$
Al_3NiY	$Al_{0.60}Ni_{0.20}Y_{0.20}$
$AlNi_2Y_2$	$Al_{0.20}Ni_{0.40}Y_{0.40}$
$AlNi_3Y_2$	$Al_{0.17}Ni_{0.50}Y_{0.33}$

2 EXPERIMENTAL

The heats of formation are determined using a high temperature reaction calorimeter with a typical accuracy of ±1 kJ/mol. The measurements are generally made with the calorimeter set at (1 473 ±2) K, and using a protective argon atmosphere. In one case a calorimeter temperature of 1 373 K was used. The calorimeter is calibrated using purecopper. Samples are produced by mixing elemental powders in a mortar in the required mole fraction, as given in Table 1, and pressing them into a small pellet. Typical sample mass is about 100 mg. The nickel powder used was reduced in hydrogen prior to preparation of the samples to remove oxygen and carbon which would be a source of errors. The yttrium powder was obtained by filing an ingot immediately prior to sample preparation.

The enthalpy of reaction, ΔH_R, is obtained first by dropping the pellet into the calorimeter from room temperature. A total of 6 separate samples are measured. The pellets are subsequently removed and again dropped from room temperature into the calorimeter to obtain the heat content of the compound, ΔH_H. If the alloy is liquid at the temperature set by the calorimeter, the ingot removed after the first set of experiments is crushed and re-pelletized for the heat content measurements. The difference between the two measurements yields the heat of formation at 298 K. The results are the averages of the 6 individual measurements. With the standard deviations from the reaction and heat content experiments designated as δ_1 and δ_2 and from the calibration as δ_3 the overall uncertainty in the measurements, δ, was determined from $\delta = (\delta_1^2 + \delta_2^2 + \delta_3^2)^{1/2}$.

Material from the reacted compound is used to obtain an X-ray diffraction pattern to confirm that the reacted sample is the desired compound.

3 RESULTS AND DISCUSSION

By using direct synthesis, the standard enthalpy of formation, $\Delta H_f(298\ K)$, is calculated from:

$$a\mathrm{Al}(s, 298\ K) + b\mathrm{Ni}(s, 298\ K) + c\mathrm{Y}(s, 298\ K) = \mathrm{Al}_a\mathrm{Ni}_b\mathrm{Y}_c(1\ 473\ K) \quad (1)$$

$$\mathrm{Al}_a\mathrm{Ni}_b\mathrm{Y}_c(s, 298\ K) = \mathrm{Al}_a\mathrm{Ni}_b\mathrm{Y}_c(1\ 473\ K) \quad (2)$$

The actual condition of the compound at 1 473 K is not relevant, the important factor is that the final state is the same in both experiments and that the sample used in the heat content experiment should be the desired compound at 298 K. Likewise, the final temperature is not important except in the sense that the reaction should be complete in the experiment time, but must be the same in both experiments.

From Eqns. (1) and (2), we get

$$a\mathrm{Al}(s, 298\ K) + b\mathrm{Ni}(s, 298\ K) + c\mathrm{Y}(s, 298\ K) = \mathrm{Al}_a\mathrm{Ni}_b\mathrm{Y}_c(s, 298\ K) \quad (3)$$

The standard enthalpy of formation is thus obtained:

$$\Delta H_f(298\ K) = \Delta H_R - \Delta H_H \quad (4)$$

where ΔH_R and ΔH_H are molar enthalpy changes for Eqns. (1) and (2).

By using Miedema's semi-empirical model extended for ternary alloys, the standard enthalpy of formation, $\Delta H_f(298\ K)$, can be calculated from

$$\Delta H_f(298\ K) = x_A f_B^A \Delta H_I(\mathrm{A\ in\ B}) + x_A f_C^A \Delta H_I(\mathrm{A\ in\ C}) + x_B f_C^B \Delta H_I(\mathrm{B\ in\ C}) \quad (5)$$

where x_A and x_B are the mole fractions of A and B elements respectively in the corresponding compounds, f_B^A is the degree of surface contact of an A atom with B neighbors, f_B^C is the degree of surface contact of a C atom with B neighbors while the f_C^A is the degree of surface contact of an A atom with C neighbors. ΔH_I is interfacial enthalpy.

The enthalpies of formation of Al-Ni-Y compounds are listed in Table 2, together with values calculated in this work based on Miedema's model. The results are also plotted in Fig. 2, together with binary compound enthalpy values from the reference. Values for the Ni-Y and Al-Ni systems are taken from Ref. [6] respectively, except for AlNi which is from Ref. [7]. Values for the Al-Y compounds are from Refs. [8~11]. The Miedema model predictions show the correct trend but are in most cases significantly less exothermic than the measured values.

Table 2 Summary of high temperature reaction calorimetry results and Miedema's semi-empirical model results) Calorimeter temperature set at 1 473 K except as noted)

Compound	ΔH_R /(kJ·mol^{-1})	ΔH_H /(kJ·mol^{-1})	Experimental ΔH_f /(kJ·mol^{-1})	Miedema's model ΔH_f/(kJ·mol^{-1})	Melting point/K
$Al_{0.67}Ni_{0.17}Y_{0.16}$	−2.0±0.5	52.0±0.5	−54.0±0.8	−44.8	1241
$Al_{0.50}Ni_{0.25}Y_{0.25}$	−31.6±1.5	31.2±0.2	−62.8±1.5	−54.6	1 418
$Al_{0.18}Ni_{0.55}Y_{0.27}$	0.0±1.0	48.5±0.8	−48.5±1.5	−45.3	1250
$Al_{0.80}Ni_{0.15}Y_{0.05}$ ①	10.3±0.5	46.1±1.3	−35.7±1.4	−25.4	1 407
$Al_{0.60}Ni_{0.07}Y_{0.33}$	−23.9±1.0	32.8±1.1	−56.7±1.5	−59.8	
$Al_{0.53}Ni_{0.14}Y_{0.33}$ ②	−12.5±1.9	39.0±1.2		−58.6	1 421
$Al_{0.33}Ni_{0.33}Y_{0.33}$	−7.0±0.4	47.1±0.3	−54.1±0.9	−54.5	1 413
$Al_{0.50}Ni_{0.33}Y_{0.17}$	−30.0±1.2	32.9±1.0	−62.8±2.3	−49.2	1 423
$Al_{0.25}Ni_{0.58}Y_{0.17}$	−4.1±0.8	44.2±1.6	−48.3±2.5	−42.3	1 426
$Al_{0.15}Ni_{0.68}Y_{0.17}$	−11.1±0.7	36.2±0.4	−47.3±1.1	−37.6	1 479
$Al_{0.05}Ni_{0.78}Y_{0.17}$	−1.1±1.1	35.1±1.1	−36.1±1.8	−30.1	1 569
$Al_{0.08}Ni_{0.67}Y_{0.25}$	5.2±1.5	43.1±1.7	−37.9±2.5	−39.2	
$Al_{0.58}Ni_{0.25}Y_{0.17}$				−49.2	1 408

①—Calorimeter set at 1 373 K; ②—Reacted sample was not predominantly single phase.

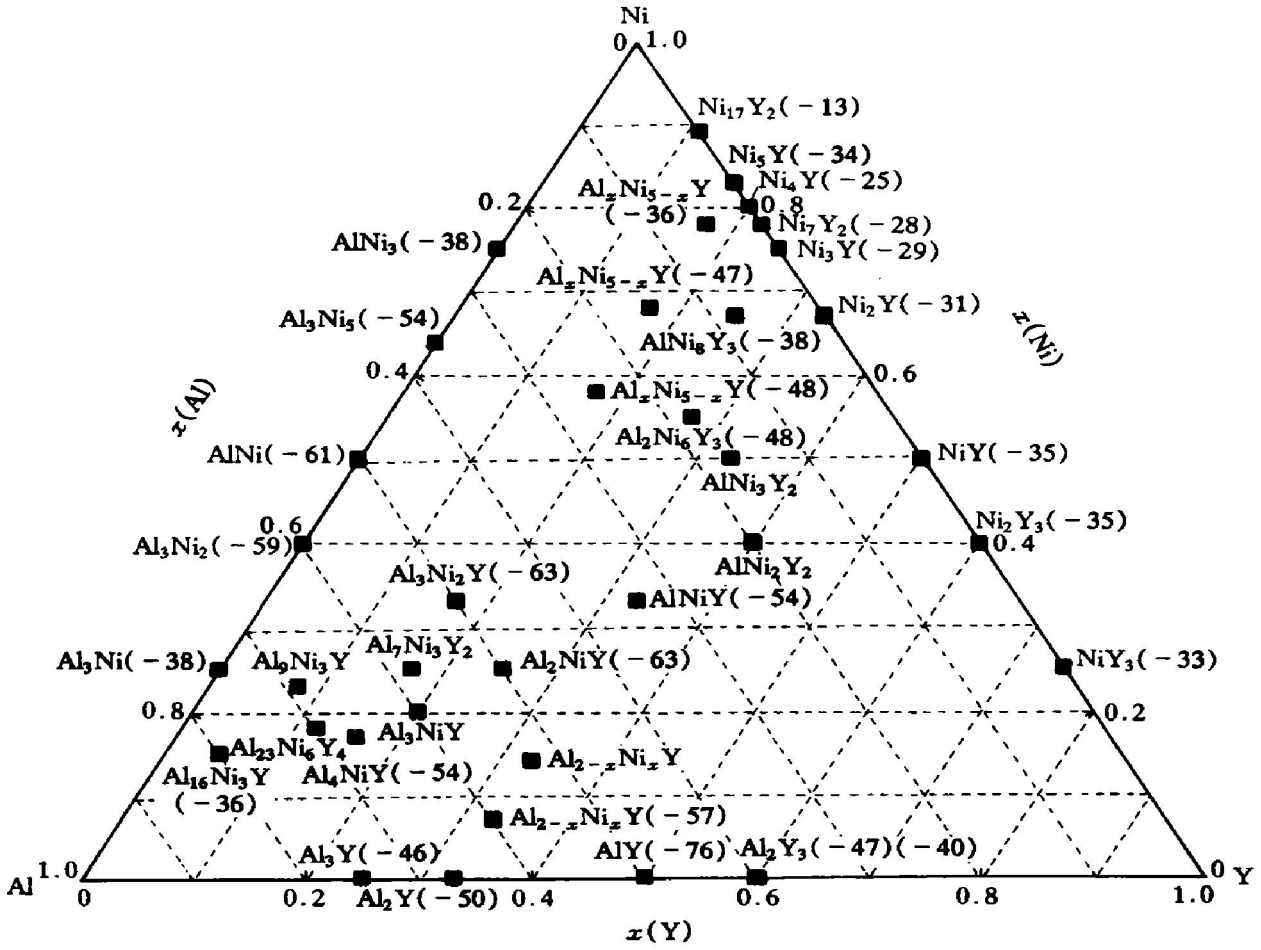

Fig. 2 Enthalpies of formation (kJ/mol) for compounds in Al-Ni-Y system

The measured enthalpy values for $Al_xNi_{5-x}Y$ with increasing Al content show a significant increase from −34 kJ/mol for Ni_5Y to −48 kJ/mol for $Al_{0.34}Ni_{4.66}Y$ due to the Al-Y and Al-Ni interactions.

The only enthalpy of formation value for a ternary phase in this system is for Al_4NiY with a value of −60 kJ/mol. This is considerably more exothermic than the value measured in this work, −54 kJ/mol. From Fig. 2 it is clear that the highest heats of formation in this system occur along the sec-

tion with constant 50% Al(mole fraction). This results from the fact that the Al—Y and Al—Ni bonds are stronger than Ni-Y bonds as indicated by the much lower enthalpy of formation of the binary NiY compared to AlNi and AlY.

Measurements of the enthalpy of formation of amorphous Al-Ni-Y alloys[8] are consistently less exothermic than the corresponding crystalline compounds measured in this work. This is expected since the amorphous phase is less stable than the crystalline compounds.

The binary compounds Al_2Y and Ni_5Y exhibit substantial solubility in the ternary system. Both of the compounds extend along lines of constant yttrium content indicating substitution of Ni for Al in Al_2Y and Al for Ni in Ni_5Y. This is confirmed by observations of simulated X-ray diffraction pattern peak intensities. In the case of Al_2Y there is an analogous compound in the Ni-Y binary, Ni_2Y, which has an identical crystal structure. According to the published phase diagram[2] there is little solubility of Al in Ni_2Y. The replacement of Al with Ni on the Al_2Y lattice leads to an initial increase in the enthalpy of formation of the compound from − 50 to − 57 kJ/mol when adding 7% Ni. However, further additions appear to lead to a decrease since the stability of the phase is limited. Unfortunately the Al_2Y compound containing 14% Ni was not predominantly single phase and the enthalpy of formation has not been determined.

It is worth noting that the ternary compounds tend to occur along lines of constant yttrium content, consistent with the extensions of the binary compounds. This implies that Al and Ni can substitute for each other on the same sublattice but not on the yttrium sublattice. In Fig. 3 the measured and predicted enthalpies of formation in $Al_xNi_{5-x}Y$ alloys are plotted as a function of Ni content across the section of constant yttrium content of 17%. It can be seen that the maximum negative heat of formation corresponds to the 50% Al composition. The Miedema model values are consistently smaller than the measured values, mainly due to the underestimation of the heats of formation of the binary compound Ni_5Y by about − 10 kJ/mol. However, they show the correct trend with a maximum negative value at 50% Al. For the $Al_{2-x}Ni_xY$ alloys the data, shown in Fig. 4, also indicate a maximum negative heat of formation at 50% Al in the section with constant yttrium content of 33%. However for this section the Miedema model predictions are mostly more negative which perhaps is the result of the over estimation of the heats for the binary compounds Al_2Y and Ni_2Y by about − 10 kJ/mol.

Based on the alloying behavior described above and the appearance of the binary phases, one might expect that ternary compounds with compositions $AlNiY_3$ and $AlNiY_2$ will exist in this system. The binary phases corresponding to these ratios will exhibit some solubility for the third element with the solubility extension occurring along constant yttrium contents of 60% and 50% respectively.

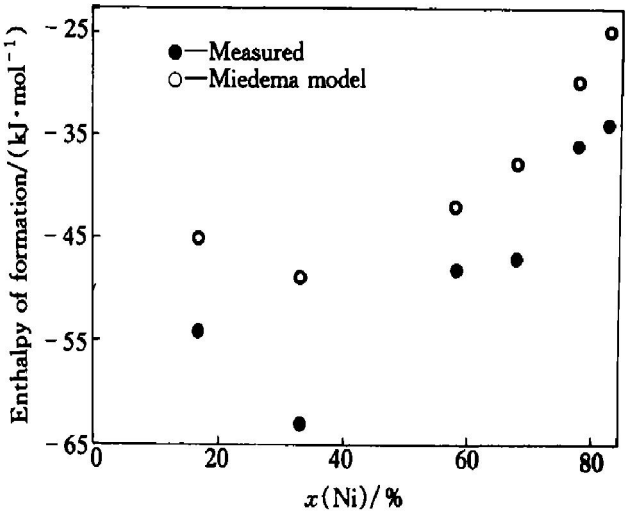

Fig. 3 Measured and predicted enthalpies of formation in $Al_xNi_{5-x}Y$ alloys

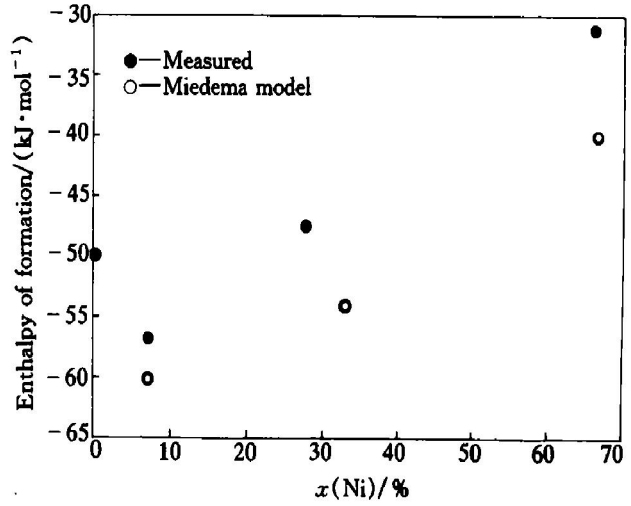

Fig. 4 Measured and predicted enthalpies of formation in $Al_{2-x}Ni_xY$ alloys

In most cases the X-ray diffraction patterns obtained from the reacted samples showed diffraction lines only from the compound being measured. Occasionally a few weak peaks corresponding to Y_2O_3 or other phases were observed. The results of the X-ray diffraction experiments are summarized in Table 3. In the case of $Al_{0.53}Ni_{0.14}Y_{0.33}$ the X-ray diffraction pattern indicated that it consisted of $Al_{2-x}Ni_xY$, Al_4NiY and another phase, consequently the heat of formation for this compound is not reported in Table 2.

4 SUMMARY

The heats of formation of a number of Al-Ni-Y ternary compounds have been measured by direct syn-

Table 3 Crystal structure data of Al-Ni-Y intermetallic compound phase

Compound	Prototype	Pearson symbol	Space group	Spacegroup No.	Lattice parameter			Ref.
					a/ Å	*b*/ Å	*c*/ Å	
$Al_{0.67}Ni_{0.17}Y_{0.16}$	Al_4NiY	oC24	Cmcm	63	4.059	15.192	6.643	[4]
$Al_{0.50}Ni_{0.25}Y_{0.25}$	BRe_3	oC16	Cmcm	63	4.259	10.215	6.824	[2]
$Al_{0.18}Ni_{0.55}Y_{0.27}$	Ag_8Ca_3	cI44	$Im\bar{3}m$	229	8.948			[2, 9]
$Al_{0.80}Ni_{0.15}Y_{0.05}$	$Al_{16}Ni_3Y$	oC*	Cmcm	63	4.08	16.04	27.29	[2]
$Al_{0.60}Ni_{0.07}Y_{0.33}$	$Al_2Y(Cu_2Mg)$	cF24	$Fd\bar{3}m$	227	7.804			
$Al_{0.53}Ni_{0.14}Y_{0.33}$	$Al_2Y(Cu_2Mg)$	cF24	$Fd\bar{3}m$	227	7.789			
$Al_{0.33}Ni_{0.33}Y_{0.33}$	Fe_2P	hP9	$P\bar{6}2m$	189	7.050		3.794	[2]
$Al_{0.50}Ni_{0.33}Y_{0.17}$	Al_3Ni_2Y	hP12	P6/ mm	191	9.015		4.070	[2]
$Al_{0.25}Ni_{0.58}Y_{0.17}$	$Ni_5Y(CaCu_5)$	hP6	P6/ mm	191	5.033		4.052	
$Al_{0.15}Ni_{0.68}Y_{0.17}$	$Ni_5Y(CaCu_5)$	hP6	P6/ mm	191	4.940		4.205	
$Al_{0.05}Ni_{0.78}Y_{0.17}$	$Ni_5Y(CaCu_5)$	hP6	P6/ mm	191	4.915		4.147	
$Al_{0.08}Ni_{0.67}Y_{0.25}$	$CeNi_3$	hP24	$P6_3$/ mmc	194	5.138	16.340		[11]
$Al_{0.58}Ni_{0.25}Y_{0.17}$					17.841	4.219		[2]
$Al_{0.70}Ni_{0.18}Y_{0.12}$*	$Al_{23}Ni_6Y_4$	mC66	C2/ m	12	15.836	4.068	18.311	[5]
$Al_{0.69}Ni_{0.23}Y_{0.08}$	$ErNi_3Al_9$	hR78	R32	155	7.289		27.430	[7]
$Al_{0.60}Ni_{0.20}Y_{0.20}$	Al_3NiY	oP20	Pnma	62	8.156	4.046 2	10.638	[6]
$Al_{0.40}Ni_{0.40}Al_{0.20}$	Mo_2NiB_2	oI10			5.418	8.420	4.181	[10, 11]
$Al_{0.17}Ni_{0.50}Y_{0.33}$	$MgZn_2$	hP12			5.330		8.600	[8]

* $\beta = 112.970°$

thesis drop calorimetry. The heats of formation exhibit maximum negative values in the section containing 50% Al. Miedema model predictions are generally less exothermic than the measured values. Ternary compounds appear mostly at a few fixed $x(Y)/x(Ni + Al)$ ratios such as 1∶5, 1∶3 and 1∶2. Based on this alloying behavior it is predicted that ternary compounds with compositions $AlNiY_3$ and $AlNiY_2$ will exist in this system and that the binary phases corresponding to these ratios will exhibit some solubility for the third element.

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