J MATER SCI **41** (2006) 631–641

Review: Experimental enthalpies of formation of compounds in Al-Ni-X systems

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The published experimental enthalpies of formation for compounds in the Al-Ni-X ternary system are reviewed. Most of these experimental data were obtained by either solution calorimetry or high temperature direct synthesis calorimetry. Data for the Al-Ni-Cu compounds determined by the current authors using direct synthesis calorimeter are presented for the first time.

1. Introduction

The enthalpy of formation, ΔH_f, as the leading term of Gibbs free energy, is an important parameter in alloy development because of its strong influence on phase equilibria in an alloy system. While predictive methods for determining ΔH_f have been developed, including the Miedema semi-empirical method [1, 2] and more recently first principle techniques [3, 4], the most reliable technique remains experimental determination by calorimetry.

Ni-Al based ternary or high order alloys have attracted a lot of attention in recent years because of their potential in high temperature structural applications [5–7]. In particular, β-NiAl and Ni_3Al are of interest due to high temperature strength and high corrosion resistance. To improve the room temperature brittleness of their polycrystalline alloys, many studies have been conducted on alloying third or more elements [8–12]. The ductility of Ni-rich Al-Ni-X (X: Fe, Cr, Co, Cu and Mn) compounds can be improved through the presence of the ductile γ phase [5]. On the other hand, Al-rich Al-Ni-X systems (X: rare earth) exhibit strong glass-forming ability that could have potential as the hydrogen storage materials [13]. Interest has also been shown in these alloys for structural application [14]. Ferromagnetic shape memory alloys in Al-Ni-Co system [15] and Al-Ni-Cu Shape Memory Alloys [16] should provide choices for smart materials.

1.1. CALPHAD methodology

Reliable thermodynamic data and accurate phase diagrams are the prerequisite for the further development of these alloys. Thermodynamic modeling of phase diagrams provides an efficient manner to evaluate the phase equilibria aspects for alloy development than extensive experimentally studies. Pioneered by L. Kaufman [17], the CALPHAD methodology has become a powerful tool in multicomponent phase equilibrium calculations. In contrast to treatments that attempt to locate phase boundaries by the consideration of factors such as a critical electron-atom ratio, electron density or electron vacancy number, the thermochemical basis of the CALPHAD approach between two or more competing phases provides an elegant nonempirical approach to the problem. It develops a thermodynamic description for the free energy of each phase as a function of composition and temperature and then computes the minimum in free energy for a particular composition at a given temperature. The CALPHAD method can predict the phase behavior of highly complex, multicomponent materials based on the extrapolation to high-order properties from their low-order binary and ternary systems, using for example Miedema's semi-empirical model [18] and Hillert's model [19]. Furthermore, the method can be coupled with kinetic formalisms to help understand and predict how materials behave in conditions well away from equilibrium, thus considerably enhancing its value [20].

Of course, the reliability of thermodynamic modeling and the computed diagram is dependent on the accuracy of the thermodynamic data used in the free energy descriptions of the phases, and the enthalpy of formation is a major contribution to the Gibbs free energy. This paper reviews the available data on the enthalpies of formation of Al-Ni-X compounds. The data provided in this paper have been referred to 298 K and solid Al, Ni and third element component when possible.

1.2. Enthalpies of formation and calorimetry

Vapor pressure measurements, the EMF technique and high temperature calorimetry are the experimental

0022-2461
DOI: 10.1007/s10853-006-6479-x

methods commonly used to obtain the thermodynamic properties (ΔG and ΔH respectively) of multi-component alloys. Since enthalpy usually outweighs the entropy and is the main part of the Gibbs free energy, especially at low temperature, and because of the difficulties, problems and errors frequently met in the evaluation of ΔH from EMF or vapor pressure, data from EMF and vapor pressure techniques have often been underlined [21–24], so calorimetry is the preferred technique to obtain the enthalpy of formation.

High temperature direct synthesis calorimetry, or drop calorimeter, is one of the popular experimental techniques because it provides determination of the enthalpy of formation at 298 K [25]. The thermodynamic basis for the method is:

$$aX(s, T_0) + bY(s, T_0) + cZ(s, T_0) = X_aY_bZ_c(T) \quad \Delta H_1 \tag{1}$$

$$X_aY_bZ_c(s, T_0) = X_aY_bZ_c(T) \quad \Delta H_2 \tag{2}$$

where a, b and c are mole of elements X, Y and Z respectively, s refers to the solid state, and $X_aY_bZ_c$ is the corresponding compound formed. From reaction (1) and (2) we get

$$aX(s, T_0) + bY(s, T_0) + cZ(s, T_0) = X_aY_bZ_c(s, T_0)$$

The standard enthalpy of formation at T_0 is thus obtained:

$$\Delta H_f^{T_0}(X_aY_bZ_c) = \Delta H_1 - \Delta H_2$$

ΔH_1 and ΔH_2 are molar enthalpy changes for reaction (1) and (2). Usually T_0 is 298 K.

From 1952, Kleppa built a series of high temperature reaction calorimeters to measure the enthalpies of formation, from the "conventional" type calorimeter to the Calvet-type calorimeter to the recent Kleppa calorimeter, which is based on the same principle as a commercial Setaram unit and can work at high temperature, usually above 1400 K [25]. Recently, a new Kleppa type calorimeter was built by W.G. Jung in which two sets of thermopiles was used to increase the measurement precision [26]. See Fig. 1.

Solution calorimetry is another indirect technique to obtain the enthalpy of formation; usually aluminum or tin is used as the solvent [27]. At room temperature the solid alloy samples and those of the components are dropped down the calibration tube into the liquid solvent. The enthalpy of formation is obtained:

$$aX(s, T_0) + \text{solvent } (1, T) = \text{solvent}(1, T) \ \Delta H_1 \tag{1}$$

$$bY(s, T_0) + \text{solvent } (1, T) = \text{solvent}(1, T) \ \Delta H_2 \tag{2}$$

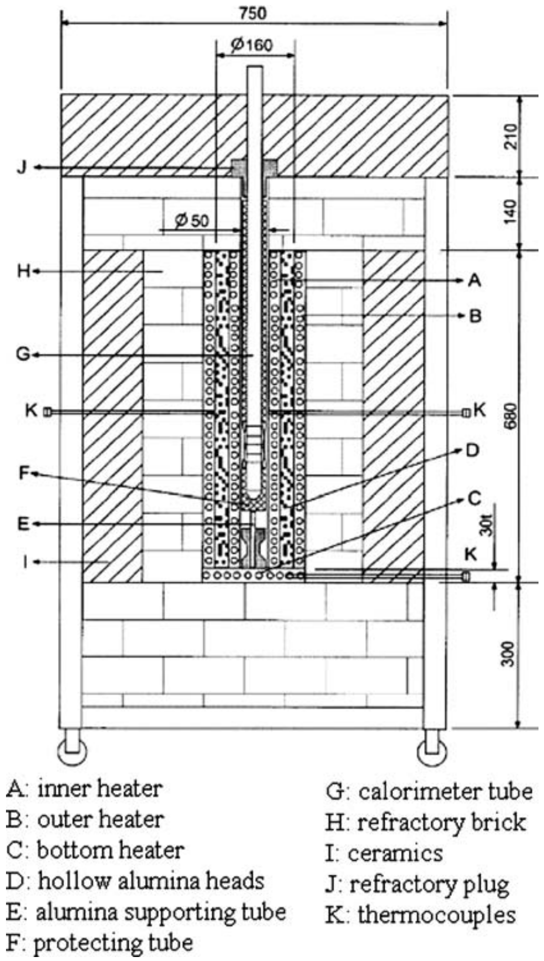

Figure 1 A new Kleppa type calorimeter.

$$bY(s, T_0) + \text{solvent } (1, T) = \text{solvent}(1, T) \ \Delta H_3 \tag{3}$$

$$X_aY_bZ_c(s, T_0) + \text{solvent } (1, T) = \text{solvent}(1, T) \ \Delta H_4 \tag{4}$$

(1)+(2)+(3)−(4), we get:

$$aX(s, T_0) + bY(s, T_0) + cZ(s, T_O) = X_aY_bZ_c(s, T_0)$$

In the above equations, s and l refer to the solid and liquid state respectively. The enthalpy of formation of $X_aY_bZ_c$, $\Delta H_f^{T_o}(X_aY_bZ_c) = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4$.

By using an alternating electromagnetic field instead of an electrical heater, the levitation mixing calorimeter can measure the enthalpy of formation and enthalpy of mixing of refractory alloys at much higher temperatures [28].

This work focused on the experimental enthalpies of formation of Al-Ni-X ternary system determination and aimed to summarize data for computational thermodynamic equilibriums and first principle calculation of Al-Ni-X systems.

TABLE I Standard enthalpy of formation of Al-Ni-Y compounds at 298 K.

Compound	$\Delta H_f^{298\mathrm{K}}$ (kJ/mol)	Experimental method
$Al_{0.67}Ni_{0.17}Y_{0.16}$	−54.0±0.8 [34]	HTDSC
$Al_{0.50}Ni_{0.25}Y_{0.25}$	−62.8±1.5 [34]	HTDRC
$Al_{0.18}Ni_{0.55}Y_{0.27}$	−48.5±1.5 [34]	HTDRC
$Al_{0.80}Ni_{0.15}Y_{0.05}$	−35.7±1.4 [34]	HTDRC
$Al_{0.66}Ni_{0.17}Y_{0.17}$	−60.25±2.0 [35]	HTIC
$Al_{0.60}Ni_{0.07}Y_{0.33}$	−56.7±1.5 [34]	HTDRC
$Al_{0.33}Ni_{0.33}Y_{0.33}$	−54.1±0.9 [34]	HTDRC
$Al_{0.50}Ni_{0.33}Y_{0.17}$	−62.8±2.3 [34]	HTDRC
$Al_{0.25}Ni_{0.58}Y_{0.17}$	−48.3±2.5 [34]	HTDRC
$Al_{0.15}Ni_{0.68}Y_{0.17}$	−47.33±1.1 [34]	HTDRC
$Al_{0.05}Ni_{0.78}Y_{0.17}$	−36.14±1.8 [34]	HTDRC
$Al_{0.08}Ni_{0.67}Y_{0.25}$	−37.9±2.5 [34]	HTDRC
$Al_{0.50}Y_{0.50}$	−84.8 [36]	Calculation
$Al_{0.50}Ni_{0.50}$	−61.8±1.1 [37]	HTDRC
$Al_{0.75}Y_{0.25}$	−46.4±1.8 [35]	HTIC
$Al_{0.67}Y_{0.33}$	−53.47±2.5 [35]	HTIC
$Al_{0.40}Y_{0.60}$	−46.88±3.9 [35]	HTIC
$Al_{0.40}Y_{0.60}$	−40.00±1.6 [38]	HTDRC

Standard enthalpies of formation: enthalpies of formation referred to solid Al, solid Ni and solid Y respectively;
HTDRC: High temperature direct reaction calorimeter
HTIC: high temperature isoperibolic calorimeter

2. Experimental measurements of enthalpies of formation

2.1. Al-Ni-Y system

The improvement of metallurgical properties of Al-Ni intermetallics by small Y additions has been reported [29]. Al-rich Al-Ni-Y alloys present an excellent mixture of properties such as low density, heat and corrosion resistance and high glass-forming ability [30–32]. Compared with Al-Y system, Al-Ni-Y system has considerably wider glass forming composition range which might be due to the larger enthalpies of formation and strong chemical interaction between components when Ni substitutes for part of Al [33].

The enthalpies of formation of crystalline Al-Ni-Y compounds at 298K were measured by high temperature direct synthesis calorimetry, see Table I. For the $Al_{5-x}Ni_xY$ and $Al_{2-x}Ni_xY$ alloys, the enthalpies of formation showed the maximum negative value at 50 at% Al, which is in accordance with the results obtained by Miedema's model [34]. This is due to the higher enthalpies of formation of AlY [36] and AlNi [37] compared to Al_3Y, Al_2Y and Al_2Y_3 [35, 38], which are also listed in Table I.

The microstructures and phase equilibria in the Al-rich region of the Al-Ni-Y system have been reported by Raggio *et al.* [39], which provide the phase information for Al-Ni-R potential glassy metals development [40]. By using isoperibolic solution calorimeter, Tomilin [33, 41] obtained the formation enthalpies of amorphous Al-Ni-Y compounds, Table II. Both of the experimental results showed the reinforcement of chemical interaction between components in Al-Ni-Y alloys with nickel content increasing in the $Al_{90-x}Ni_xY_{10}$ and indicated the potential metallic glass in this system [41].

The composition in the Table I were selected to be single phase alloys while those in Table II may or may not be single phase in the crystalline state. Consequently, only one composition is comparable in the two sets of data.

Comparing the enthalpy of formation data of amorphous $Al_{0.80}Ni_{0.15}Y_{0.05}$ (Table II) with the crystalline one (Table I), the amorphous value is less than that of the crystalline, as expected. However, the difference is much larger (∼20 kJ/mol) than expected (∼5–10 kJ/mol), which casts some doubt on the accuracy of the results. More work is needed to resolve this issue.

2.2. Al-Ni-RE system (rare earth element)

Aluminum-Nickel-Rare earth compounds have received much attention due to the hydrogen storage capacity and glass-forming ability [42, 43].

$AlNi_4RE$ (RE: La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Tm) compounds are found to crystallize in the hexagonal $CaCu_5$-type structure and are potential hydrogen storage materials, which are more promising than the binary $RENi_5$ [44–46].

The standard enthalpies of formation at 300 K of the AlNiRE phases (RE = rare earth) have been obtained by

TABLE II Enthalpy of Formation of Amorphous Al-Ni-Y compounds by high temperature isoperibolic calorimeter

Compound	$\Delta H_f^{300\mathrm{K}}$ (kJ/mol)	Compound	$\Delta H_f^{298\mathrm{K}}$ (kJ/mol)
$Al_{0.90}Y_{0.10}$	−13.21±2.00 [33]	$Al_{0.90}Y_{0.10}$	−16.2±3.1 [41]
$Al_{0.88}Ni_{0.02}Y_{0.10}$	−21.37±8.05 [33]	$Al_{0.88}Ni_{0.02}Y_{0.10}$	−17.9±2.4 [41]
$Al_{0.85}Ni_{0.05}Y_{0.10}$	−20.50±2.71 [33]	$Al_{0.85}Ni_{0.05}Y_{0.10}$	−20.4±2.4 [41]
$Al_{0.82}Ni_{0.08}Y_{0.10}$	−22.76±2.62 [33]	$Al_{0.82}Ni_{0.08}Y_{0.10}$	−22.9±3.0 [41]
$Al_{0.80}Ni_{0.10}Y_{0.10}$	−25.38±3.09 [33]	$Al_{0.80}Ni_{0.10}Y_{0.10}$	−24.6±3.7 [41]
$Al_{0.75}Ni_{0.15}Y_{0.10}$	−22.01±2.04 [33]	$Al_{0.85}Ni_{0.09}Y_{0.06}$	−19.3±2.3 [41]
$Al_{0.70}Ni_{0.20}Y_{0.10}$	−38.71±4.03 [33]	$Al_{0.80}Ni_{0.12}Y_{0.08}$	−24.4±2.8 [41]
$Al_{0.85}Ni_{0.09}Y_{0.06}$	−19.30±2.31 [33]		
$Al_{0.80}Ni_{0.12}Y_{0.08}$	−24.41±2.82 [33]		
$Al_{0.80}Ni_{0.15}Y_{0.05}$	−15.04±2.53 [33]		

Reference state: crystalline elements.

TABLE III Standard enthalpy of formation of solid AlNiRE at 300 K

Phase	$\Delta H_f^{300\mathrm{K}}$ (kJ/mol)	Phase	$\Delta H_f^{300\mathrm{K}}$ (kJ/mol)
AlNiY	−59.0±2 [47]	AlNiDy	−62.0±2 [47]
AlNiLa	−49.0±2 [47]	AlNiHo	−61.0±2 [47]
AlNiCe	−54.0±2 [47]	AlNiEr	-61.0±2 [47]
AlNiPr	−56.0±2 [47]	AlNiYb	−45.0±2 [47]
AlNiNd	−55.0±2 [47]	$AlNi_{623}Er_4$	−47.6±1.1*
AlNiSm	−54.0±2 [47]	Al_4NiEr	−50.2±1.8*
AlNiGd	−57.5±2 [47]	$AlNi_4La$	−169.7 [49]

*$\Delta H_f^{298\mathrm{K}}$, Unpublished research data, H. Su and P. Nash (2003), available from http://tptc.iit.edu/Center/research/PhaseDiagram/index.htm

using a high temperature direct reaction drop calorimeter and an isoperibolic calorimeter, see Table III. In addition, the composition dependence of the enthalpies of formation in the Ce-Ni-Al ternary system was investigated by Borzone *et al*. [50].

Table III shows the systematic increase of enthalpies of formation from the light to the heavy rare earth, except AlNiYb [47], which may be because its electron configuration is similar to that of inert element and the element has low reactivity.

The recent interest in developing intermetallic hydrides based on a system of substituted LaNi5 compounds is due to the large and continuous variation in their thermodynamic properties in addition to their very high hydrogen content.

2.3. Al-Ni-Ti system

Al-rich Al-Ni-Ti amorphous phase has formed over a wide composition range, and some of the compounds showed promising ductility [51]. Reactive rapid prototyping provided a new economic method to make the Al-Ni-Ti intermetallic compounds [52]. The transformation behavior and shape memory characteristics of Ti-rich Al-Ni-Ti alloys with near equiatomic Ti/Ni ratio were reported [53]. Isoperibolic calorimetery was used to determine the total and partial enthalpies of mixing Al-Ni-Ti melts at 1770 ± 5 K, the experiment showed the formation of liquid Al-Ni-Ti alloys was accompanied by high exothermic effects [54]. And the pseudobinary section Ni_3Al-Ni_3Ti of the ternary Al-Ni-Ti system was investigated by thermal analysis and Knudsen effusion mass spectrometry [55]. Kubaschewski *et al*. used the room temperature solution calorimeter and obtained the standard enthalpies of formation of Al-Ni-Ti compounds at 298 K [56], see Table IV.

Table IV showed the smaller enthalpy of formation of Ni-rich Al-Ni-Ti compounds than that of Al-rich corner, which is due to the weaker bonding between Ni and Ti atoms than Al and Ti atoms. For the enthalpies of formation of $Al_{0.3}Ni_{0.7-y}Ti_y$, $Al_{0.4}Ni_{0.6-y}Ti_y$ and $Al_{0.5}Ni_{0.5-y}Ti_y$, with the Ti content increased, there exists a maximum at Ti = 0.2, 0.1 and 0 respectively.

TABLE IV Standard enthalpy of formation of Al-Ni-Ti compounds at 298 K[56]

Compound	$\Delta H_f^{298\mathrm{K}}$ (kJ/mol)	Compound	$\Delta H_f^{298\mathrm{K}}$ (kJ/mol)
$Al_{0.05}Ni_{0.75}Ti_{0.20}$	−36.7	$Al_{0.4}Ni_{0.4}Ti_{0.2}$	−54.2
$Al_{0.05}Ni_{0.45}Ti_{0.50}$	−35.2	$Al_{0.4}Ni_{0.3}Ti_{0.3}$	−50.5
$Al_{0.06}Ni_{0.90}Ti_{0.04}$	−9.6	$Al_{0.4}Ni_{0.2}Ti_{0.4}$	−45.4
$Al_{0.1}Ni_{0.75}Ti_{0.15}$	−37.2	$Al_{0.4}Ni_{0.1}Ti_{0.5}$	−39.2
$Al_{0.1}Ni_{0.50}Ti_{0.4}$	−42.3	$Al_{0.45}Ni_{0.05}Ti_{0.5}$	−38.7
$Al_{0.1}Ni_{0.40}Ti_{0.5}$	−37.7	$Al_{0.5}Ni_{0.5}$	−58.8
$Al_{0.15}Ni_{0.75}Ti_{0.1}$	−37.7	$Al_{0.5}Ni_{0.45}Ti_{0.05}$	−57.8
$Al_{0.15}Ni_{0.35}Ti_{0.5}$	−39.6	$Al_{0.5}Ni_{0.4}Ti_{0.1}$	−57.3
$Al_{0.2}Ni_{0.8}$	−29.3	$Al_{0.5}Ni_{0.35}Ti_{0.15}$	−53.9
$Al_{0.2}Ni_{0.75}Ti_{0.05}$	−38.1	$Al_{0.5}Ni_{0.3}Ti_{0.2}$	−52.1
$Al_{0.2}Ni_{0.6}Ti_{0.2}$	−48.8	$Al_{0.5}Ni_{0.25}Ti_{0.25}$	−52.1
$Al_{0.2}Ni_{0.5}Ti_{0.3}$	−50.8	$Al_{0.5}Ni_{0.2}Ti_{0.3}$	−50.3
$Al_{0.2}Ni_{0.3}Ti_{0.5}$	−40.5	$Al_{0.5}Ni_{0.15}Ti_{0.35}$	−46.2
$Al_{0.2}Ni_{0.2}Ti_{0.6}$	−33.5	$Al_{0.5}Ni_{0.1}Ti_{0.4}$	−45.3
$Al_{0.25}Ni_{0.5}Ti_{0.25}$	−56.1	$Al_{0.5}Ni_{0.05}Ti_{0.45}$	−40.3
$Al_{0.25}Ni_{0.25}Ti_{0.5}$	−40.5	$Al_{0.55}Ni_{0.45}$	−58.9
$Al_{0.3}Ni_{0.7}$	−43.1	$Al_{0.6}Ni_{0.4}$	−57.7
$Al_{0.3}Ni_{0.6}Ti_{0.1}$	−47.7	$Al_{0.6}Ni_{0.3}Ti_{0.1}$	−52.1
$Al_{0.3}Ni_{0.5}Ti_{0.2}$	−57.7	$Al_{0.6}Ni_{0.2}Ti_{0.2}$	−45.3
$Al_{0.3}Ni_{0.4}Ti_{0.3}$	−54.1	$Al_{0.65}Ni_{0.35}$	−50.5
$Al_{0.3}Ni_{0.3}Ti_{0.4}$	−46.6	$Al_{0.75}Ni_{0.25}$	−37.7
$Al_{0.3}Ni_{0.2}Ti_{0.5}$	−40.2	$Al_{0.75}Ni_{0.2}Ti_{0.05}$	−38.6
$Al_{0.35}Ni_{0.15}Ti_{0.5}$	−41.2	$Al_{0.75}Ni_{0.15}Ti_{0.1}$	−39.1
$Al_{0.4}Ni_{0.6}$	−50.5	$Al_{0.75}Ni_{0.1}Ti_{0.15}$	−38.7
$Al_{0.4}Ni_{0.55}Ti_{0.05}$	−52.2	$Al_{0.75}Ni_{0.05}Ti_{0.2}$	−36.0
$Al_{0.4}Ni_{0.5}Ti_{0.1}$	−57.9		
$Al_{0.4}Ni_{0.45}Ti_{0.15}$	−54.6		

TABLE V Standard enthalpies of formation of Al-Ni-Hf compounds at 298 K[65]

Compound	$\Delta H_f^{298\mathrm{K}}$ (kJ/mol)	Compound	$\Delta H_f^{298\mathrm{K}}$ (kJ/mol)
$Al_{0.25}Ni_{0.50}Hf_{0.25}$	−58.2 ± 1.7	$Al_{0.19}Ni_{0.75}Hf_{0.06}$	−39.6 ± 1.3
$Al_{0.30}Ni_{0.50}Hf_{0.20}$	−60.3 ± 1.3	$Al_{0.23}Ni_{0.74}Hf_{0.02}$	−37.8 ± 1.1
$Al_{0.04}Ni_{0.75}Hf_{0.21}$	−44.4 ± 1.1	$Al_{0.26}Ni_{0.54}Hf_{0.20}$	−56.3 ± 1.4
$Al_{0.08}Ni_{0.715}Hf_{0.205}$	−47.6 ± 1.4	$Al_{0.26}Ni_{0.50}Hf_{0.24}$	−61.0 ± 1.2
$Al_{0.13}Ni_{0.67}Hf_{0.20}$	−50.5 ± 1.2		

2.4. Al-Ni-Zr system

By rapid quenching from the liquid state, ternary Al-Ni-Zr alloys have good glass forming ability [57], which can be obtained at low cooling rate [58]. The thermodynamic properties of liquid Al-Ni-Zr alloys, like enthalpies of mixing [59], heat capacity [60, 61] were determined. Enthalpies of formation from pure crystalline elements at 298 K were investigated for Al-Ni-Zr amorphous alloys by using the solution calorimetry method in a high temperature isoperibolic calvet type solution calorimeter described in [62]. The amorphous alloys were prepared by melt spinning technique under purified argon. The experimental values of $\Delta H_f^{298\mathrm{K}}((Zr_{0.60}Ni_{0.40})_{1-x}(Zr_{0.60}Al_{0.40})_x^{\mathrm{am}})$ in concentration range $0 \leq x \leq 0.5$ were measured, using least squares regression, the enthalpies of formation was fitted to:

TABLE VI Enthalpy of formation of Al-Ni-Nb compounds at 298 K[65]

Compound	$\Delta H_{f,B2}^{298\text{K}}$ (kJ/mol)	Compound	$\Delta H_{f,B2}^{298\text{K}}$ (kJ/mol)
$Al_{0.33}Ni_{0.33}Nb_{0.33}$	-40.9 ± 1.5	$Al_{0.75}$ $Ni_{0.17}Nb_{0.08}$	-40.3 ± 1.1
$Al_{0.25}Ni_{0.50}Nb_{0.25}$	-38.6 ± 1.1	$Al_{0.40}$ $Ni_{0.20}Nb_{0.33}$	-46.2 ± 1.3
$Al_{0.27}Ni_{0.40}Nb_{0.33}$	-39.1 ± 1.6	$Al_{0.20}$ $Ni_{0.76}Nb_{0.04}$	-28.4 ± 0.8

TABLE VII Standard enthalpy of formation of Al-Ni-Cr compounds at 298 K [74]

Compound	$\Delta H_f^{298\text{K}}$ (kJ/mol)	Experiment method
$Al_{0.23}Ni_{0.72}Cr_{0.05}$	-36.7 ± 1.4	SC
$Al_{0.22}Ni_{0.70}Cr_{0.08}$	-35.2 ± 1.4	. . .
$Al_{0.21}Ni_{0.67}Cr_{0.12}$	-34.9 ± 1.3	. . .

SC: Solution calorimeter.

TABLE VIII Standard enthalpy of formation of Al-Ni-Fe compounds at 298 K [79]

Compound	$\Delta H_{f,B2}^{298\text{K}}$ (kJ/mol)	Compound	$\Delta H_{f,B2}^{298K}$ (kJ/mol)
$Al_{0.82}Ni_{0.09}Fe_{0.09}$	-25.8 ± 1.4	$Al_{0.40}Ni_{0.20}Fe_{0.40}$	-32.8 ± 2.7
$Al_{0.72}Ni_{0.14}Fe_{0.14}$	-36.7 ± 1.6	$Al_{0.40}Ni_{0.30}Fe_{0.30}$	-35.4 ± 3.1
$Al_{0.18}Ni_{0.75}Fe_{0.07}$	-28.3 ± 1.2	$Al_{0.40}Ni_{0.40}Fe_{0.20}$	-42.8 ± 1.9
$Al_{0.25}Ni_{0.25}Fe_{0.50}$	-27.9 ± 1.4	$Al_{0.40}Ni_{0.50}Fe_{0.10}$	48.8 ± 1.5
$Al_{0.25}Ni_{0.50}Fe_{0.25}$	-30.6 ± 1.8	$Al_{0.50}Ni_{0.10}Fe_{0.40}$	-29.8 ± 1.9
$Al_{0.30}Ni_{0.40}Fe_{0.30}$	-34.2 ± 1.1	$Al_{0.50}Ni_{0.25}Fe_{0.25}$	-44.5 ± 0.9
$Al_{0.33}Ni_{0.10}Fe_{0.57}$	-24.7 ± 1.1	$Al_{0.50}Ni_{0.4\ 0}Fe_{0.10}$	-47.7 ± 1.2
$Al_{0.33}Ni_{0.17}Fe_{0.50}$	-32.3 ± 1.8	$Al_{0.33}Fe_{0.67}$	-22.2 ± 0.9
$Al_{0.33}Ni_{0.33}Fe_{0.33}$	-39.4 ± 1.3	$Al_{0.40}Fe_{0.60}$	-25.9 ± 1.2
$Al_{0.33}Ni_{0.45}Fe_{0.22}$	-41.2 ± 1.2	$Al_{0.50}Fe_{0.50}$	-26.5 ± 1.1
$Al_{0.33}Ni_{0.50}Fe_{0.17}$	-41.5 ± 1.2	$*Al_{0.50}Ni_{0.50}$	-61.8 ± 1.1[80]
$Al_{0.33}Ni_{0.57}Fe_{0.10}$	-43.8 ± 1.3	$*\ Al_{0.40}Ni_{0.60}$	-52[80]
$Al_{0.40}Ni_{0.10}Fe_{0.50}$	-28.3 ± 2.6		

Experimental technique: HTDRC.

$\Delta H_f^{298\text{K}}((Zr_{0.60}Ni_{0.40})_{1-x}(Zr_{0.60}Al_{0.40})_x^{\text{am}}) = -52.15 + 88.06x - 215.31x^2$ (kJ/mol) [63]. The negative value of enthalpies of formation of the amorphous alloys indicated the existence of these amorphous alloys. A maximum presented at about $x = 0.2$.

2.5. Al-Ni-Hf system

Al-Ni-X systems (X is a refractory element) are playing an increasingly important role in superalloy development including eutectic alloy systems [64]. To develop these promising alloys, the standard enthalpies of formation of Al-Ni-Hf compounds were measured by high temperature direct reaction calorimeter [65].

2.6. Al-Ni-Nb system

Nb and Ti as γ' strengthening element of Ni-based super alloys have been investigated [66, 67]. High temperature direct synthesis calorimeter was used to measure the enthalpies of formation of Al-Ni-Nb compounds, seen the Table VI.

With Al increasing, the enthalpies of formation of (Al, Ni)$_{0.67}$Nb$_{0.33}$ increase, which might be due to the higher bonding energy of Al-Nb than that of Ni-Nb.

2.7. Al-Ni-Cr system

Different elements have different effects on the mechanical properties of NiAl binary compounds. NiAl exhibits excellent high-temperature oxidation resistance when doped with zirconium or hafnium, and excellent high-temperature corrosion resistance when doped with chromium or yttrium [68–71]. When elements such as Ti, Si and Nb are added to NiAl, the As temperature of NiAl martensite decreases rapidly with an increase in their content. Because Ti, Si, Nb additions help the Ms temperature of NiAl martensite to drop sharply, these elements would be effective in showing shape-memory effect in Ni-33Al-X alloys [72]. Ni-Al-Cr system is the most important ternary system for Ni-based superalloys used in gas turbines and jet engines [73], and enthalpies of formation of Ni rich portion of Al-Ni-Cr compounds by solution calorimeter are listed in Table VII [74].

2.8. Al-Ni-Fe system

NiAl-based intermetallic alloys containing Fe up to 25% were produced by reactive casting, which enables one to cast high-melting-point intermetallic alloys without external heating, the addition of Fe increased the room temperature Vickers hardness, bending strength and wear resistance of the NiAl, while decreased its Young's modulus [75]. Sauthoff *et al.* found for B2-NiAl the addition of Fe or Cr possibly resulted in its higher ductility [76]. Between FeAl and NiAl two binary systems are a series of solid soltion CsCl-phases that have been shown to exhibit some rather unusual magnetic and mechanical properties [77, 78]. Hsin *et al.* reported the enthalpies of formation of Al-Ni-Fe B2 compounds at 298 K by using the synthesis calorimeter [79], with Fe content increasing, the enthalpies of formation of $Al_{0.50}Ni_{0.50-x}Fe_x$, $Al_{0.40}Ni_{0.6-x}Fe_x$ and $Al_{0.33}Ni_{0.67-x}Fe_x$ decreased; and Wagner-schottky model was used to investigate the constitutional defects in these compounds. Lattice parameters indicated the Fe could substitute both Al and Ni atoms when changing the atom ratio of Fe, Ni and Al [81].

Table IX shows the standard enthalpies of formation of Al-Ni-Fe compounds measured by the solution calorimeter [82]; the data have been referred to solid Ni, solid Fe and solid Al at 1073 K by using the latent heat of Al from Kubaschewski *et al.* [83]. Enthalpies of formation in Table IX show the same tendency with those obtained by direct synthesis calorimeter at 298 K, that is, with Fe content increasing, the enthalpies of formation of

TABLE IX Standard enthalpy of formation of Al-Ni-Fe compounds at 1073 K [82]. Data were modified from original by referring to solid Al

Compound	$\Delta H_{f,B2}^{1073\mathrm{K}}$ (kJ/mol)	Compound	$\Delta H_{f,B2}^{1073\mathrm{K}}$ (kJ/mol)
$Al_{0.50}Ni_{0.08}Fe_{0.42}$	-48.13 ± 0.28	$Al_{0.45}Ni_{0.275}Fe_{0.275}$	-56.735 ± 0.14
$Al_{0.50}Ni_{0.16}Fe_{0.34}$	-54.08 ± 0.22	$Al_{0.45}Ni_{0.27}Fe_{0.18}$	-62.885 ± 0.11
$Al_{0.50}Ni_{0.25}Fe_{0.25}$	-59.77 ± 0.24	$Al_{0.45}Ni_{0.46}Fe_{0.09}$	-67.925 ± 0.06
$Al_{0.50}Ni_{0.34}Fe_{0.16}$	-66.21 ± 0.23	$Al_{0.45}Ni_{0.55}$	-70.195 ± 0.10
$Al_{0.50}Ni_{0.42}Fe_{0.08}$	-71.09 ± 0.27	$Al_{0.35}Ni_{0.06}Fe_{0.59}$	-34.665 ± 0.24
$Al_{0.45}Ni_{0.09}Fe_{0.46}$	-44.685 ± 0.23	$Al_{0.35}Ni_{0.12}Fe_{0.53}$	-39.205 ± 0.31
$Al_{0.45}Ni_{0.18}Fe_{0.37}$	-50.555 ± 0.05	$Al_{0.35}Ni_{0.505}Fe_{0.145}$	-55.265 ± 0.29

$Al_{0.50}Ni_{0.50-x}Fe_x$, $Al_{0.45}Ni_{0.55-x}Fe_x$ and $Al_{0.35}Ni_{0.65-x}Fe_x$ decreased.

2.9. Al-Ni-Ru system

The element Ru, as a new addition to Ni-based super alloys for improving alloy strengthening and oxidation-resistance, has been proposed for investigation. And Ruthenium posses lower metal and oxide vapour pressure and has the lowest high-temperature diffusion coefficient in fcc γ-Ni among the six elements in the second transition series from Nb to Ag with the exception of Tc; Ru has good potentials to be used as the bond coat layer in the turbine blades and vanes. Partial substitution ruthenium with nickel could provide the ability to tailor the properties [84] because of the extensive B2 phase field that some claim [85] extends from NiAl to RuAl. While varying results have been obtained as the extension of AlRu and AlNi phase fields into the Al-Ni-Ru ternary system [86–88].

The enthalpies of formation of the Al-Ni-Ru compounds obtained by high temperature direct reaction calorimeter are listed in Table X. It can be observed that as the Al content increases, the enthalpy tends to be more exothermic. And the enthalpy results for compounds in the B2 phase region between NiAl and RuAl showed a decrease around 0.1 mole fraction of Ru indicating a reduction in stability which will likely result in a miscibility gap. The effect diminishes on reducing the Al concentration below stoichiometry. The relation observed in the enthalpy results of constant Al content in Al-Ni-Ru system is quite different from the linear relations previously reported in the Al-Ni-Fe system [79]. Unusual behavior is observed for the composition dependence of the enthalpy of formation suggesting that formation of a miscibility gap in the B2 phase field between AlNi and AlRu occurs [89].

TABLE X Standard enthalpy of formation of Al-Ni-Ru compounds at 298 K[89]

Compound	$\Delta H_{f,B2}^{298\mathrm{K}}$ (kJ/mol)	Compound	$\Delta H_{f,B2}^{298\mathrm{K}}$ (kJ/mol)
$Al_{0.50}Ni_{0.50}$	-61.8 ± 1.1[80]	$Al_{0.45}Ni_{0.10}Ru_{0.45}$	-56.1 ± 0.8
$Al_{0.50}Ni_{0.10}Ru_{0.40}$	-62.0 ± 1.3	$Al_{0.45}Ni_{0.20}Ru_{0.35}$	-56.9 ± 1.9
$Al_{0.50}Ni_{0.20}Ru_{0.30}$	-63.1 ± 0.8	$Al_{0.45}Ni_{0.30}Ru_{0.25}$	-58.1 ± 1.5
$Al_{0.50}Ni_{0.25}Ru_{0.25}$	-64.04 ± 2.2*	$Al_{0.45}Ni_{0.35}Ru_{0.20}$	-57.6 ± 0.6
$Al_{0.50}Ni_{0.30}Ru_{0.20}$	-61.5 ± 1.1	$Al_{0.45}Ni_{0.45}Ru_{0.10}$	-55.5 ± 1.2
$Al_{0.50}Ni_{0.35}Ru_{0.15}$	-58.2 ± 2.0	$Al_{0.40}Ni_{0.40}Ru_{0.20}$	-51.6 ± 1.0
$Al_{0.50}Ni_{0.40}Ru_{0.10}$	-55.9 ± 2.1	$Al_{0.40}Ni_{0.50}Ru_{0.1}$	-49.5 ± 1.4
$Al_{0.50}Ni_{0.45}Ru_{0.05}$	-58.7 ± 2.4	$Al_{0.82}Ni_{0.12}Ru_{0.06}$	-31.5 ± 1.5
$Al_{0.50}Ru_{0.50}$	-54.5 ± 1.2		

* This work.

2.10. Al-Ni-Co system

NiAl and CoAl are isostructural and between them in the ternary phase diagram is a wide B2 phase region. That is, Co has great solubility in the NiAl compounds, which offers a considerable alloying potential and has been added to NiAl to improve its ductility [90]. By introducing a second phase in Co-Al-Ni system, for example, B2/γ' two phase alloys exhibited excellent compressive ductility from room temperature to 1273 K [91]. On the other hand, the effect of Co addition to the NiAl increased the tendency of martensite formation by increasing the Ms temperature, reducing the transformation strain anisotropy and reducing the transformation temperature hysteresis, optimizing Co content should allow martensitic transformation toughening process to overcome the ambient temperature brittleness of NiAl alloys [92, 93].

The enthalpies of formation and the constitutional defects of the ordered B2 $(Ni, Co)_{1-x}Al_x$ phase were investigated by Grün *et al.* [94], which can be described by the disorder model of Wagner and Schottky in the whole B2 phase region with high precision. A more recent Bragg-williams model was used to evaluate the triple defects in the (Co, Ni) Al B2 intermetallic compounds [95]. Table XI shows the enthalpy results for 1073 K obtained by using a differential solution calorimeter [96]. The derived values at 298 K have been added to Table XI. To derive the enthalpies of formation from 1073 K to 298 K, the Neumann-Kopp rule was used to get the heat capacity of the compounds, that is,

$$C_{p,}(Al_{0.5}Ni_{0.5-x}Co_x)$$
$$= xC_{p,}(AlNi) + (0.5-x)C_{p,}(CoAl)$$

TABLE XI Standard enthalpies of formation of Al-Ni-Co B2 phase compounds

Compound	ΔH_f^{1073K} (kJ/mol)	Experimental technique	$\Delta H_f^{298K}*$ (kJ/mol)
$Co_{0.5}Al_{0.5}$	-66.05 ± 0.05[94]	IHFDSC	-55.93 ± 0.05
$Ni_{0.08}Co_{0.42}Al_{0.5}$	-66.31 ± 0.10[94]		-56.41 ± 0.10
$Ni_{0.17}Co_{0.33}Al_{0.5}$	-66.65 ± 0.32[94]	...	-56.99 ± 0.32
$Ni_{0.25}Co_{0.25}Al_{0.5}$	-67.24 ± 0.06[94]	...	-57.8 ± 0.06
$Ni_{0.33}Co_{0.17}Al_{0.5}$	-68.48 ± 0.06[94]	...	-59.26 ± 0.06
$Ni_{0.42}Co_{0.08}Al_{0.5}$	-70.04 ± 0.12[94]	...	-61.07 ± 0.12
$Ni_{0.5}Al_{0.5}$	-71.27 ± 0.13[94]	...	-62.52 ± 0.13
$Ni_{0.20}Co_{0.38}Al_{0.42}$	-54.25 ± 0.08[94]	...	
$Ni_{0.29}Co_{0.29}Al_{0.42}$	-55.10 ± 0.15[94]	...	
$Ni_{0.38}Co_{0.20}Al_{0.42}$	-57.39 ± 0.14[94]	...	
$Ni_{0.30}Co_{0.15}Al_{0.55}$	-66.73 ± 0.07 [94]	...	

IHFDSC: Isoperibolic heat flux differential solution calorimeter. $\Delta H_f^{298K}*$ ——-Derived value from 1073 K by using the Neumann-Kopp rule

Then the enthalpies of formation of $Al_{0.5}Ni_{0.5-x}Co_x$ at 298 K is:

$$\begin{aligned}\Delta H_f^{298K}(Al_{0.5}Ni_{0.5-x}Co_x) &= \Delta H_f^{1073K}(Al_{0.5}Ni_{0.5-x}Co_x) \\ &\quad - \left(\int_{298K}^{1073K} C_p, (Al_{0.5}Ni_{0.5-x}Co_x) - 0.5 \right. \\ &\quad \times \int_{298K}^{1073K} C_p, Al - (0.5-x) \int_{298K}^{1073K} \\ &\quad \left. \times\, C_p, Ni - x \int_{298K}^{1073K} C_p, Co \right)\end{aligned}$$

Seen from Table XI, the enthalpies of formation decrease with Co content increasing both for $Al_{0.50}Ni_{0.5-x}Co_x$ and $Al_{0.42}Ni_{0.58-x}Co_x$. The model in [94] exhibited 8% (Ni, Co) antistructure atoms in $(Ni_xCo_{1-x})_{0.58}Al_{0.42}$ and $(Ni_xCo_{1-x})_{0.45}Al_{0.55}$ 8% vacancies and 1% Al antistructure atoms, which is in agreement with the calculation results from Parlinski [97].

Fig. 2 showes the standard enthalpies of formation derived from data of Sommer [94], which measured by solution calorimeter at 1073 K.

TABLE XII Standard enthalpies of formation of $(Ni, Cu)_{1-x}Al_x$ and $x_{Ni}/x_{Cu} = 11; 5$[96] at 1100 K. Data were modified from original by referring to solid Al

Compound	ΔH_f^{1100K} (kJ/mol)	Compound	ΔH_f^{1100K} (kJ/mol)
$Al_{0.40}Ni_{0.55}Cu_{0.05}$	-63.78	$Al_{0.40}Ni_{0.5}Cu_{0.1}$	-62.61
$Al_{0.43}Ni_{0.522}Cu_{0.047}$	-67.59	$Al_{0.43}Ni_{0.475}Cu_{0.095}$	-66.03
$Al_{0.46}Ni_{0.495}Cu_{0.045}$	-71.09	$Al_{0.46}Ni_{0.45}Cu_{0.09}$	-68.13
$Al_{0.48}Ni_{0.477}Cu_{0.043}$	-72.79	$Al_{0.48}Ni_{0.433}Cu_{0.087}$	-69.62
$Al_{0.50}Ni_{0.458}Cu_{0.042}$	-73.64	$Al_{0.50}Ni_{0.417}Cu_{0.083}$	-70.17
$Al_{0.52}Ni_{0.44}Cu_{0.04}$	-73.12	$Al_{0.52}Ni_{0.4}Cu_{0.08}$	-69.58
$Al_{0.55}Ni_{0.412}Cu_{0.037}$	-71.77	$Al_{0.55}Ni_{0.375}Cu_{0.075}$	-69.03

2.11. Al-Ni-Cu system

The Al-Ni-Cu Shape Memory Alloys (SMA) were paid a lot of attention for its possible high working temperature compared to the conventional Cu-Zn-Al and Ti-Ni SMA [98, 99], the microstructure evolution of one SMA during heating was studied [100]. Three different transformations occurred in the different composition Al-Ni-Cu alloys [101].

The standard enthalpies of formation of Al-Ni-Cu compounds in B2 phase region were determined by using an aluminum solution calorimeter [96], see the Table XII, all the data in Table XII have been referred to the solid Ni, solid Cu and solid Al at 1100 K by using the latent heat of Al from Kubaschewski *et al.* [83]. A maximum exists in $(Ni, Cu)_{1-x}Al_x$ compounds when $x = 0.5$. Same trend was observed in the results obtained by direct synthesis calorimetry for 298K by the current authors which are referred here for the first time, seen Fig. 3. This phenomenon happens in the Fe-Ni-Al and Co-Ni-Al systems.

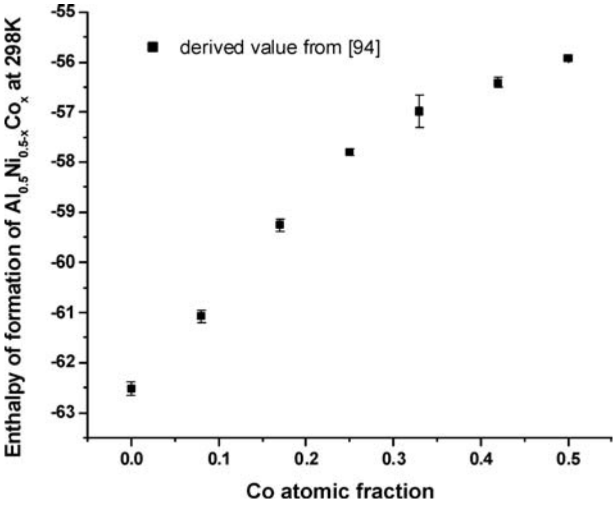

Figure 2 Standard enthalpies of formation of $Al_{0.5}Ni_{0.5-x}Co_x$ at 298 K.

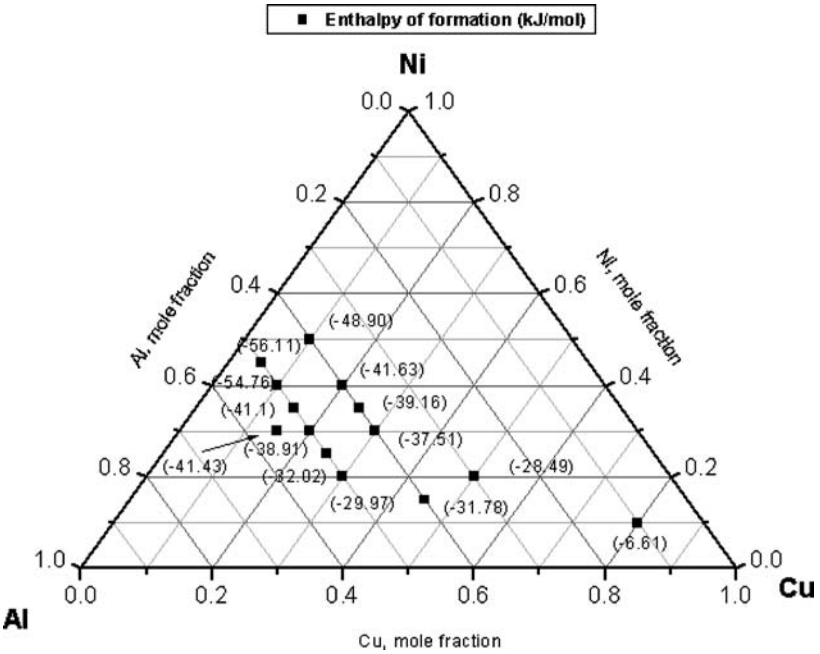

Figure 3 Standard enthalpies of formation of Al-Ni-Cu B2 phase compounds at 298 K.

Since the heat capacities of Al-Ni-Cu compounds are not available, the above enthalpies of formation at different temperatures (Table XII and Fig. 3) can not be compared directly.

3. Enthalpy comparison between different systems

3.1. Enthalpies of formation of $Al_{0.5}Ni_{0.5-y}X_y$ compounds

3.2. Enthalpies of formation of $Al_{0.4}Ni_{0.6-y}X_y$ compounds

Seen from Figs. 4 and 5, it is obvious that the enthalpies of formation of $Al_{0.5}Ni_{0.5-y}X_y$ and $Al_{0.4}Ni_{0.6-y}X_y$ decrease with the X (X: Fe, Co, Cu and Ti) content increasing, which indicates the much strong bonds between Al and Ni atoms than that between Al and X atoms; For the $Al_{0.5}Ni_{0.5-y}Y_y$ compounds, the enthalpies of formation is almost same as Y content increased; Maximum enthalpy existed for the $Al_{0.5}Ni_{0.5-y}Ru_y$ and $Al_{0.4}Ni_{0.6-y}Ru_y$ compounds, which is because of the discontinuousness between Al-Ni and Al-Ru sides [89].

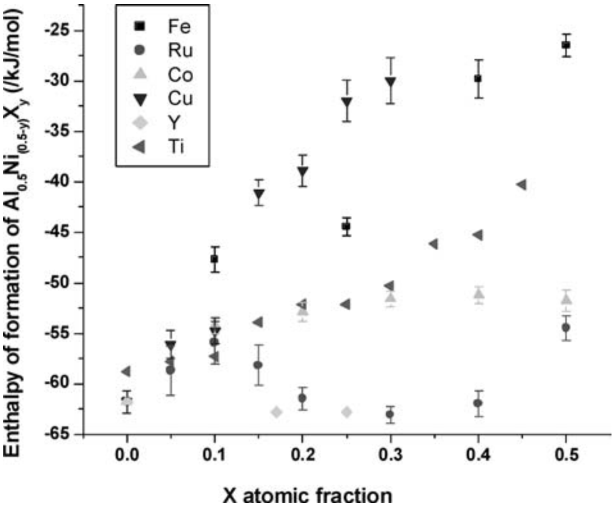

Figure 4 Enthalpy of formation of $Al_{0.5}Ni_{0.5-y}X_y$.

3.3. Enthalpies of formation of $(Al,X)_{0.25}(Ni,X)_{0.75}$ compounds

The phase diagrams of ternary systems indicate Cr, Nb, Ru, and Ti tend to substitute the Al sublattice when added to Ni_3Al; while Co, Zr, Fe and Cu tend to substitute the Ni sublattice; Hf seems like no preference sites. Figs. 6 and 7 showed the enthalpies of formation for $(Al, X)_{0.25}Ni_{0.75}$ (X: Hf, Ti, Nb and Y) and $Al_{0.25}(Ni, X)_{0.75}$ (X: Y, Fe, Cr, Nb, Ti and Hf) compounds. Both of the figures showed that Hf is the γ' phase stabilization element. $Ni_3(Al,Ti)$ and $(Ni,Y)_3(Al,Y)$ are more stable than $(Ni,Fe)_3Al$.

3.4. Enthalpies of formation of $Al_{0.33}Ni_{0.33}X_{0.33}$ compounds

Seen from Fig. 8, with the atomic number increasing, the enthalpies of formation of $Al_{0.33}Ni_{0.33}X_{0.33}$ compounds increase, which might be caused by the increase of ratio of valence electrons and atom radius.

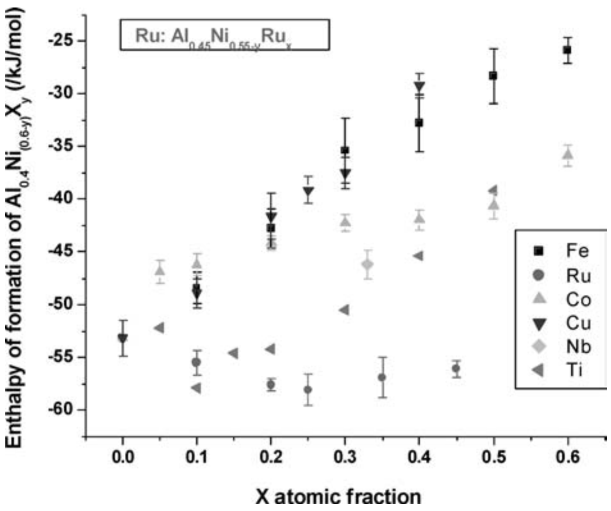

Figure 5 Enthalpy of formation of $Al_{0.4}Ni_{0.6-y}X_y$.

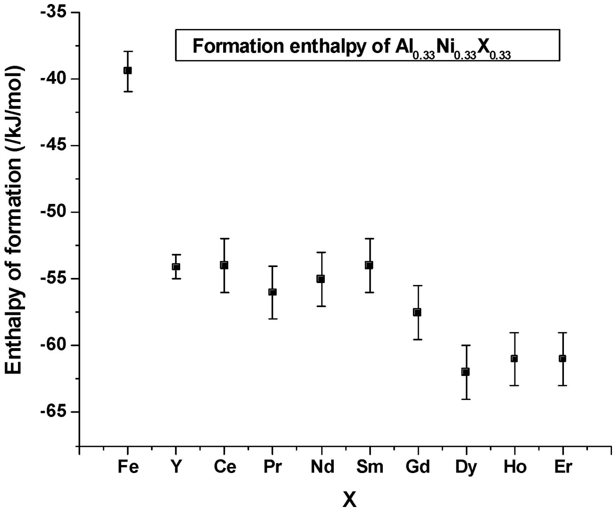

Figure 8 Enthalpy of formation of $Al_{0.33}Ni_{0.33}X_{0.33}$ compounds.

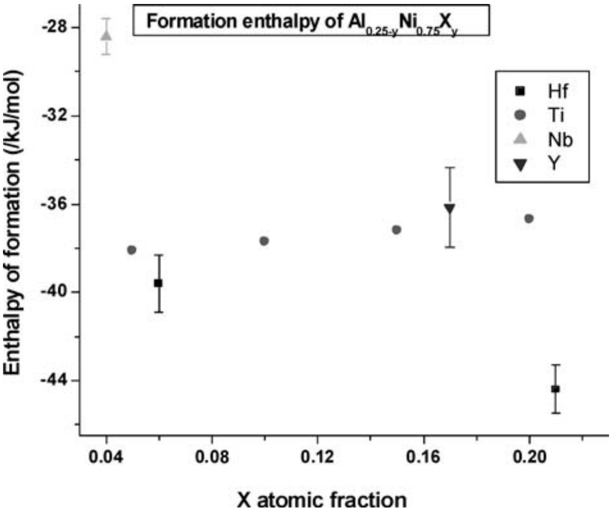

Figure 6 Enthalpy of formation of $Al_{0.25-y}Ni_{0.75}X_y$ compounds.

3.5. Enthalpies of formation of $Al_{0.5}Ni_{0.25}X_{0.25}$ compounds

To evaluate the solubility of X (fourth series elements in periodic table) in AlNi and the bonding strength between Al and X, the enthalpies of $Al_{0.5}Ni_{0.25}X_{0.25}$ (X: Cr, Mn, Fe, Co, Ni, Cu and Zn) compounds were measured by the high temperature direct synthesis calorimeter, seen in Fig. 9. It is clear that the enthalpy of formation for $Al_{0.5}Ni_{0.5}$ is the maximum, which indicates the strong bond between Al and Ni atoms. From Ni to its left side, the enthalpies decreased slower compared the slope of the right side, which might be due to the electron configuration of Cu and Zn is close to that of inert element, so the bonding between Al—Cu and Al—Zn are weak.

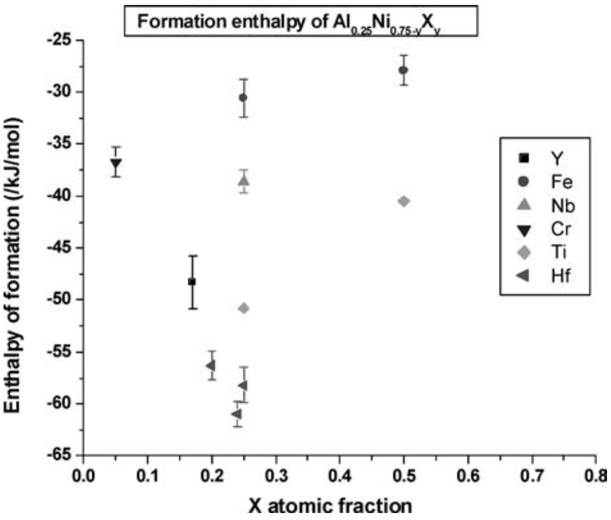

Figure 7 Enthalpy of formation of $Al_{0.25}Ni_{0.75-y}X_y$ compounds.

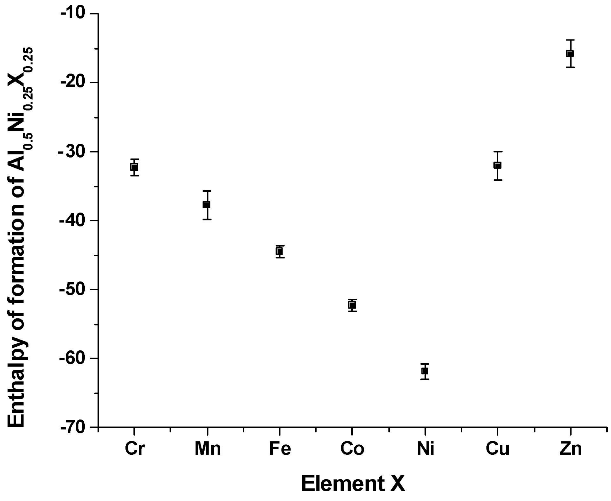

Figure 9 Enthalpies of formation of $Al_{0.5}Ni_{0.25}X_{0.25}$ compounds.

4. Conclusion

The enthalpies of formation of $Al_{0.5}Ni_{0.5-y}X_y$ and $Al_{0.4}Ni_{0.6-y}X_y$ decrease with the X (X: Fe, Co, Ti and Cu) content increasing; for the $Al_{0.5}Ni_{0.5-y}Y_y$ compounds, the enthalpies of formation are almost same as Y content increased; the maximum values of the enthalpies of formation existed in the $Al_{0.5}Ni_{0.5-y}Ru_y$ and $Al_{0.4}Ni_{0.6-y}Ru_y$ indicate the discontinuousness between Al−Ni and Al−Ru sides; enthalpies of formation of $(Al, X)_{0.25}(Ni, X)_{0.75}$ indicate that Hf is the γ' phase stabilization element; with atomic number increases, the enthalpies of formation of $Al_{0.33}Ni_{0.33}X_{0.33}$ (X: Fe, Y, Ce, Pr, Nd, Sm, Gd, Dy, Ho and Er) increase. The enthalpies of $Al_{0.5}Ni_{0.25}X_{0.25}$ (X: Cr, Mn, Fe, Co, Ni, Cu and Zn) compounds have a maximum, that is, the enthalpy of formation for $Al_{0.5}Ni_{0.5}$ compound. From Ni to both of its sides, the enthalpies of formation decreased.

Acknowledgments

This work was supported by the National Science Foundation under grand No. DMR 0208624.

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