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The enthalpy of formation of NiAl

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NiAl and NiAl based ternary metallic systems have attracted much attention in recent years for potential use as high temperature structural materials [1–6]. Alloy development of such systems requires a thorough knowledge of the phase equilibria and thermodynamics of the systems. Using high temperature calorimeters [7–9], the enthalpies of formation for many alloy systems have been measured and the results incorporated into thermodynamic databases for modeling of their phase diagrams using software such as Thermocalc® [10]. However, there exists some confusion regarding the value for the enthalpy of formation of NiAl. In one reference [11], comparison of published experimental data was made which are referred to different standard states, with the consequent conclusion that there is a wide discrepancy in the experimental NiAl data. In this paper, the enthalpies of formation of NiAl as a function of composition determined by two different calorimetric techniques are compared. The results are also compared to enthalpy of formation data for the stoichiometric alloy from several other sources.

Two kinds of calorimeters are widely used in measuring the enthalpies of formation of intermetallic compounds with high melting points: the differential solution calorimeter and the direct synthesis calorimeter. The former is an indirect method because the compound is prepared before the enthalpy of formation is determined, while the latter is a direct one since the enthalpy of formation is determined during alloy formation.

Using the differential solution calorimeter, Henig and Lukas [12] determined the enthalpy of formation of NiAl at 1100 K. During their experiment, the element Ni and the compound NiAl were dropped into the liquid aluminum separately and their heat of dissolution were measured in turn. The reactions involved in the measurement are:

$$\langle \mathrm{Ni}\rangle_{1100\ \mathrm{K}} + (\mathrm{Al})_{1100\ \mathrm{K}} \rightarrow ((\mathrm{Ni}))_{1100\ \mathrm{K}} \quad (1) \quad \Delta H_1$$

$$\langle \mathrm{NiAl}\rangle_{1100\ \mathrm{K}} + (\mathrm{Al})_{1100\ \mathrm{K}} \rightarrow ((\mathrm{Ni, Al}))_{1100\ \mathrm{K}} \quad (2) \quad \Delta H_2$$

(Al), ⟨Ni⟩, ⟨NiAl⟩ refer to liquid Al, solid Ni and solid NiAl respectively; ((Ni)), ((Ni, Al)) refer to the element Ni and compound NiAl dissolved into the liquid aluminium.

Then according to

$$(\mathrm{Al})_{1100\ \mathrm{K}} + \langle \mathrm{Ni}\rangle_{1100\ \mathrm{K}} \rightarrow \langle \mathrm{NiAl}\rangle_{1100\ \mathrm{K}} \quad (3)$$

the enthalpy of formation of NiAl, $\Delta H^{1100\ \mathrm{K}}_{\mathrm{f,Ni_{0.5}Al_{0.5}}}$, is obtained from ΔH_1 and ΔH_2, that is, $\Delta H^{1100\ \mathrm{K}}_{\mathrm{f,Ni_{0.5}Al_{0.5}}} = 0.5(\Delta H_1 + \Delta H_2)$, and the result was −72.20 kJ/mol referred to liquid Al and solid Ni at 1100 K. These authors also measured the composition dependence of the formation enthalpy for NiAl.

The enthalpy of formation of NiAl determined by direct synthesis calorimeter involves two reactions:

$$\mathrm{Al(298\ K) + Ni(298\ K) \rightarrow NiAl(1473\ K)} \quad (1) \quad \Delta H_1$$

$$\mathrm{NiAl(298\ K) \rightarrow NiAl(1473\ K)} \quad (2) \quad \Delta H_2$$

Then according to

$$\mathrm{Al(298\ K) + Ni(298\ K) \rightarrow NiAl(298\ K)} \quad (3)$$

The enthalpy of formation of NiAl at 298 K, $\Delta H^{298\ \mathrm{K}}_{\mathrm{f,Ni_{0.5}Al_{0.5}}}$, is calculated from ΔH_1 and ΔH_2:

$$\Delta H^{298\ \mathrm{K}}_{\mathrm{f,Ni_{0.5}Al_{0.5}}} = \Delta H_1 - \Delta H_2$$

The result from Nash and Kleppa [1] was −61.8 ± 1.1 kJ/mol, referred to solid Al and Ni at 298 K. These authors also measured the composition dependence of the formation enthalpy for NiAl.

To compare the data from the two methods, we used the data of heat capacities $C_{\mathrm{p,NiAl}}$, $C_{\mathrm{p,Al}}$ and $C_{\mathrm{p,Ni}}$ from Kubaschewski *et al.* [13] (seen Table I) and obtained the heat of reaction for $0.5\ \mathrm{Ni} + 0.5\mathrm{Al} \rightarrow \mathrm{Ni_{0.5}Al_{0.5}}$ from 298 to 1073 K:

$$\begin{aligned}\Delta H^{298\ \mathrm{K}\rightarrow 1073\ \mathrm{K}}_{\mathrm{Reaction}} &= \int_{298\ \mathrm{K}}^{1073\ \mathrm{K}} \left(C_{\mathrm{p,Ni_{0.5}Al_{0.5}}} - 0.5C_{\mathrm{p,Al}} - 0.5C_{\mathrm{p,Ni}}\right) \mathrm{d}T \\ &= \int_{298\ \mathrm{K}}^{1073\ \mathrm{K}} C_{\mathrm{p,Ni_{0.5}Al_{0.5}}} \mathrm{d}T - 0.5 \int_{298\ \mathrm{K}}^{1073\ \mathrm{K}} C_{\mathrm{p,Al}} \mathrm{d}T \\ &\quad - 0.5 \int_{298\ \mathrm{K}}^{1073\ \mathrm{K}} C_{p,Ni} \mathrm{d}T \\ &= -8.76\,\mathrm{kJ/mol}\end{aligned}$$

The enthalpy of melting of aluminum was taken as10.7 kJ/mole [13].

Using the above heat content we derived the enthalpy of formation of NiAl at 298 K from the data of

TABLE I Heat capacities of Al, Ni and NiAl from [13]

Substance	Phase	T (K)	$C_p = A + BT + C/T^2 + DT^2$ (J/deg mol) A	B $\times 10^3$	C $\times 10^{-5}$	D $\times 10^6$	Ht (kJ/mol)
Al	fcc	298	31.38	−16.40	−3.6	20.75	–
	liq	934	31.76	–	–	–	10.7
Ni	fcc	298	11.17	37.78	3.18	–	–
	fcc	631	20.54	10.08	15.40	–	–
	liq	1728	38.91	–	–	–	17.2
$Ni_{0.5}Al_{0.5}$	cubic	298	20.92	6.91	–	–	–
	liq	1912	35.56	–	–	–	31.4

TABLE II Enthalpy of formation of $Ni_{0.5}Al_{0.5}$ determined by different technique

Experimental method	Enthalpy of formation from reference (kJ/mol)	Standard state for referenced data	$\Delta H^{298\,\mathrm{K}}_{\mathrm{f,Ni_{0.5}Al_{0.5}}}$, referred to ⟨Ni⟩ and ⟨Al⟩ (kJ/mol)
Solution calorimeter	−71.27 ± 0.13 [2]	⟨Ni⟩ and (Al) at 1073 K	−62.51
	−72.20 [12]	⟨Ni⟩ and (Al) at 1100 K	−63.37
	−72.7 [10]	⟨Ni⟩ and (Al) at 1100 K	−63.87
Direct synthesis calorimeter	−61.8 ± 1.1 [1]	⟨Ni⟩ and ⟨Al⟩at 298 K	−61.8 [1]
	−63.6 [14]	⟨Ni⟩ and (Al) at 1073 K	−54.7
	−65.7 ± 1.1 [15]	⟨Ni⟩ and ⟨Al⟩ at 1136 K	−62
	−58.3 ± 1.1 [16]	⟨Ni⟩ and ⟨Al⟩ at 298 K	−58.3 [16]
	−58.7 [17]	⟨Ni⟩ and ⟨Al⟩ at 298 K	−58.7 [17]
EMF technique	−62.0 [18]	⟨Ni⟩ and ⟨Al⟩ at 298 K	−62.0 [18]
Water calorimeter	−69.0 [19]	⟨Ni⟩ and ⟨Al⟩ at 298 K	−69.0 [19]

*(Al), ⟨Ni⟩ and ⟨Al⟩ refer to liquid Al, solid Ni and solid Al respectively.

Grün *et al.* [2], that is, $\Delta H^{298\mathrm{K}}_{\mathrm{f,Ni_{0.5}Al_{0.5}}} = \Delta H^{1073\mathrm{K}}_{\mathrm{f,Ni_{0.5}Al_{0.5}}} - \Delta H_{\mathrm{reaction}} = -71.27$ kJ/mol $-(-8.76$ kJ/mol$) = -62.51$ kJ/mol, which is in good agreement with the data determined by direct synthesis calorimetry [1]. At the same time, the enthalpies of formation of $Ni_{1-x}Al_x$ ($0.42 < x < 0.54$) determined by solution calorimeter at 1100 K [12] were referenced to 298 K assuming the heat capacities of $Ni_{1-x}Al_x$ ($0.42 < x < 0.54$) are not composition dependent, Fig. 1. The derived values agree well with those obtained by direct synthesis calorimetry.

The enthalpy of formation values in the literature are often not directly comparable due to the different standard states, Table II. Using the heat contents in Table I and the enthalpy of melting of Al, the enthalpy data have been referred to 298 K and solid Ni and solid Al.

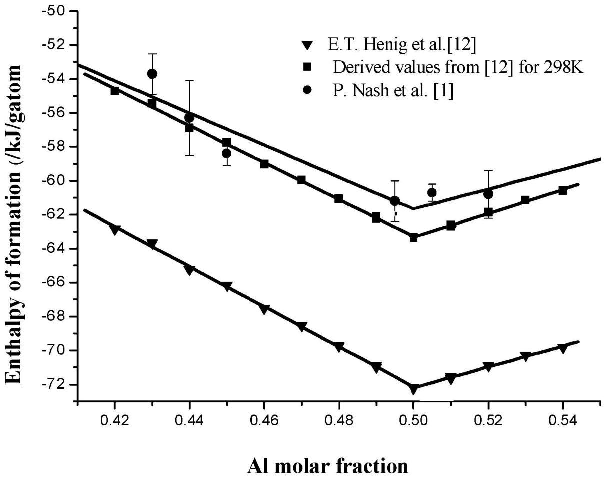

Figure 1 Enthalpy of formation of $Ni_{1-x}Al_x$ determined by different calorimeter.

The results are shown in the last column of Table II. It can be seen that six independent determinations of enthalpy of formation of NiAl at 298 K using three different experimental techniques fall within the range −61 to −64 kJ/mol. Taking a value of −62 ± 2 kJ/mol results in agreement with most of the experimental data.

In conclusion, the preponderance of the experimental data suggests that a value of −62 ± 2 KJ/mol should be taken for the enthalpy of formation of stoichiometric NiAl at 298 K.

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