

Composition dependence of the enthalpies of formation of NiAl

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Abstract

The enthalpy of formation of $\text{Ni}_x\text{Al}_{1-x}$ as a function of composition has been determined by high temperature reaction calorimetry over the range $0.44 \leq x \leq 0.58$. The value for the $\text{Ni}_{0.5}\text{Al}_{0.5}$ composition is -61.8 ± 1.1 kJ/mol. The present results are compared with previously published results on the enthalpy of formation of $\text{Ni}_x\text{Al}_{1-x}$. In several cases the experiments were performed at two different calorimeter temperatures and the difference in heat content values is compared with the heat capacity of NiAl. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The intermetallic compound NiAl is of interest as a potential high temperature structural material. However, to achieve the properties required the material will have to have additional alloying elements or reinforcing phases added. To ensure compatibility of the NiAl with the reinforcement and to provide a knowledge of the phase equilibria with ternary and higher order alloying additions, it is necessary to understand the thermodynamic behavior of the phase. Several studies of the heats of formation of $\text{Ni}_x\text{Al}_{1-x}$ as a function of composition have been made [1–4], as well as measurements for the stoichiometric composition only [5,6]. The published results show differences of up to 10 kJ/mol. As part of a broader program on heats of formation of Ni–Al–X compounds it was considered worthwhile to determine the composition dependence of the heat of formation of NiAl using a high temperature reaction calorimeter.

2. Experimental procedure

The heats of formation were determined using a high temperature reaction calorimeter with a typical accuracy of ± 1 kJ/mol [7] (in this paper mol refers to mole of atoms).

The measurements were generally made with the calorimeter set at 1473 ± 2 K, and using a protective argon atmosphere. In some cases a calorimeter temperature of 1373 K was used. The calorimeter was calibrated using pure copper. Samples were produced by mixing elemental powders in the required molar ratio in a mortar and pressing them into a small pellet. Typical sample weight was ~ 100 mg. The nickel powder used was reduced in hydrogen prior to preparation of the samples to remove oxygen and carbon impurities which would be a source of error particularly in the presence of aluminum. The compositions quoted are values obtained by wet chemical analysis (ASTM E 1409) of the reacted pellets. Oxygen contents of the samples were typically ~ 0.3 wt.%, carbon content ~ 0.02 wt.% and nitrogen content 0.01 wt.% or less.

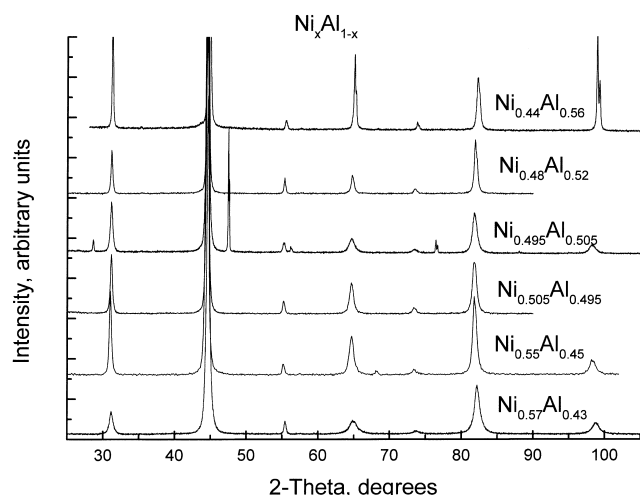
The enthalpy of reaction, $\Delta H_{\text{Reaction}}$, was obtained first by dropping the pellet into the calorimeter from room temperature. A minimum of four separate samples were measured. The pellets were subsequently removed and again dropped from room temperature into the calorimeter to obtain the heat content of the compound, $\Delta H_{\text{Heat Content}}$. The difference between the two measurements yields the heat of formation at 298 K. Material from the reacted compound was used to obtain an X-ray diffraction pattern to confirm that the reacted sample was the desired compound.

3. Results and discussion

X-ray diffraction patterns for the $\text{Ni}_x\text{Al}_{1-x}$ alloys after

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Fig. 1. X-ray diffraction patterns for $\text{Ni}_x\text{Al}_{1-x}$ alloys.

reacting in the calorimeter are shown in Fig. 1. Only diffraction peaks from the NiAl phase, with the CsCl prototype structure, were observed except for the $\text{Ni}_{0.495}\text{Al}_{0.505}$ alloy where some Si powder was added to the X-ray sample for calibration purposes. The results indicate that the samples completely reacted to the NiAl compound in the calorimeter.

The standard enthalpy of formation, $\Delta H_f^{298\text{ K}}$, is calculated from:

$$\Delta H_f^{298\text{ K}} = \Delta H_{\text{Reaction}} - \Delta H_{\text{Heat Content}}$$

The enthalpies of formation of $\text{Ni}_x\text{Al}_{1-x}$ alloys for $0.44 \leq x \leq 0.58$ were determined and the results are shown in Fig. 2 and Table 1. The results are the averages of four to seven individual measurements. With the standard deviations from the reaction and heat content experiments

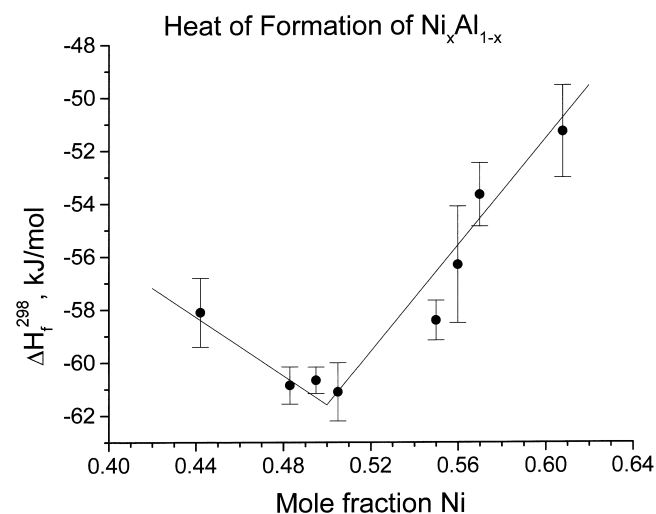
Fig. 2. Enthalpies of formation for $\text{Ni}_x\text{Al}_{1-x}$ alloys determined in this work.

Table 1

Summary of high temperature reaction calorimetry results for $\text{Ni}_x\text{Al}_{1-x}$ ^a

Composition	$\Delta H_{\text{Reaction}}^*$ kJ/mol	$\Delta H_{\text{Heat Content}}^*$ kJ/mol	$\Delta H_{\text{formation}}^{298\text{ K}}$ kJ/mol
$\text{Al}_{0.56}\text{Ni}_{0.44}^b$	-26.5 ± 0.7	31.6 ± 0.5	-58.1 ± 1.3
$\text{Al}_{0.52}\text{Ni}_{0.48}^b$	-32.0 ± 0.6	29.0 ± 0.6	-61.0 ± 0.7
$\text{Al}_{0.52}\text{Ni}_{0.48}$	-29.7 ± 0.6	31.1 ± 0.6	-60.8 ± 1.4
$\text{Al}_{0.505}\text{Ni}_{0.495}$	-29.9 ± 0.2	30.7 ± 0.5	-60.7 ± 0.5
$\text{Al}_{0.495}\text{Ni}_{0.505}^b$	-29.5 ± 0.9	31.5 ± 0.4	-61.0 ± 1.1
$\text{Al}_{0.495}\text{Ni}_{0.505}^b$	-32.9 ± 1.1	28.30 ± 0.2	-61.2 ± 1.2
$\text{Al}_{0.45}\text{Ni}_{0.55}^b$	-27.1 ± 0.4	31.3 ± 0.6	-58.4 ± 0.7
$\text{Al}_{0.44}\text{Ni}_{0.56}^b$	-27.4 ± 2.2	28.9 ± 0.3	-56.3 ± 2.2
$\text{Al}_{0.43}\text{Ni}_{0.57}$	-21.9 ± 0.4	31.7 ± 0.4	-53.7 ± 1.2
$\text{Al}_{0.39}\text{Ni}_{0.61}$	-19.5 ± 0.3	31.8 ± 0.7	-51.3 ± 1.7

^a Calorimeter temperature set at 1473 K except as noted. $\Delta H_{\text{formation}}^{298\text{ K}}$ refers to $\text{Ni(s)} + \text{Al(s)} \rightarrow \text{NiAl(s)}$.

^b Calorimeter set at 1373 K.

designated as δ_1 and δ_2 and from the calibration as δ_3 , the overall uncertainty in the measurements, δ , was determined from $\delta = (\delta_1^2 + \delta_2^2 + \delta_3^2)^{1/2}$. The data were fit with two linear fits on either side of stoichiometry, corresponding to a Wagner–Schottky defect model [8] with different defect structures on either side of stoichiometry.

Note that for several compositions the enthalpies of formation were determined with the calorimeter at two different temperatures, 1373 and 1473 K. In those cases the enthalpies of formation are seen to be identical, demonstrating the excellent reproducibility of results from the calorimeter. For these alloys a rough estimate may be made of the heat capacity from the slope of the $\Delta H_{\text{Heat Content}}$ versus T plot, resulting in values of 21 and 32 J/mol.K for $\text{Ni}_{0.48}\text{Al}_{0.52}$ and $\text{Ni}_{0.505}\text{Al}_{0.495}$, respectively. This difference results from the large error involved in determining the slope from two values rather than from a real composition effect. Nevertheless these values are consistent with published values for stoichiometric NiAl [9–11].

The composition dependence of the enthalpy of formation of $\text{Ni}_x\text{Al}_{1-x}$ is clearly not symmetric around the stoichiometric composition (Fig. 2). The rate of decrease in enthalpy of formation on the Al-rich side is lower than that on the Ni-rich side. This results from the fact that there is a change in the type of defect structure necessary to accommodate the non-stoichiometric compositions on either side of stoichiometry. It is well established that on the Ni-rich side of stoichiometry Ni atoms substitute for Al on the Al sub-lattice [12] resulting in an increasing number of Ni–Ni bonds. On the Al-rich side the excess Al ratio is accommodated by having vacancies on the Ni-rich sublattice, resulting in a decrease in enthalpy of formation due to fewer bonds and an increasing number of vacancies.

Selected enthalpy of formation results from previous studies are shown in Fig. 3. The data are all referred to Al(s) and Ni(s) standard states. It has been stated that there is a discrepancy in the experimental values of as much as 13 kJ/mol [13]. However, this is incorrect since the

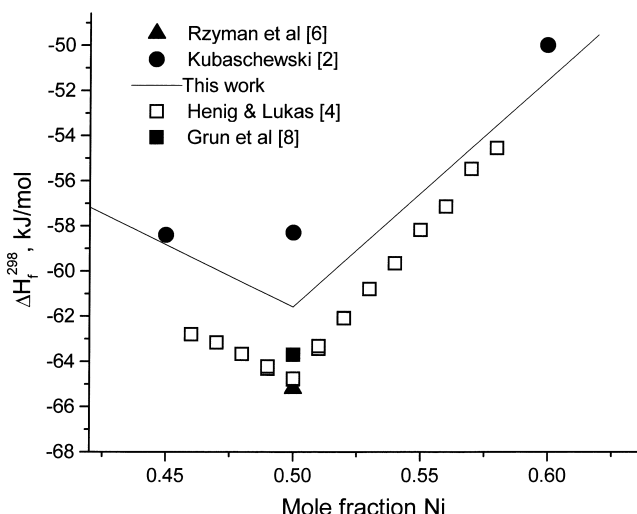


Fig. 3. Comparison of enthalpies of formation of $\text{Ni}_x\text{Al}_{1-x}$ determined in several studies.

comparison was made without taking into account the different standard states used in different studies, where in some cases the results reported are referred to Al(liquid) and Ni(solid). Taking this into account reduces the discrepancy in the data to ~ 8 kJ/mol, or 13%. In addition some of the data are referred to the reaction or dissolution temperature while others are referred to 298 K. The data may be referred to 298 K if the heat capacities of the product and reactants are known as a function of temperature up to the reaction or dissolution temperature:

$$\Delta H_{298} = \Delta H_T - \int_{298}^T \Delta C_p dT$$

$$\Delta C_p = C_{p, \text{NiAl}} - 0.5C_{p, \text{Ni}} - 0.5C_{p, \text{Al}}$$

Using data for $C_{p, \text{NiAl}}$, $C_{p, \text{Al}}$ and $C_{p, \text{Ni}}$ from Kubaschewski et al. [11] we calculate that ΔH_{1100} is more negative than ΔH_{298} by -0.85 kJ/mol. Rzyman et al. [6] fit their experimental data for ΔH_T over the range 298–1140 K to give $\Delta H_{f, \text{NiAl}} = -65.915 - 0.0014118T$ kJ/mol, which gives ΔH_{1100} as more negative than ΔH_{298} by -1.1 kJ/mol between 298 and 1100 K. Using the more recent data of Perring et al. [10] for $C_{p, \text{NiAl}}$ we calculate that ΔH_{1100} is more negative than ΔH_{298} by -2.2 kJ/mol. We have chosen to use the data from Ref. [10] and applying the enthalpy correction for temperature to the data of Henig and Lukas [4] their data are then ~ 2.2 kJ/mol less negative when referred to 298 K. The data of Henig and Lukas [4] presented in Fig. 2 are referred to Ni(s), Al(s) and 298 K after applying the 2.2-kJ/mol correction for all compositions.

After adjusting the data of Henig and Lukas the differences between their data and the present results over the composition range measured vary from 0.5 to 3 kJ/mol. The difference tends to be smaller on the Ni-rich side and

Table 2

Experimental values of $\Delta H_f^{298 \text{ K}}$ for $\text{Ni}_{0.5}\text{Al}_{0.5}$ referred to Ni(s), Al(s)

$\Delta H_f^{298 \text{ K}}$, kJ/mol	Experimental technique	Ref.
-58.7	Reaction calorimeter	[2]
-64.2 ± 2.0	Solution calorimeter	[3]
-64.8	Solution calorimeter	[4]
-58.0 ± 3.0	Solution calorimeter	[5]
-65.2 ± 1.3	Solution calorimeter	[6]
-63.7 ± 0.13	Solution calorimeter	[8]
-62.0	EMF	[14]
-61.8 ± 1.1	Reaction calorimeter	This work

larger on the Al-rich side. The data of Dannöhl and Lukas [3] are more scattered but tend to lie between the results of this work and those of Henig and Lukas. The agreement for most of the composition range lies within the expected experimental error range for the two studies. Additional experimental data points of Kubaschewski [2], are shown on the figure. Data for the enthalpy of formation of $\text{Ni}_{0.5}\text{Al}_{0.5}$ from several studies are given in Table 2, all referred to 298 K and the standard states of the components. The data were derived from several different experimental techniques but nevertheless show agreement to within 10%. Although all of the data are referred to 298 K the fact that reaction and dissolution experiments are performed at different temperatures may result in slightly different heats of formation being determined. One would expect that at higher temperatures a certain amount of disorder would be introduced into the lattice due to the increase in thermal vacancies. This effect has been confirmed by experiments (see for example Refs. [15,16]). This would mean that experiments at higher temperatures would determine a lower ΔH_{298} due to the less ordered structure of the compound. This could explain part or all of the difference in the ΔH_{298} values determined in the present work and the results from dissolution calorimetry at lower temperatures [3,4,8].

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