Enthalpies of formation in the Al–Ni–Ru system by direct reaction synthesis calorimetry

Hsin-Ning Su, Philip Nash *

Thermal Processing Technology Center, Illinois Institute of Technology, Chicago, IL 60616, USA

Abstract

The enthalpies of formation of ternary compounds in the Al–Ni–Ru system have been determined by high temperature reaction calorimetry. The composition dependence of the enthalpy of formation and lattice parameter of the compounds with B2 structure were determined in the region of $0.40 \leq Al \leq 0.5$ mole fraction. 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 occurs. For some compositions, the experimental enthalpy data therefore represent the formation enthalpy of the metastable B2 phase.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

The Al–Ni–Ru system is of practical interest since the RuAl intermetallic compound has shown potential for high temperature application [1] and partial substitution for ruthenium by nickel could provide the ability to tailor the properties [2] because of the extensive B2 phase field that some claim [3] extends from NiAl to RuAl.

The B2 structure can be visualized as an ordered bcc lattice. Unlike a bcc lattice one type of atom occupies the body-centered position and another type occupies the cube corners. This results in only one lattice point per unit cell and the lattice is therefore primitive cubic. When the composition deviates from stoichiometry constitutional defects must be introduced to preserve the crystal structure. The simple cubic lattice on which the Al atoms reside may be designated β and the corresponding transition metal lattice may be designated α.

In NiAl, it is well established that on the Al-rich side of stoichiometry vacancies are present on the α sublattice [4]. On the Ni-rich side, the excess Ni atoms occupy the β sublattice creating anti-structure defects. In the RuAl compound, the constitutional defect structure appears different from NiAl but is not well understood [5]. Due to the different constitutional defect structure between NiAl and RuAl, it is not straightforward to define the B2 phase field between NiAl and RuAl in the Al–Ni–Ru phase equilibria. The available phase equilibria data indicate that the B2 phase field between NiAl and RuAl exhibits either a miscibility gap [6–9] or complete miscibility [3,10].

It would be very helpful if enthalpy of formation data and lattice parameter data are available to help resolve the issue of the continuity of the B2 phase field and to provide data to thermodynamically optimize the Al–Ni–Ru system by the Calphad method. This paper reports on determinations of enthalpies of formation and precise lattice parameter measurements in the B2 phase field of this system.

2. Experimental procedure

The heats of formation were determined using a high temperature reaction calorimeter with a typical accuracy

---

* Corresponding author.
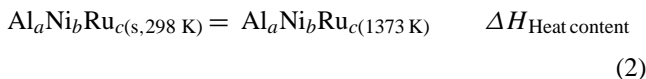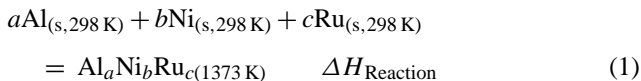*E-mail address:* nash@iit.edu (P. Nash).

of ± 1 kJ/mol [11]. The measurements were made with the calorimeter set at 1373 ± 2 K, and using a protective argon atmosphere. The calorimeter was calibrated using pure copper. Samples were produced by mixing elemental powders in a mortar in the required molar ratio, and pressing them into a small pellet. Typical sample weight was about 100 mg. The nickel and iron powders used were reduced in hydrogen at 873 K prior to preparation of the samples to remove oxygen and carbon, which would be a source of errors.

The enthalpy of reaction is measured in two steps. $\Delta H_{\text{Reaction}}$ is obtained first by dropping the pellet into the calorimeter from room temperature. A minimum of six 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. The results are averages of the six 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 was used to obtain an X-ray diffraction pattern to confirm that the reacted sample was the desired compound.

3. Enthalpy of formation calculation

By using direct synthesis, the standard enthalpy of formation, $\Delta H_{\text{f}}^{298\,\text{K}}$, is calculated from:

$$a\text{Al}_{(s,298\,\text{K})} + b\text{Ni}_{(s,298\,\text{K})} + c\text{Ru}_{(s,298\,\text{K})}$$
$$= \text{Al}_a\text{Ni}_b\text{Ru}_{c(1373\,\text{K})} \qquad \Delta H_{\text{Reaction}} \qquad (1)$$

$$\text{Al}_a\text{Ni}_b\text{Ru}_{c(s,298\,\text{K})} = \text{Al}_a\text{Ni}_b\text{Ru}_{c(1373\,\text{K})} \qquad \Delta H_{\text{Heat content}}$$
$$(2)$$

From reactions (1) and (2), we get

$$a\text{Al}_{(s,298\,\text{K})} + b\text{Ni}_{(s,298\,\text{K})} + c\text{Ru}_{(s,298\,\text{K})} = \text{Al}_a\text{Ni}_b\text{Ru}_{c(s,298\,\text{K})}$$

The standard enthalpy of formation is thus obtained.

$$\Delta H_{\text{f}}^{298\,\text{K}} = \Delta H_{\text{Reaction}} - \Delta H_{\text{Heat content}}$$

$\Delta H_{\text{Reaction}}$ and $\Delta H_{\text{Heat content}}$ are molar enthalpy changes for reactions (1) and (2).

4. Lattice parameter calculation

X-ray diffraction was performed using Cu Kα radiation. Scans were taken over a 2θ range of 5–120°. A NIST alumina reference material was used as a standard to correct

d-spacing. The lattice parameter was calculated using seven to nine peaks. The Nelson–Riley method was used for correcting for systematic errors [12].

5. Prediction of enthalpies of formation

For comparison with our experimental results we have used Miedema's semi-empirical model extended for ternary alloys [13] to calculate the standard enthalpy of formation, $\Delta H_{\text{f}}^{298\,\text{K}}$:

$$\Delta H_{\text{f}}^{298\,\text{K}} = C_{\text{A}} f_{\text{B}}^{\text{A}} \Delta H^{\text{inter}}(\text{A in B})$$
$$+ C_{\text{A}} f_{\text{C}}^{\text{A}} \Delta H^{\text{inter}}(\text{A in C})$$
$$+ C_{\text{B}} f_{\text{B}}^{\text{C}} \Delta H^{\text{inter}}(\text{B in C})$$

C_{A} and C_{B} are the molar ratios of A and B elements, respectively, in the corresponding compounds, f_{B}^{A} the degree of surface contact of an A atom with B neighbors, while f_{C}^{A} is the degree of surface contact of an A atom with C neighbors. ΔH^{inter} is interfacial enthalpy.

6. Enthalpy of formation results

The enthalpies of formation of the Al–Ni–Ru compounds and measured lattice parameters are listed in Table 1, together with values calculated in this work based on Miedema's model. It can be observed that as the Al content increases, the enthalpy tends to be more exothermic. The Miedema model predicts less exothermic values than the measured values for all compositions. Fig. 1 shows the enthalpy results for compounds in the supposed B2 phase region between NiAl and RuAl.

Figs. 2 and 3 show the enthalpies of formation of compounds along constant 45 at.% Al indicated as $\text{Al}_{0.45}\text{Ni}_{(0.55-X)}\text{Ru}_X$ and 50 at.% Al indicated as $\text{Al}_{0.50}$
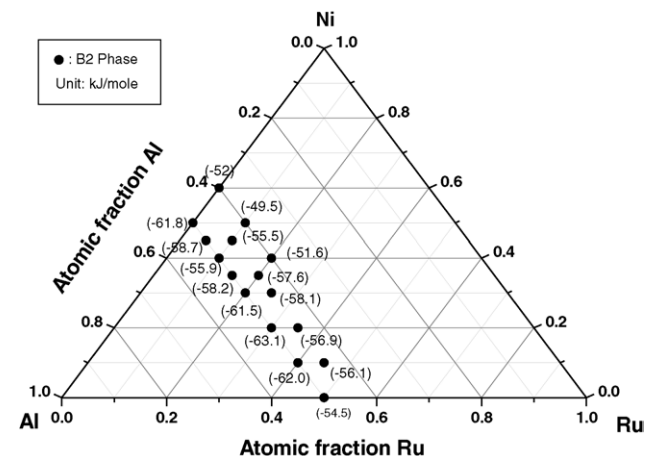

Fig. 1. Enthalpies of formation in B2 phase field of Al–Ni–Ru system.