Thermodynamic properties of the Al–Fe–Ni system acquired via a hybrid approach combining calorimetry, first-principles and CALPHAD

Lijun Zhang [a], Jiong Wang [a], Yong Du [a,*], Rongxiang Hu [b], Philip Nash [b], Xiao-Gang Lu [c], Chao Jiang [a]

[a] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, China*
[b] *Thermal Processing Technology Centre, Illinois Institute of Technology, 10 West, 32nd Street, Chicago, IL 60616, USA*
[c] *Thermo-Calc Software AB, Björnnäsvägen 21, 113 47 Stockholm, Sweden*

Abstract

A reaction calorimeter coupled with first-principles calculations was employed to obtain enthalpies of formation for τ_1 (Al_9FeNi) and τ_2 ($Al_{10}Fe_3Ni$) compounds. The previous thermodynamic model for describing the disorder/order transition (fcc_A1/L1$_2$) in the Al–Fe–Ni system was modified to extrapolate this model to quaternary and higher-order systems. The first-principles energy calculations for the end-members of sub-lattice models in ternary compounds and L1$_2$ phase were performed to facilitate subsequent modeling. The existence of the experimentally observed miscibility gap for ternary B2-ordered phase is detected by the present calculation. Such a feature cannot be identified with available thermodynamic software due to the tiny difference between the Gibbs energies associated with different phase assemblages. A set of thermodynamic parameters for the Al–Fe–Ni system was obtained via thermodynamic modeling. Numerous experimental data including phase diagram, thermodynamic properties and site occupation of Fe in B2 phase are well accounted for by the present modeling.
© 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Aluminium alloys; First-principle electron theory; CALPHAD; High-temperature reaction calorimeter; Nickel aluminides

1. Introduction

The Al–Fe–Ni system has been subject to numerous investigations due to its important technological applications, which include high-temperature alloys, magnetic materials and shape memory devices. Knowledge of the phase equilibria and thermodynamic properties in the Al–Fe–Ni system is indispensable to optimize alloy composition and control processing conditions for Al–Fe–Ni-based alloys.

Zhang et al. [1,2] have conducted experimental investigations and thermodynamic assessment for the Al–Fe–Ni

system. In view of the number of newly measured phase equilibria [3–5], the previous thermodynamic description needs to be updated in order to reproduce these experimental data [3–5]. The refined thermodynamic description can be incorporated into a thermodynamic database for multi-component Al-based commercial alloys, which is being established in our group [6–8]. In the thermodynamic modeling due to Zhang et al. [1,2], only the CALPHAD approach [9] is employed. The essence of this approach is to evaluate the parameters of thermodynamic models for the Gibbs energies of the individual phases via a thermodynamic optimization applied to the measured thermodynamic and phase equilibrium data. With the optimized thermodynamic parameters, any kind of phase equilibria and thermodynamic properties can be computed. However,

---

this approach cannot predict the thermodynamic properties in a metastable state. Due to this limitation, the Gibbs energies of the metastable state for the end-members of sub-lattice models used for ternary compounds and $L1_2$ phases are given fictitious values in the previous modeling [1,2].

Recent studies have indicated that the incorporation of first-principles calculations based on density functional theory (DFT) [10] into the CALPHAD framework can be quite fruitful [11]. Using the atomic numbers and crystal structure information as input, first-principles calculations can compute thermodynamic and structural properties for both stable and metastable phases. The integration of first-principles calculation and CALPHAD provides an efficient way to obtain reliable thermodynamic parameters when thermodynamic quantities in the metastable state need to be defined. Although first-principles calculation can be used to provide missing thermodynamic properties, its predictive reliability should be verified experimentally. The enthalpy of formation, as the leading term in the Gibbs energy, is the predominant quantity among various thermodynamic properties. Calculation of this thermodynamic quantity is one of the main focuses targeted by first-principles calculations. To the best of our knowledge, however, almost all of the previous enthalpies of formation computed via first-principles methods are only compared with the literature data, which are not reliable in some cases. It is necessary to perform a key experiment, such as a calorimetric investigation, in order to verify the reliability of the first-principles calculations.

In the present work, we develop a hybrid approach that combines calorimetry, first-principles and CALPHAD to acquire thermodynamic properties for the Al–Fe–Ni system spanning wide composition and temperature ranges. Thus, the main objectives of this study are: (i) to determine the enthalpies of formation for τ_1 (Al_9FeNi) and τ_2 ($Al_{10}Fe_3Ni$) using a high-temperature reaction calorimeter (HTRC) coupled with first-principles calculations; (ii) to perform first-principles calculations to obtain the enthalpies of formation for the end-members in the sub-lattice

models describing τ_1 and τ_2 ternary compounds, as well as those for Al_2FeNi, $AlFe_2Ni$ and $AlFeNi_2$ in the ordered $L1_2$ structure; and (iii) to obtain a consistent set of thermodynamic parameters for the Al–Fe–Ni system based on all the critically reviewed literature data and the present work, and validate the hybrid approach by comparing the calculated phase diagrams, thermodynamic properties, and site occupation of Fe in B2 phase with the corresponding experimental values.

2. Evaluation of the recent literature data

To facilitate reading, the symbols to denote the phases in the Al–Fe–Ni system are listed in Table 1. Since Zhang and Du [1] and Eleno et al. [12] have reviewed all the literature data in the Al–Fe–Ni system up to 2006, only those newly published results will be described here. These new investigations on phase equilibria and crystal structures are summarized in Table 2 and concisely categorized in the following.

Table 1
List of the symbols used to denote the phases in the Al–Fe–Ni system.

Symbol	Phase
L	Liquid
(Al)	Solid solution based on Al with fcc_A1 structure
γ	Solid solution based on (γFe) and (Ni) with fcc_A1 structure
$\alpha\delta$	(δFe) and (αFe) are modeled as the bcc_A2 phase
β	Solid solution based on AlFe and AlNi with bcc_B2 structure
$Al_{13}Fe_4$	Solid solution based on $Al_{13}Fe_4$
Al_5Fe_2	Solid solution based on Al_5Fe_2
Al_2Fe	Solid solution based on Al_2Fe
ε	Solid solution based on Al_5Fe_4
γ'	$AlNi_3$ and $FeNi_3$ are modeled as the $L1_2$ phase
Al_3Ni_5	Solid solution based on Al_3Ni_5
Al_3Ni_2	Solid solution based on Al_3Ni_2
Al_3Ni	Solid solution based on Al_3Ni
τ_1	Ternary compound Al_9FeNi
τ_2	Ternary compound $Al_{10}Fe_3Ni$
τ_3	Ternary compound $Al_{71}Fe_5Ni_{24}$
θ	Both $\alpha\delta$ and β phases
λ	Both γ and γ' phases

Table 2
Recent investigations on phase equilibria and crystal structures of the Al–Fe–Ni system since 2006.

Ref.	Type of paper	Description of the main contributions	Experimental technique	Quoted mode[a]
[1]	Experiment	Phase transition temperatures in Al-rich region	DTA	□
	Modeling	Thermodynamic modeling	/	/
[2]	Experiment	Isothermal sections at 850 and 627 °C in Al-rich region	XRD, EPMA SEM/EDX	■
[3]	Experiment	Isothermal section at 850 °C in Al-rich region	XRD, EPMA	■
		A series of vertical sections in Al-rich region	DTA	■
		Crystal structures of ternary τ_1 and τ_2 compounds	Single-crystal XRD	■
[4]	Experiment	Phase transition temperatures along the Ni_3Al–Ni_3Fe section	DTA	■
[5]	Experiment	Phase equilibria at 1200, 1100, 1000 and 900 °C close to Fe–Ni side	XRD, EPMA	■

KEMS, Knudsen effusion mass spectrometry; XRD, X-ray diffraction; EPMA, electron probe microanalysis; DTA, differential thermal analysis; SEM/EDX, scanning electron microscopy with energy dispersive X-ray analysis.
[a] Indicates whether the data are used or not used in the parameter optimization: ■, used; □, not used but used for checking the modeling.