JPEDAV (2009) 30:559–563
DOI: 10.1007/s11669-009-9573-3
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Enthalpy of Formation in the Al-Ni-Ti System

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(Submitted March 22, 2009; in revised form July 12, 2009)

The Al-Ni-Ti ternary system forms the basis of several alloy systems of practical importance. This study was undertaken to provide additional experimental thermodynamic data for the modeling of the Al-Ni-Ti system. High-temperature direct reaction calorimetry has been used to determine the standard enthalpy of formation of several Al-Ni-Ti alloys. The stability of the $L2_1$ structure over the B2 structure at the stoichiometric composition of $Ni_{0.5}Al_{0.25}Ti_{0.25}$ was estimated from the enthalpy results to be 6.8 kJ/mol. The lattice parameters and melting temperatures of these compounds are also reported.

Keywords thermodynamics, enthalpy of formation, Al-Ni-Ti, stability

1. Introduction

The Al-Ni-Ti system contains several interesting composition regions which form the basis of many technologically important alloys. NiAl-based alloys can be used for the oxidation protection coating of Ni-based superalloys[1] and for electrical contacts to metallize *n*-GaN.[2] NiAl is a potential high-temperature structural material and the addition of Ti to NiAl increases the creep strength due to the large size mismatch,[3] and beyond the solubility limit the semi-coherent precipitation of $AlNi_2Ti$ occurs.[4] Another application is shape memory alloys based on NiTi B2 phase.[5] Ni-based γ/γ' superalloys (γ is the fcc nickel solid solution and γ' is based on the Ni_3Al $L1_2$ phase) are used for the high-temperature/high-strength turbine applications, Ti addition increases the amount of the γ' phase. Another region with potential structural applications is Al-rich Al-Ni-Ti where an amorphous phase can be formed over a wide composition range, and some of the alloys show promising ductility.[6]

The Al-Ni-Ti phase diagram has been reviewed recently, and some discrepancies and incompleteness were identified.[7] Thermodynamic modeling of the system could benefit from additional thermodynamic data especially with regard to the enthalpy of formation of compounds in the system.

This study was undertaken to provide additional thermodynamic data for the modeling of the Al-Ni-Ti system. In this paper we report on enthalpy of formation measurements, lattice parameter measurements and some phase equilibria results. Measurements of specific heat capacity of selected compounds have been reported elsewhere.[8]

2. Experimental Procedure

2.1 Enthalpy of Formation Determination

A high-temperature direct synthesis calorimeter[9] was used to determine the enthalpy of formation at 298 K. The enthalpy is measured in two steps: first, elemental powders are mixed in a mortar in the required molar ratio and then pressed into a small pellet. This pellet is dropped from room temperature into the high-temperature calorimeter to form the compound:

$$a\text{Al (298 K)} + b\text{Ni (298 K)} + c\text{Ti (298 K)} = \text{Al}_a\text{Ni}_b\text{Ti}_c \text{ (1373 K)} \qquad \Delta H_{\text{reaction}} \qquad \text{(Eq 1)}$$

where a, b, and c are moles of elements Al, Ni and Ti, respectively, and $Al_aNi_bTi_c$ is the correspondingly formed compound. The pellets were subsequently removed and again dropped from room temperature into the calorimeter to obtain the heat content of the compound, $\Delta H_{\text{heat content}}$:

$$\text{Al}_a\text{Ni}_b\text{Ti}_c \text{ (298 K)} = \text{Al}_a\text{Ni}_b\text{Ti}_c \text{ (1373 K)} \qquad \Delta H_{\text{heat content}} \qquad \text{(Eq 2)}$$

From reactions 1 and 2, that is, 1 − 2, we obtain

$$a\text{Al (298 K)} + b\text{Ni (298 K)} + c\text{Ti (298 K)} = \text{Al}_a\text{Ni}_b\text{Ti}_c \text{ (298 K)}$$

The difference between the two measurements yields the heat of formation at 298 K:

$$\Delta H_f^{298\text{K}} (\text{Al}_a\text{Ni}_b\text{X}_c) = \Delta H_{\text{reaction}} - \Delta H_{\text{heat content}}$$

This article is an invited paper selected from participants of the 14th National Conference and Multilateral Symposium on Phase Diagrams and Materials Design in honor of Prof. Zhanpeng Jin's 70th birthday, held November 3-5, 2008, in Changsha, China. The conference was organized by the Phase Diagrams Committee of the Chinese Physical Society with Drs. Huashan Liu and Libin Liu as the key organizers. Publication in *Journal of Phase Equilibria and Diffusion* was organized by J.-C. Zhao, The Ohio State University; Yong Du, Central South University; and Qing Chen, Thermo-Calc Software AB.

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Details of this high-temperature calorimeter have been published previously.[9] The calorimeter is maintained continuously at 1373 K and uses a protective argon atmosphere, which passes through titanium chips at 1173 K. The sample weight used was about 120 mg. The nickel powder was reduced in hydrogen prior to preparation of the samples to remove oxygen and carbon, which would be a source of errors if they reacted with the aluminum or titanium. 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 $\delta = (\delta_1^2 + \delta_2^2 + \delta_3^2)^{1/2}$.

Table 1 Standard enthalpy of formation of Al-Ni-Ti compounds at 298 K, ΔH_f^0 (kJ/mol)

Compound	$\Delta H_{reaction}$, kJ/mol	$\Delta H_{heat\ content}$, kJ/mol	$\Delta H_{formation}$, kJ/mol	Database[11]	Melting point, K
$Ni_{0.5}Ti_{0.5}$	−3.1 ± 0.7	33.0 ± 2.1	−36.1 ± 2.3	−34.1	…
$Al_{0.05}Ni_{0.75}Ti_{0.20}$	−4.3 ± 1.6	30.6 ± 5.1	−34.9 ± 5.4	−38.7	1623
$Al_{0.05}Ni_{0.5}Ti_{0.45}$	−9.0 ± 0.3	31.7 ± 2.1	−40.7 ± 2.1	−40.0	1628
$Al_{0.11}Ni_{0.74}Ti_{0.15}$	−10.7 ± 2.5	28.9 ± 1.6	−39.6 ± 2.9	−41.3	1628
$Al_{0.16}Ni_{0.74}Ti_{0.1}$	0	32.2 ± 1.7	−32.2 ± 1.7	−42.5	1628
$Al_{0.2}Ni_{0.5}Ti_{0.3}$	−24.1 ± 0.6	30.8 ± 2.9	−54.9 ± 3.0	−57.8	1405
$Al_{0.21}Ni_{0.74}Ti_{0.05}$	4.0 ± 0.8	28.6 ± 2.9	−24.6 ± 3.0	−43.0	…
$Al_{0.25}Ni_{0.5}Ti_{0.25}$	−26.1 ± 1.5	29.7 ± 1.6	−55.8 ± 2.2	−63.8	1513
$Al_{0.3}Ni_{0.5}Ti_{0.2}$	−24.0 ± 0.8	30.0 ± 1.0	−54.0 ± 3.9	−66.2	1517 (a)
$Al_{0.3}Ni_{0.5}Ti_{0.2}$	−28.5 ± 2.9	30.2 ± 2.6	−58.7 ± 3.9	−66.2	1517 (a)
$Al_{0.4}Ni_{0.6}$	…	…	−51.9 ± 1.7[12]	−56.7	…
$Al_{0.4}Ni_{0.5}Ti_{0.1}$	−28.4 ± 1.9	31.7 ± 1.5	−60.1 ± 2.4	−66.2	1709 (a)
$Al_{0.4}Ni_{0.55}Ti_{0.05}$	−24.9 ± 1.5	31.9 ± 1.7	−56.8 ± 2.3	−61.5	…
$Al_{0.45}Ni_{0.5}Ti_{0.05}$	−30.0 ± 1.6	29.4 ± 2.1	−59.4 ± 2.7	−66.2	>1709
$Al_{0.45}Ni_{0.55}$	…	…	−58.4 ± 0.7[12]	−61.4	…
$Al_{0.54}Ni_{0.46}$	…	…	−59.6 ± 1.3[12]	−64.1	>1709
$Al_{0.5}Ni_{0.5}$	…	…	−62.0 ± 2.0[13]	−66.1	>1709

(a) With small amount of second phase

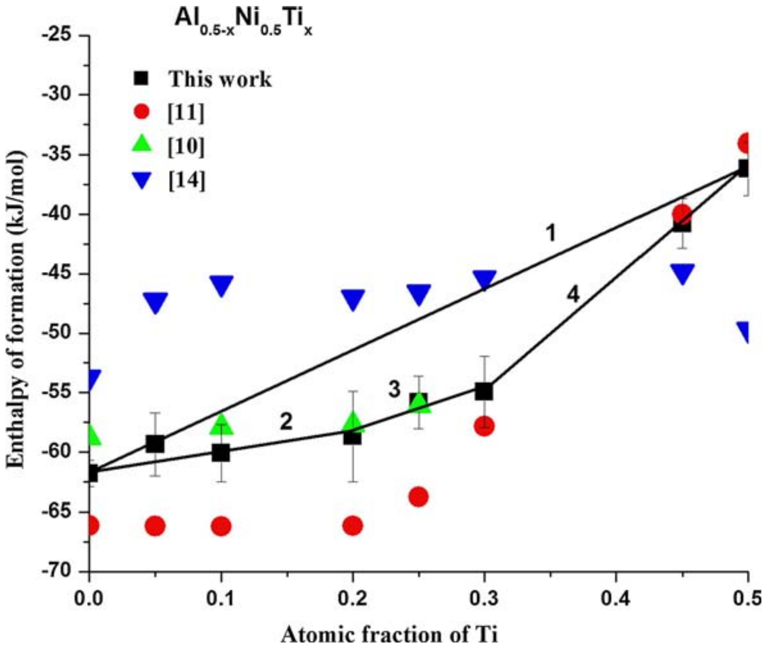

Fig. 1 Enthalpies of formation of $Al_{0.5-x}Ni_{0.5}Ti_x$ alloys

2.2 XRD and EDS/EPMA

X-ray diffraction spectra were obtained using a θ-θ x-ray diffractometer. The lattice parameters were determined by the least squares refinement of the diffraction data. One reacted sample from each alloy composition was examined to determine that complete reaction had occurred, and in all cases no unreacted material was observed. Furthermore, all alloys were single phase or contained only traces of second phase estimated at less than 5% and these are noted in Table 1.

2.3 Differential Thermal Analysis (DTA)

Differential thermal analysis was performed in argon gas using a Setsys 16/18 calorimeter (Setaram, Caluire, France), to determine the transition or melting points of the compounds. The samples used for this test were from the enthalpy of formation measurement experiments.

3. Results and Discussion

3.1 Enthalpies of Formation

Enthalpies of formation of Al-Ni-Ti compounds measured in this work by high-temperature reaction calorimeter are shown in Table 1, together with previous experimental data[10] and calculated values from a thermodynamic database.[11]

Figure 1 shows the enthalpy comparison between the experimental results and calculated values from the extended Miedema model[14] and the thermodynamic database.[11]

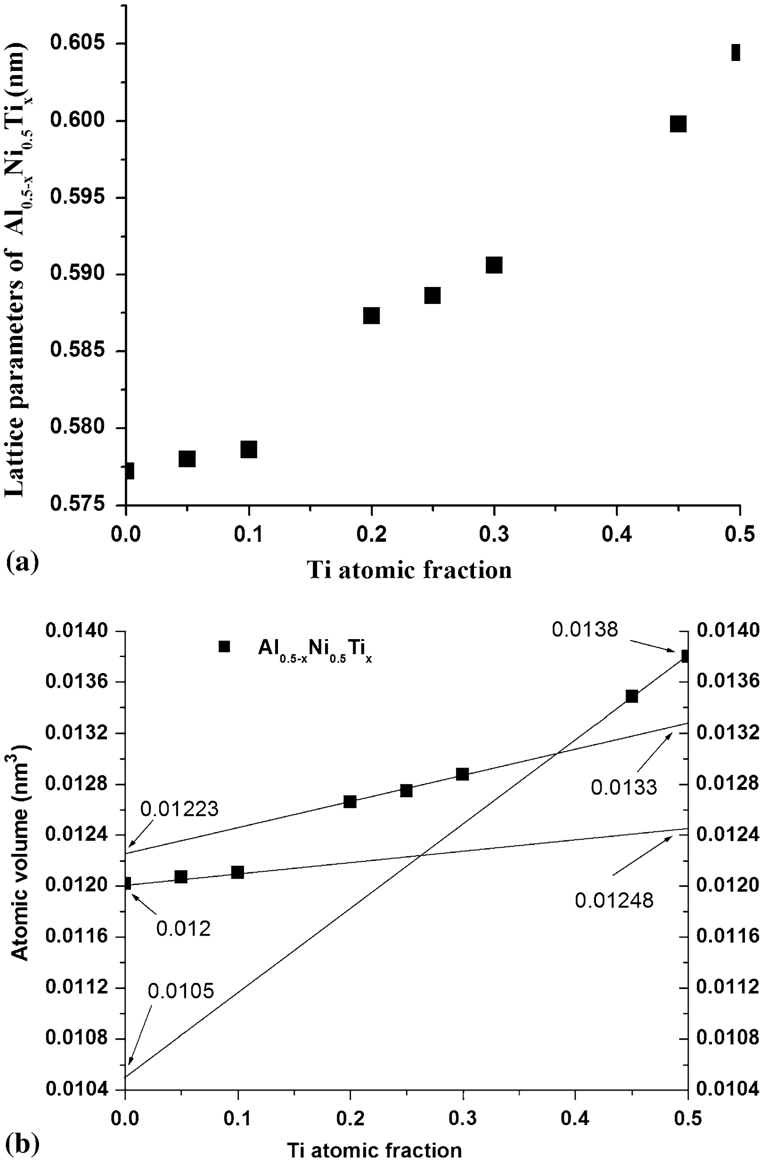

Fig. 2 Lattice parameters of $Al_{0.5-x}Ni_{0.5}Ti_x$ (B2 parameters doubled for comparison to $L2_1$)

Table 2 Lattice parameters and EDS/EPMA result in Al-Ni-Ti system

Compound composition, at.%				Lattice parameters, pm			
Al	**Ni**	**Ti**	**Phases**	***a***	***c***	**Liquidus, K**	**Reference**
50	50	0	NiAl	288.6	···	>1709	This work
···	···	···	NiAl	289.7	···	···	[17]
···	···	···	NiAl	289.3	···	···	[16]
54	46	0	NiAl	286.6	···	>1709	This work
45	50	5	NiAl	289	···	>1709	This work
45	50	5	NiAl	290	···	···	[18]
40	55	5	NiAl	288.2	···	>1709	This work
···	···	···	NiAl	288.2	···	···	[16]
40	50	10	NiAl	289.3	···	>1709	This work
30	50	20	$AlNi_2Ti$	587.3	···	>1709	This work
···	···	···	Ni_3Ti (a)	505	818.3	···	This work
25	50	25	$AlNi_2Ti$	588.6	···	>1709	This work
20	50	30	$AlNi_2Ti$	590.6	···	>1709	This work
5	50	45	NiTi	299.9	···	1613	This work
···	···	···	NiTi	···	···	···	[16]
0	50	50	NiTi	302.2	···	···	This work
21	74	5	$AlNi_3$	352.8	···	···	This work
16	74	10	$AlNi_3$	358.2	···	1595	This work
11	74	15	$AlNi_3$	358.4	···	1593	This work
···	···	···	$AlNi_3$	359.5	···	···	[16]
7	75	18	$AlNi_3$	359.2	···	···	[19]
5	75	20	Ni_3Ti	509.5	···	1589	This work

(a) Small amount

The two sets of experimental results, Ref 10 and this work, are in good agreement with each other. The calculated results from the database[11] show the same trend with composition but are generally more exothermic than the experimental results over the composition range between NiAl and Ni_2AlTi. This is obviously due to the use of a more exothermic value for the enthalpy of formation of NiAl, which previous work has shown to be incorrect.[13] As a matter of fact, if one examines Fig. 1 in the present work and Fig. 9 of Ref 8 at the same time, one can readily conclude that the discrepancies between experiments and calculations on both formation enthalpy and heat content are due to the inadequacy in the heat capacity model used in the assessment. The Miedema model gives substantially less exothermic results as has been observed previously with Al-Ni-X alloy systems.[15] From Fig. 1, it is seen that the composition dependence of enthalpies is different in NiAl, Ni_2AlTi, and NiTi phases, i.e., the slopes of line 2, 3, and 4 are different. The extrapolation of the enthalpy dependence of the B2 phase gives a good prediction of the Heusler enthalpy on their respective composition sides. The enthalpies of formation of $Al_{0.5-x}Ni_{0.5}Ti_x$ ($0 \le x \le 0.5$) change little for $x(\mathrm{Ti}) < 0.3$ where the structure is B2 but decreases (becomes less negative) dramatically for higher titanium compositions when the structure becomes $L2_1$ (Heusler) and NiTi two phase range. With increasing Ti content, the electron valence ratio *e*/*a* increases, which results in a small change in the enthalpies for the B2 phase. As Ti content increases beyond 30 at.%, the bonding type for the compounds changes from the sp-d bonds between Al and Ni (Ti) in the NiAl and Heusler phases to the d-d bonds between Ni and Ti in the NiTi phase which results in a decrease in the enthalpies of formation.

On the other hand, the enthalpies of the Heusler compounds are below the line 1, which corresponds to the enthalpies of the ideal mixing of NiTi and NiAl. This is consistent with the stability of this phase over the B2 structure. The additional ordering enthalpy for the $L2_1$ over the B2 structure of the stoichiometric composition of $Ni_{0.5}Al_{0.25}Ti_{0.25}$ can be estimated from Fig. 1 as about 6.8 kJ/mol.

3.2 Lattice Parameters and Melting Points

Figure 2 shows the lattice parameters of $Al_{0.5-x}Ni_{0.5}Ti_x$ plotted along a constant 50 at.% Ni section. The lattice parameters in Fig. 2 for NiAl and NiTi B2 phase are for two unit cells in order to make a comparison with the Heusler phase, which is a super-ordered B2 structure and has a unit cell that corresponds to eight unit cells of the B2 structure. With increasing Ti content, the lattice parameters increase, as expected since Ti has a larger atomic size than Al. It is noteworthy that the lattice parameter shows a linear variation through B2 and Heusler phase with the compositional dependence through the Heusler phase being intermediate between that for NiAl and NiTi.

Table 2 shows all the lattice parameter data of the Al-Ni-Ti alloys measured in this study, in comparison with selected literature values.[16-18] The lattice parameters increase when Ti substitutes for either Ni or Al, which is due to the larger atomic size of Ti. The results from this work are consistent with other reported values.[16-18]

The melting points of selected alloys determined in this work are summarized in Table 2. The experimental data in this work are consistent with the liquidus in Ref 7. Experiments showed the NiAl (B2) and $AlNi_2Ti$ phase have high melting points, beyond the temperature limit of our DTA over most of the composition region.

4. Conclusions

The enthalpy of formation of several compounds in the Al-Ni-Ti system were determined by direct synthesis drop calorimetry. The enthalpy of formation of $Al_{0.5-x}Ni_{0.5}Ti_x$ alloys decreased (became less negative) with increasing Ti content. The enthalpies of formation in this study are in good agreement with other experimental data and show the same trend as calculated values from a thermodynamic database using Thermo-Calc software. The Miedema model gave generally less exothermic values for the enthalpies of Al-Ni-Ti compounds as has been observed previously for similar alloys. The stability of the $L2_1$ structure over the B2 structure at the stoichiometric composition of $Ni_{0.5}Al_{0.25}Ti_{0.25}$ was estimated to be 6.8 kJ/mol. The lattice parameters of Al-Ni-Ti alloys increased with increasing Ti content. The measured liquidus points are consistent with previous work.

Acknowledgment

This work was supported by the National Science Foundation under grant DMR 0600690.

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