ARCHIVES OF METALLURGY AND MATERIALS
Volume 51 2006 Issue 4

Z. MOSER*, W. GĄSIOR*, K. RZYMAN**, A. DĘBSKI*

CALORIMETRIC STUDIES OF THE ENTHALPIES OF FORMATION OF $NiTi_2$, NiTi AND Ni_3Ti

BADANIA KALORYMETRYCZNE ENTALPII TWORZENIA $NiTi_2$, NiTi I Ni_3Ti

Solution calorimetry operated with the liquid Al bath have been used for the determination of enthalpies of formation of intermetallic compounds of the Ni-Ti system. These are needed for extensive studies on the quaternary system Al-Fe-Ni-Ti within the COST 535 program on advanced aluminides. At first, there were obtained enthalpies of solution of Ni and Ti in liquid Al amounting respectively: -150 ± 0.4 (kJ/g.atom) for Ni and -128.8 ± 0.7 (kJ/g.atom) for Ti. Using these values of enthalpies of solution, the following values of enthalpies of formation were obtained: -25.3 ± 1.7 (kJ/mol of atoms) for $NiTi_2$, -31.1 ± 1.1 (kJ/mol of atoms] for NiTi and -43.8 ± 1.6 (kJ/mol of atoms) for Ni_3 Ti, respectively. The resulting values are in good agreement with literature data, both experimental and from theoretical calculations.

Technika kalorymetryczna (rozpuszczanie w ciekłym aluminium) została zastosowana do wyznaczania entalpii tworzenia związków międzymetalicznych z układu Ni-Ti. Dane te są potrzebne do badań układu czteroskładnikowego Al-Fe-Ni-Ti w ramach programu COST 535. W pierwszym etapie, wyznaczono entalpie rozpuszczania niklu i tytanu w ciekłym Al wynoszące -150 ± 0.4 (kJ/g.atom) dla Ni i -128.8 ± 0.7 (kJ/g.atom) dla Ti. Używając tych danych entalpii rozpuszczania, otrzymano następujące wartości entalpii tworzenia: -25.3 ± 1.7 (kJ/mol of atoms) dla $NiTi_2$, -31.1 ± 1.1 (kJ/mol of atoms) dla NiTi i -43.8 ± 1.6 (kJ/mol of atoms) dla Ni_3 Ti. Otrzymane wartości są w dobrej zgodności z danymi literaturowymi.

1. Introduction

The Institute of Metallurgy and Materials Science (IMIM) of the Polish Academy of Sciences (PAS) have for many years undertaken extensive studies on the thermodynamics of alloys with the cooperation of various foreign partners. IMIM participates in COST 535 Action to perform calorimetric studies on Al-Fe-Ni-Ti system. Intermetallic phases from Al-Ni and Al-Ti were studied by [1], [2], and [3] by calorimetric techniques. In Ref. [2] were presented results of enthalpies of formation obtained by solution and direct reaction method. Data for Al_3Ti from both techniques was nearly the same, however for AlTi and $AlTi_3$ it was different. The reason for this is connected with the sequence of formation of intermetallic compounds. The first phase formed is the Al_3Ti. For the other two phases AlTi and $AlTi_3$, as found from the analysis of the products from direct reaction method, the reaction of a given phase formation is not completed in the calorimeter. It is the result of difference between two methods. Thus, we decided to use in our study of enthalpies of formation of remaining phases from Al-Ni-Ti-Fe the solution method. In the first stage, enthalpies of solution of Ni and Ti in liquid Al were determined. Then the enthalpies of formation of phases from Ni-Ti system were performed.

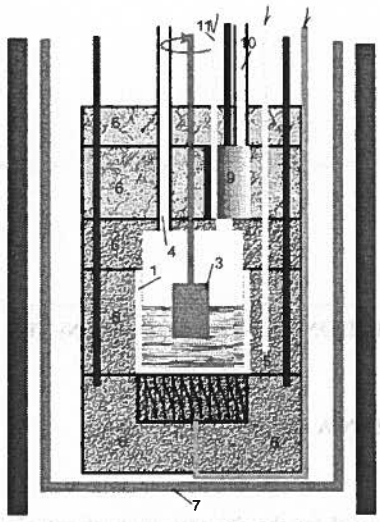
2. Principles of determination of enthalpies of formation of intermetallic phases by solution calorimetry

The enthalpy of formation $\Delta_f H$ of the considered phase, determined by this method, is obtained from the difference of heat effects accompanying the dissolution in the aluminium bath of the studied phase and its components. In the case of two-component phase the following equation is applied:

$$\Delta_f H = X_A \Delta H_A^{ef.0} + X_B \Delta H_B^{ef.0} - \Delta H_{X_A X_B}^{ef.0},$$

where: $\Delta_f H$ – formation enthalpy of the alloy, X_A, X_B – concentrations (mole fractions) of the alloy components, $\Delta H_A^{ef.0}, X_B \Delta H_B^{ef.0}, \Delta H_{X_A X_B}^{ef.0}$ – heat effects accompanying the dissolution of the components and the alloy in the bath.

* INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, 30-059 KRAKÓW, 25 REYMONTA STR., POLAND
** SILESIAN UNIVERSITY OF TECHNOLOGY, FACULTY OF MATERIALS SCIENCES AND METALLURGY, 40-019 KATOWICE, 8 KRASIŃSKIEGO STR., POLAND



1. Alumina crucible.
2. Thermopile NiAl-NiCr.
3. Ceramic stirrer.
4. Device for delivery of the samples from room temperature into crucible with Al bath.
5. Thermocouple for temperature measurements of the calorimeter block.
6. The block of the calorimeter.
7. Heat-resistant tube.
8. Calorimetric furnace.
9. Intermediate container.
10. Device of the intermediate container for the samples.
11. Thermocouple for temperature measurements of the intermediate container.

Fig. 1. Schematic representation of solution calorimeter

The solid state of Ni and Ti was chosen as the reference state. Experiments were undertaken in high-temperature solution calorimeter shown in Fig. 1.

Before each experimental run, the calorimeter was evaluated and flushed with high purity argon (99.999%). Numerous runs were done in a steady argon atmosphere with continuous stirring of the bath. Calibrations was done at the beginning of a run by adding several Al samples into the Al bath. Details of experimental technique were described in details in Ref. 3.

The calculation of enthalpies of formation was facilitated by coupling of the calorimeter with a computer. In this manner the voltage signal from the thermopile was amplified and transformed to digital form, the planimetration was done automatically, and the enthalpies of formation were calculated directly from the recorded enthalpy effects.

Samples of investigated intermetallic compounds Ni_3Ti, NiTi and $NiTi_2$ were obtained from pure metals by melting in glove-box under purified circulated gas free of nitrogen, oxygen and and moisture.

3. Results of calorimetric results

In calculations of the partial enthalpy of solution of Ni in Al (for infinitive dilution of Ni) and for Ti in Al (for infinitive dilution of Ti) and for determination of enthalpy of formation of intermetallic phases of Ni-Ti system, thermochemical data from Thermo-Calc (The SGTE Substances Database of 2001 update: March 1, 2002, Thermo-Calc Software) were used.

The obtained values of enthalpy of solution of Ni and Ti in Al at the temperature 1247 K are presented in Table 1. The mean values of this study are nearly the same as reported in [1] ($\Delta H^0_{Ni} = -148.9 \pm 0.6$ [kJ·g·atom^{-1}] and $\Delta H^0_{Ti} = -128.3 \pm 1.4$ [kJ·g·atom^{-1}]).

TABLE 1
Values of enthalpies of solution of Ti ΔH^0_{Ti} and Ni ΔH^0_{Ni} in liquid Al Temperature of the bath 1273±2 [K].

Element	Measurement No.	ΔH^0_i [kJ·g·atoms^{-1}]
Ni	1	−149.7
	2	−149.6
	3	−150.4
	4	−150.5
	5	−149.8
	Average	−150.0
	Standard Dev.	0.4
Ti	1	−129.3
	2	−128.7
	3	−129.5
	4	−129.8
	5	−128.1
	6	−128.6
	7	−129.3
	8	−127.4
	9	−128.9
	Average	−128.8
	Standard Dev.	0.7

The enthalpies of solution of Ni and Ti in liquid Al presented in Table 1 were used for calculations of the enthalpies of formation of phases of Ni-Ti system. Results are presented in Table 2 and are plotted in Fig. 2 with other References from literature. In Table 3, results of formation enthalpies obtained by various authors both experimental (solution and direct reaction) methods and calculated are presented.

TABLE 2

Values of formation enthalpies of intermetallic phases $NiTi_2$, NiTi and Ni_3Ti at room temperature. Temperature of Al bath: 1273 ± 2 [K].

Intermetallic phase	Temperature [K]	Measurement No.	Heat effect ΔH^{ef} [kJ/mol of atoms]	Enthalpy of formation $\Delta_f H$ [kJ/mol of atoms]
Ni_3Ti	298	1	−52.65	−46.0
		2	−56.45	−42.2
		3	−55.65	−43.0
		4	−54.57	−44.1
		Average	−54.83	−43.8
		Standard Dev.	1.6	1.6
NiTi	298	1	−63.0	−31.7
		2	−64.8	−29.9
		3	−62.7	−31.9
		Average	−63.5	−31.1
		Standard Dev.	1.1	1.1
$NiTi_2$	300	1	−65.1	−26.8
		2	−67.6	−24.4
		3	−65.4	−26.6
		4	−68.6	−23.4
		Average	−66.7	−25.3
		Standard Dev.	1.9	1.7

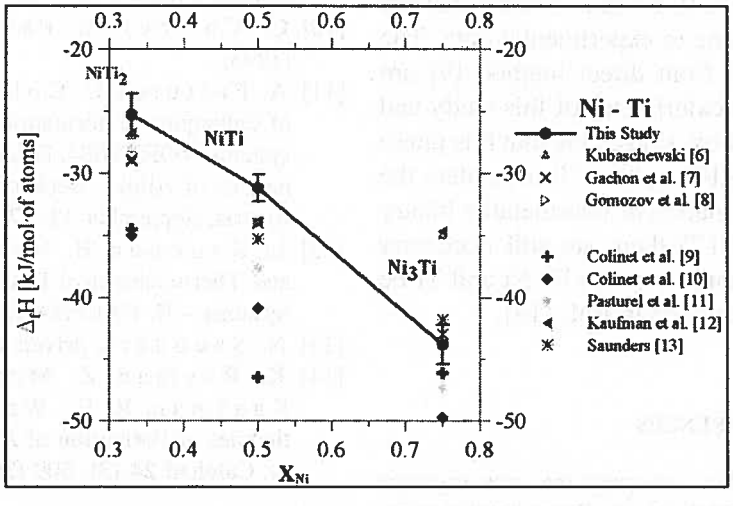


Fig. 2. Enthalpy of formation of the intermetallic phases of Ni-Ti system at 298 [K]

TABLE 3

Comparison of enthalpies of formation of this study with various references from literature Enthalpies of formation of compounds are referred to Ni (A1) and Ti (A3)

$\Delta_f H$ [kJ/mol of atoms]									
Phase	TB Recursion	LMTO	FPLMTO LDA	Experimental				Phase diagram optimization	
				Direct reaction method		Solution method			
	[9]	[10]	[11]	[6]	[7]	[8]	This Study	[12]	[13]
$NiTi_2$	−34.5	−35.0	−28.1	−27	−29		−25.3	−26.8	−28.9
NiTi	−46.5	−40.9	−37.7	−34	−34	−34	−31.1	−33.9	−35.3
Ni_3Ti	−46.1	−49.7	−47.3	−35	−43		−43.8	−34.7	−41.8

Note: TB Recursion (The tight- binding recursion method), LMTO (Linear Muffin Tin Orbital), FPLMTO (Full potential linear muffin tin orbital) and LDA (The local density approximation) were described in Ref. 9–11.

4. Conclusions

By means of solution calorimetry, enthalpies of solution of Ni and Ti in liquid Al as well as enthalpies of formation of $NiTi_2$, NiTi and Ni_3Ti were determined. The values of the enthalpies of formation of phases from Ni-Ti system decrease with the increase of Ni concentration from -25.3 ± 1.7 (kJ/mol of atoms) for $NiTi_2$, to -31.1 ± 1.1 (kJ/mol of atoms) for NiTi and finally to -43.8 ± 1.6 (kJ/mol of atoms) for Ni_3Ti. It should be noted that the higher the melting temperature, the lower the enthalpy of formation was observed. The comparison of the results of this study presented in Fig. 2 with various references shows the highest deviations for NiTi compound. It may result from the fact that this compound has a range of homogeneity in contrary to both other two stoichiometric intermetallic phases $NiTi_2$ and Ni_3Ti. In addition, numerous values referred in Table 3 based on theoretical calculations Refs. 9, 10 and 11 show that the newest results are more close to experimental data. The results for Ni_3Ti obtained from direct method [9] are close to this from solution calorimetry of this study and to phase diagram optimization, suggesting that this phase forms first, like Al_3Ti in Al-Ti system. To complete the studies of enthalpies of formation of intermetallic binary phases existing in Al-Fe-Ni-Ti there are still necessary investigations of the remaining systems Fe-Ni and Ti-Fe as these for AlFe were presented in Ref. [14].

REFERENCES

[1] K. Rzyman, Efekty energetyczne towarzyszące tworzeniu faz międzymetalicznych, Praca habilitacyjna, Kraków 2002.

[2] K. Rzyman, Z. Moser, J. C. Gachon, Calorimetric Studies of the Enthalpies of Formation of Al_3Ti, AlTi, $AlTi_3$ and Al_2Ti, Archs. Metall. and Mater. **49**, 543-563 (2004).

[3] K. Rzyman, Z. Moser, Calorimetric Studies of the Enthalpies of Formation of Al_3Ni_2, AlNi and $AlNi_3$, Prog. Mat. Sc. **49**, 581-606 (2004).

[4] C. Colinet, A. Pasturel, Ab Initio Calculation of Thermodynamic Data and Phase Diagram of Binary Transition Metal Based Alloys, J. Phase Equilib. **15 (3)**, 330-338 (1994).

[5] O. Kubaschewski, W. A. Dench, The Heats of Formation in the Systems Titanium-Aluminium and Titanium-Iron, Acta Metall. **3**, 339-346 (1955).

[6] O. Kubaschewski, The Heats of Formation in the System Aluminium+Nickel+Titanium, Trans. Faraday Soc. **54**, 814-820 (1958).

[7] J. C. Gachon, M. Notin, J. Hertz, The Enthalpy of Mixing of the Intermediate Phase in the Systems FeTi, CoTi and NiTi by Direct Reactions Calorimetry, Thermochim. Acta **48**, 155-164 (1981).

[8] P. A. Gomozov, Yu. V. Zasypalov, B. M. Mogutnov, Russ. J. Phys. Chem. **60**, 1865-1867 (1986).

[9] C. Colinet, P. Hicter, A. Pasturel, J. Phys. Condens. Matter. **3**, (1991).

[10] C. Colinet, A. Pasturel, Phisica B **192**, 238 (1993).

[11] A. Pasturel, C. Colinet, Ab initio determination of enthalpies of formation in Al, Fe, Ni, and Ti based systems, TOFA 2004, Discussion Meeting on Thermodynamics of Alloys, Book of Abstracts, Program, Vienna, Austria, September 12–17, 2004.

[12] L. Kaufman, H. Nesor, Coupled Phase Diagram and Thermochemical Data for Transition Metal Binary Systems – II, CALPHAD, **2 (1)**, 81-108 (1978).

[13] N. Saunders, private communication (1991).

[14] K. Rzyman, Z. Moser, P. Miodownik, L. Kaufman, R. E. Watson, M. Weinert, Enthalpies of Formation of AlFe: Experiment versus Theory. Calphad **24 (3)**, 309 (2000).

Received: 20 September 2006.