



Enthalpies of formation of the compounds of ternary phases equilibria in the Al-Ni-Ti system at 1073 K

F.Z. Chrifi-Alaoui*, M. Nassik, S. Kardellass, H. Azza, N. Selhaoui

Laboratoire de thermodynamique et énergétique, Université Ibn Zohr, Faculté des Sciences, B.P. 28/S, 80000 Agadir, Morocco.

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frchrifialaoui@gmail.com ;
Phone: +212661735393

Abstract

Ternary phases in the Al-Ni-Ti system have been investigated by direct reaction calorimetry at high temperature at $T = 1073$ K. Enthalpies of formation of ternary intermetallic compounds of various phases have been measured.

The results have been compared with the available experimental values based on calorimetric measurements and with the calculated values from theoretical models.

X-Ray powder Diffraction (XRD) and Electron Probe MicroAnalysis (EPMA) were used to check the crystal structure and the homogeneity of the calorimetric products. The concentration variation effect on the enthalpies of formation values has been studied, for any given element at temperature of 1073 K.

1. Introduction

The Al-Ni-Ti ternary system deserves more investigation because of its interesting high temperature properties. This ternary system is still badly known in spite of its obvious industrial interest and some sixty years which passed by since the first publications relative to the diagram of phase. Raman and Schubert[1] studied the Al-Ni-Ti ternary diagram, by diffraction of X-rays, in the temperature at 1073 K. Markiv et al. [2] determined the complete section of the system at 1073 K, by optical microscopy and by diffraction of X-rays.

Kaufman and Nesor [3] modelled the diagram with various temperatures 1023K and 1273K and compared their results with the experimental diagrams found by Taylor and Floyd [4] and by Raman and Schubert [1]. Nash et al.[5] made an estimation of the Al-Ni-Ti ternary diagram at the temperature 1073 K resting on the data of the studies of Taylor and Floyd [4], Raman and Schubert [1], and Markiv et al. [2].

The assessed phase diagram of the Al-Ni-Ti system was determined by Lee and Nash[6] at 1073 K and results from the work of Nash et al.[5] and Okamoto[7]. Moreover, Huneau et al.[8] have estimated an isothermal section of the Al-Ni-Ti ternary system at 1073 K.

Recently, Schuster et al.[9] have determined an isothermal section at 1273 K. In 2009, Bursik and Broz[10], have analysed by electron probe microanalysis (EPMA), the compositions of compounds of the system Al-Ni-Ti and have modelised this system.

The Open Quantum Materials Database (OQMD) is used to compare the DFT predictions with experimental measurements of the enthalpies of formation of compounds[11,12].

The targeted aim of this work is to give a new set of enthalpies of formation of the ternary intermetallic compounds of various ternary phases in the Al-Ni-Ti system determined by direct reaction calorimetry at high temperature $T = 1073$ K: $\text{Ni}_{0.50}(\text{Al}_{0.25+x}\text{Ti}_{0.25-x})$ $0 \leq x \leq 0.14$, $\text{Al}_{0.36}\text{Ni}_{0.28}\text{Ti}_{0.36}$, $\text{Al}_{0.43}\text{Ni}_{0.26}\text{Ti}_{0.31}$ and $\text{Al}_{0.61}\text{Ni}_{0.10}\text{Ti}_{0.29}$.

Our results are compared with available experimental data and with predicted ones based on semi-empirical and theoretical models. The calorimetric products were examined by X-Ray powder Diffraction (XRD) and Electron Probe MicroAnalysis (EPMA) to check their structures and compositions and to ascertain the absence of unreacted phases.

2. Experimental procedure

2.1. Pure metals

Table 1, gives the characteristics of the pure metals which have been used in this work.

Table1: Characteristics of the pure metals, which have been used throughout this work.

Metal	Purity (mass%)	Size (μm)	Packaging atmosphere	Supplier
Aluminium	> 99.0	2-5	Air	Prolabo
Nickel	> 99.8	4-7	Argon	Goodfellow
Titanium	> 99.7	< 44	Argon	Alpha Ventron
Alumina ^(*)	> 99.7	--	--	--
Argon	> 99.99	--	--	Air products

(*) mass alumina: 30 g.

2.2. Calorimetry

The calorimetric method, which was used, has already been described in [13]. The calorimeter has been devised for measuring heat effects at temperatures ranging from 800 to 1800 K. It is heated in a vertical furnace (SETARAM 2400) specially built for the calorimetric applications. The support is made from a massive piece of alumina sawed off a tube (outside diameter 20 mm, inside 15 mm).

The calorimetric cell is located in the cylindrical part (height 9 cm) which warrants the symmetry of the thermal exchanges. The above part is a half cylinder with two alumina two bore tubes cemented on its edges to drive the output wires up to the top of the support. The dissymmetry of this part does not alter the measurements as shown by comparative experiments made with symmetrical devices.

The calorimetric cell is made from 17 (PtRh6%, PtRhSO%) thermocouples connected in series and supported by alumina two-bore tubes at two different levels around the working crucible. This disposition coupled with the length of the junctions (about 1 cm) ensures that if the part of the heat transfer between the sample and the calorimeter passing through the thermocouples i) maximal, ii) the effect of the filling of the crucible is minimized. All the junctions of one type are around the working crucible while the junctions of the other type (all at the same level) surround the inert crucible.

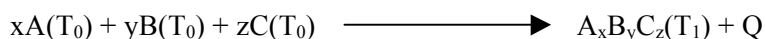
The integral of the calorimetric signal is proportional to the heat transfer between the sample and the calorimeter. A calibration provides the converting factor;

The samples are introduced in the vacuum tight entrance lock of the calorimeter and, after being put under argon, are driven down in the crucible by an alumina tube taking place in the half cylinder of the support.

The crucible temperature is given by the e.m.f. of one junction of the cell in touch with the working crucible. The calorimetric signal is electronically amplified, integrated and graphically recorded.

- Number of measurement samples : 5;
- Number of calibration samples "alumina α " : 6 ;99.7 % of purity ;
- measurement sample mass : ~ 50 mg ;
- calibration sample mass "alumina α ": ~ 30 mg ;

Fine powders of Al, Ni, and Ti are mixed in suitable proportions manually, by pounding in a mortar of porcelain for ten minutes to ensure a mix as intimate as possible and compressed at 298 K under purified argon in a glove box. The samples still at this temperature were then dropped under argon into the crucible of the calorimeter, which was kept at a temperature of 1073 K in order to induce the interdiffusion of the components. The temperature was measured with error limit estimated at temperature of 2 K.



T_0 : room temperature, T_1 : calorimeter's temperature,

$\text{Q} = \Delta_f\text{H}(\text{A}_x\text{B}_y\text{C}_z, \text{T}_1) + x\text{H}(\text{T}_0, \text{T}_1) (\text{A}) + y\text{H}(\text{T}_0, \text{T}_1) (\text{B}) + z\text{H}(\text{T}_0, \text{T}_1) (\text{C})$,

$\text{H}(\text{T}_0, \text{T}_1) (i)$: heating of pure metal i between room T_0 and calorimeter T_1 temperatures,

$\Delta_f\text{H}(\text{A}_x\text{B}_y\text{C}_z, \text{T}_1)$: enthalpy of formation of the compound at T_1 .

The global thermal effect includes a term due to the heating of pure metals between room (T_0) and calorimeter (T_1) temperatures. The enthalpies of formation of the alloys are referred to the pure compounds in their equilibrium state at temperature T_1 .

The enthalpy increments of the elements were taken from Barin et al. [14]. The calorimetric calibration was achieved by dropping cold alumina samples (50-100 mg) into the working crucible, the corresponding enthalpy increments being taken from the work of NIST group [15]. Most often, during one experiment, six pieces of alumina and five metallic samples of one composition are used.

After each experiment, X-Ray powder Diffraction (XRD) and Electron Probe MicroAnalysis (EPMA) were used to check structure and composition of the products. X-Ray powder Diffraction was performed with molybdenum $K\alpha_1$ radiation ($\lambda = 0.070926$ nm) on samples crushed into powder. In order to compute X-ray patterns of the phases we have used the "Lazy pulverix" program [16]. No experimental X-Ray diffractogram was published to our knowledge at least. The chemical compositions were determined by Wavelength Dispersive Spectroscopy (WDS) on a camera microprobe (available in Service Commun de MicroAnalyse, Henri Poincaré University, Nancy 1, France).

3. Experimental

The seed oil had Figure 1 shows the experimental isothermal section of the Al-Ni-Ti ternary phase diagram at $T = 1073$ K, this section is published by Lee and Nash [6] and results from the work of Nash et al. [5] and Okamoto [7], with four ternary compounds with composition ranges more or less extended. We have prepared and studied based on our calorimeter by using direct reaction at $T = 1073$ K between powders of pure metals all the ternary phases: "H", " λ ": $Al_{0.36}Ni_{0.28}Ti_{0.36}$, " μ ": $Al_{0.43}Ni_{0.26}Ti_{0.31}$, and " π ": $Al_{0.61}Ni_{0.10}Ti_{0.29}$ phases.

The experimental enthalpies of formation, of these ternary phases are summarized in Table 2. The pressure, started temperature T_0 , calorimeter's temperature T_1 , $H(T_0, T_1)$ heating of pure metals Al, Ni and Ti between T_0 and T_1 temperatures obtained in two separate series are given in Table 2. The current denomination of the phases was respected in the presentation of our results.

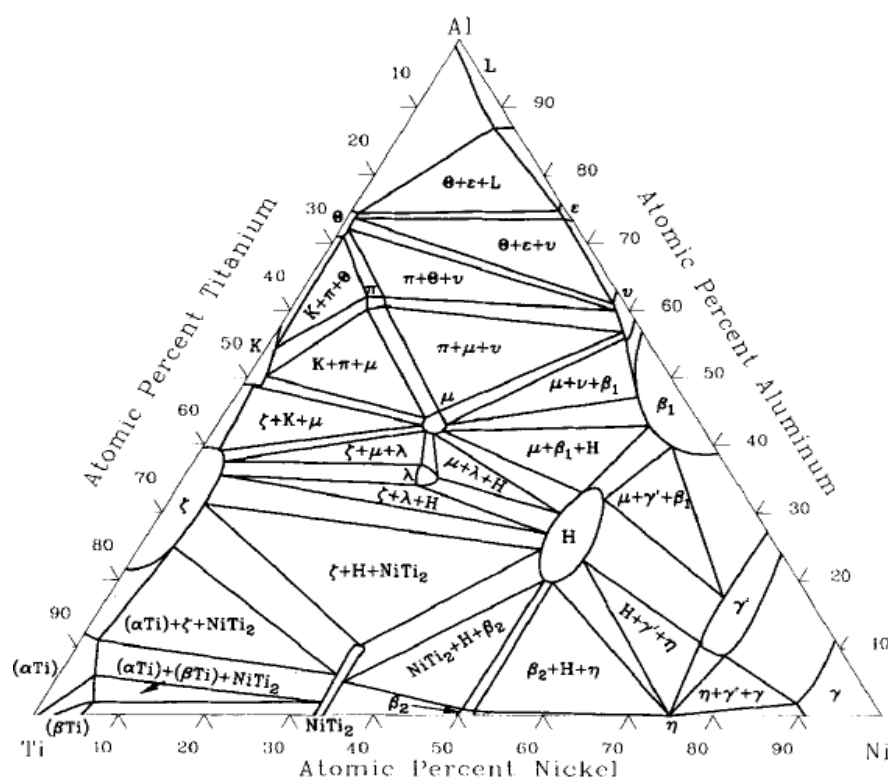


Figure 1: Experimental isothermal section of the Al-Ni-Ti phase diagram at $T = 1073$ K established by Lee and Nash [6].

4. Results and Discussion

4.1. Phase "H": $Ni_{0.50}(Al_{0.25+x}Ti_{0.25-x})$, $0 \leq x \leq 0.14$

According to the published section of the Al-Ni-Ti system by Lee and Nash [6], the domain of existence of the "H" ternary phase has a shape oriented parallel near to 50 at.% Ni from 15 to 31 at.% Ti at $T = 1073$ K. This phase has a large extension which varies between 23 to 26 at.% Ti at $T = 1073$ K, according to Raman and Schubert [1] and Markiv et al. [2] and from 24 to 28 at.% Ti at $T = 1373$ K according to Sridharan et al. [17] and estimated from 24 to 28 at.% Ti at $T = 1073$ K by Huneau et al. [8] to a concentration in Ni near 50 at.%.

For the purpose to study the variation of the enthalpy of formation with the substitution of Al atoms by those of Ti at Ni constant concentration (50 at.% Ni), we have investigated the following alloys:

"H": $Al_{0.33}Ni_{0.50}Ti_{0.17}$, $Al_{0.31}Ni_{0.50}Ti_{0.19}$, $Al_{0.27}Ni_{0.50}Ti_{0.23}$, $Al_{0.25}Ni_{0.50}Ti_{0.25}$, $Al_{0.22}Ni_{0.50}Ti_{0.28}$, and $Al_{0.19}Ni_{0.50}Ti_{0.31}$.

In Table 2, we give the measured enthalpies of formation after five measurements at $T = 1073$ K of the ternary alloys. The variation of the enthalpies of formation versus concentration of aluminium of different compositions of the "H" phase was represented in Figure 2.

Table2:Our Experimental results of enthalpies of formation of ternary intermetallic compounds of the ternary phases in the Al-Ni-Ti system compared with literature data.

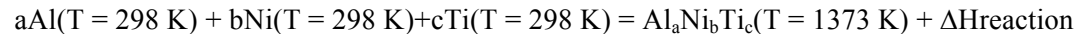
Phase [6]	Compound (Mole fraction)	Molar enthalpy of formation (kJ. mol ⁻¹ . at ⁻¹)				Structure		EPMA results (WDS)	
		Our calorimetric results at T = 1073 K	Literature			Our results	Literature	Maj. phase	Min. phase
			Exper. (Working temperature, K)	Ref.	Calc. (Working temperature, K)				
Series 1: atmosphere: argon (air products 99.9999 wt.%) at pressure p = 0.1 MPa, starting amount: x _{Al} = 19 at. % at x _{Ni} = 50 at. %, T ₀ = 298 K, T ₁ = 1073 K, H _{Al} (T ₀ ,T ₁) =33.28' H _{Ni} (T ₀ ,T ₁) =24.543, H _{Ti} (T ₀ ,T ₁) =22.967 kJ. mol ⁻¹									
0 < x ≤ 0.15 H : Ni _{0.5} (Al _{0.25+x} Ti _{0.25-x})	Al _{0.33} Ni _{0.50} Ti _{0.17}	-61.0 ± 0.7	-56.6 (548 K)	[19] ^(a)	-	-	cubic cubic [1,2,21,22]	<x _{Al} > = 31.6 ± 2.1 at. %	-
	Al _{0.31} Ni _{0.50} Ti _{0.19}	-58.0 ± 2.3	-	-	-	-		<x _{Ni} > = 52.0 ± 1.2 at. %	-
	Al _{0.30} Ni _{0.50} Ti _{0.20}	-	-57.6 (548 K)	[19] ^(b)	-	-		<x _{Al} > = 29.9 ± 1.2 at. %	-
			-58.7±3.9	[18] ^(c)	-	-		<x _{Ni} > = 51.9 ± 1.1 at. %	-
	Al _{0.27} Ni _{0.50} Ti _{0.23}	-60.0 ± 1.5	-55.0 (548 K)	[19] ^(a)	-	-		<x _{Al} > = 26.5 ± 2.4 at. %	-
	Al _{0.25} Ni _{0.50} Ti _{0.25}	-57.0 ± 1.5	-56.1 (548 K)	[19] ^(b)	-64 (300 K)	[3] ^(d)		<x _{Ni} > = 52.5 ± 1.6 at. %	-
			-55.8 ± 2.2 (571K)	[18] ^(c)	-72.1 ± 1.2 (1133 K)	[20] ^(e)		<x _{Al} > = 24.3 ± 2.3 at. %	-
	Al _{0.22} Ni _{0.50} Ti _{0.28}	-59.0 ± 0.8	-52.0 (548 K)	[19] ^(a)	-	-		<x _{Ni} > = 50.5 ± 1.6 at. %	-
	Al _{0.19} Ni _{0.50} Ti _{0.31}	-54.0 ± 1.7	-	-	-	-		<x _{Al} > = 23.2 ± 2.1 at. %	-
-			-	-	-	<x _{Ni} > = 50.2 ± 0.6 at. %	<x _{Al} > = 0.7 ± 0.2 at. %		
Al _{0.20} Ni _{0.50} Ti _{0.30}	-	-51.0 (548 K)	[19] ^(a)	-	-	<x _{Al} > = 21.5 ± 2.6 at. %	<x _{Ni} > = 51.1 ± 0.9 at. %	<x _{Ni} > = 72.9 ± 0.1	
			-54.9 ± 3.0 (571 K)	[18] ^(c)	-	-	-	-	

Serie 2: Atmosphere: argon (air products 99.9999 wt.%) at pressure p = 0.1 MPa, T ₀ = 298 K, T ₁ = 1073 K, H _{Al} (T ₀ ,T ₁) =33.287, H _{Ni} (T ₀ ,T ₁) =24.543, H _{Ti} (T ₀ ,T ₁) =22.967 kJ.										
λ	Al _{0.36} Ni _{0.28} Ti _{0.36}	-56.0 ± 2.6	-50.5 (548 K)	[19] ^(a)	-56.4 (300 K)	[3] ^(d)	Hexagonal	Hexagonal [24]	<x _{Al} > = 37.0 ± 1.3 at. %	<x _{Al} > = 27.1 ± 1.6 at. %
					-56.9 (1133 K)	[20] ^(e)			<x _{Ni} > = 27.1 ± 1.1 at. %	<x _{Ni} > = 44.9 ± 1.8 at. %
Serie 2: Atmosphere: argon (air products 99.9999 wt.%) at pressure p = 0.1 MPa, T ₀ = 298 K, T ₁ = 1073 K, H _{Al} (T ₀ ,T ₁) =33.287, H _{Ni} (T ₀ ,T ₁) =24.543, H _{Ti} (T ₀ ,T ₁) =22.967 kJ.										
μ	Al _{0.43} Ni _{0.26} Ti _{0.31}	-51.6 ± 2.1	-52.0 (548 K)	[19] ^(a)	-52.6 (300 K)	[3] ^(d)	cubic	cubic [21]	<x _{Al} > = 42.4 ± 0.3 at. %	<x _{Al} > = 42.9 ± 0.3 at. %
					-40.7 (1133 K) ^(f)	[20] ^(e)			<x _{Ni} > = 24.2 ± 0.1 at. %	<x _{Ni} > = 32.9 ± 0.5 at. %
Serie 2: Atmosphere: argon (air products 99.9999 wt.%) at pressure p = 0.1 MPa, T ₀ = 298 K, T ₁ = 1073 K, H _{Al} (T ₀ ,T ₁) =33.287, H _{Ni} (T ₀ ,T ₁) =24.543, H _{Ti} (T ₀ ,T ₁) =22.967 kJ.										
π	Al _{0.61} Ni _{0.10} Ti _{0.29}	-49.8 ± 0.9	-43.0 (548 K)	[19] ^(a)	-	-	-	-	<x _{Al} > = 63.3 ± 1.5 at. %	<x _{Al} > = 51.6 ± 1.8
									<x _{Ni} > = 07.4 ± 1.6 at. %	<x _{Ni} > = 18.3 ± 2.7

λ): Calorimetric value determined by Kubachewski [19] at temperature range (1023-1100) K,

μ): Value extrapolated at T = 548 K [19],

π): A high-temperature direct synthesis calorimeter was used by Rongxiang et al. [18] to determine the enthalpy of formation at T = 298 K. The enthalpy is measured in two steps: 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



where a, b, and c are moles of elements Al, Ni and Ti, respectively, and Al_aNi_bTi_c is the correspondingly formed compound.

μ): Utilization of computer based methods for calculation of ternary phases diagram Al-Ni-Ti, by Kaufman and Nesor [3], has been facilitated by developing explicit description of the phase stability of the pure components and the solution and compound parameters of the component binary system.

π): For the determination of the enthalpy of formation of alloys of different compositions by Debski et al. [20], the theoretical calculation of the discussed thermodynamic function was conducted by Lee and Nash [6], by the Calphad method and Bakker [25] using Miedema's model [26].

λ): for the composition Al_{0.50}Ni_{0.25}Ti_{0.25},

μ): Standard uncertainties u are:

$$u(T_1) = 2 \text{ K}, u(T_0) = 2 \text{ K}, u(p) = 16 \text{ kPa}, u(x_{\text{Al}}) = 1.00 \text{ at. \%}, u(x_{\text{Ti}}) = 1.00 \text{ at. \%}, \text{series 1: } u(\Delta H_f) = 1.4 \text{ kJ. mol}^{-1} \cdot \text{at}^{-1}, \text{serie 2: } u(\Delta H_f) = 2.6 \text{ kJ. mol}^{-1} \cdot \text{at}^{-1}, u(m) = 0.001 \text{ g}.$$

Our results are in good agreement with the ones measured at $T = 571$ K by Rongxiang et al. [18] for the compositions: $Al_{0.30}Ni_{0.50}Ti_{0.20}$, $Al_{0.25}Ni_{0.50}Ti_{0.25}$, and $Al_{0.20}Ni_{0.50}Ti_{0.30}$. The obtained results are in good agreement with the values determined by Kubaschewski [19] using calorimetric method for the compositions $Al_{0.30}Ni_{0.50}Ti_{0.20}$ and $Al_{0.25}Ni_{0.50}Ti_{0.25}$.

To obtain other values relating to the compositions not studied. Kubaschewski[19] used interpolation at temperature of 548 K, this explains the difference between our values for the other compositions of the "H" phase.

On the other hand, both calculated values found by Debski et al. [20] by using semi-empirical model (-72.1 ± 1.2 kJ. mol⁻¹. at⁻¹. at $T = 1133$ K) and by Kaufman and Nesor [3] during phase equilibria optimisation (-64 kJ. mol⁻¹. at⁻¹. at $T = 300$ K) are more exothermic than our experimental one.

The examination of the products by X-Ray diffraction confirmed the cubic structure type $AlCu_2Mn$ [1,2,21,22]. Tables 3, 4 and 5 show a comparison of intensities and d-spacings between measured and calculated peaks (Lazy Pulverix [16]).

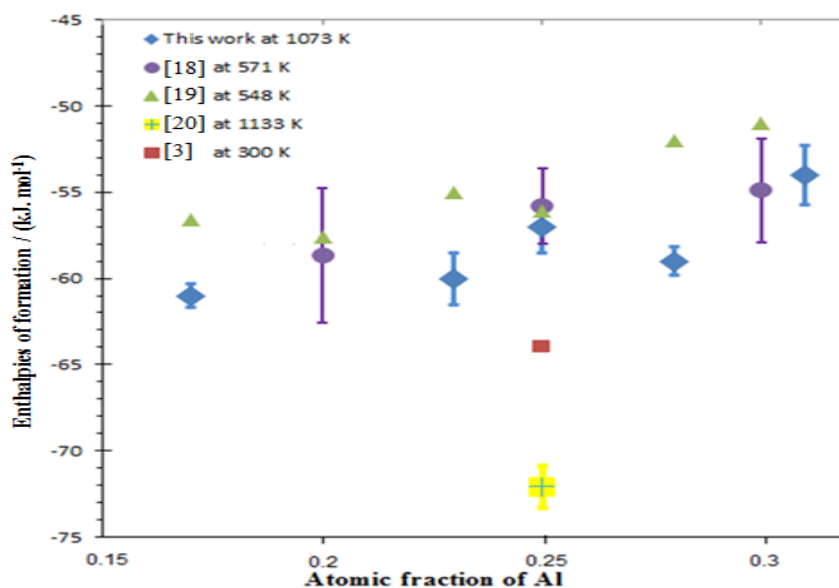


Figure 2: Variation of the enthalpy of formation as a function of the aluminum content of the compositions of the "H" large phase: $Ni_{0.50}(Al_{0.25+x}Ti_{0.25-x})$; $0 \leq x \leq 0.14$ (series 1) and compared with literature data [3,18,19,20].

Table 3: Structural controls of the compositions $Al_{0.33}Ni_{0.50}Ti_{0.17}$ and $Al_{0.31}Ni_{0.50}Ti_{0.19}$ of the "H" phase MoK α ; $\lambda = 0.070926$ nm.

Experiment:Composition $Al_{0.33}Ni_{0.50}Ti_{0.17}$ formed at $T = 1073$ K			Experiment:Composition $Al_{0.31}Ni_{0.50}Ti_{0.19}$ formed at $T = 1073$ K			Results found by "Lazy Pulverix" [4] $a = 0.585$ nm (Hughes [23])		
θ_{hkl} (deg)	d_{hkl} (nm)	I/I ₀	θ_{hkl} (deg)	d_{hkl} (nm)	I/I ₀	d_{hkl}	I/I ₀	hkl
6.95	0.2932	10	6.95	0.2932	10	0.2925	9	200
9.87	0.2069	100	9.90	0.2063	100	0.2068	100	220
11.45	0.1787	2	11.45	0.1787	3	0.1763	1	311
12.08	0.1695	2	12.15	0.1685	2	0.1688	2	222
14.04	0.1462	10	14.08	0.1458	10	0.1462	16	400
15.32	0.1342	<1	15.32	0.1342	<1	0.1342	<1	331
15.73	0.1308	<1	15.78	0.1304	2	0.1308	3	420
17.30	0.1193	18	17.32	0.1191	20	0.1194	32	422
18.36	0.1125	<1	18.36	0.1125	<1	0.1125	<1	511
18.36	0.1125	<1	18.36	0.1125	<1	0.1125	<1	333
20.04	0.1035	7	20.06	0.1034	4	0.1034	9	440

In order to verified our results, we recalculated by using Lazy Pulverix program [16], the diagram using the parameter indicated by Hughes [23]. Our experimental diffractogram is well reproduced. EPMA analysis showed that both homogeneity and stoichiometry were correct for the two compositions of this phase. The

diffractogram (shown in Table 4) shows all the lines corresponding to the cubic phase of type $AlCu_2Mn$, in addition to the amounts of the Ni_3Ti phase very discreet.

The MicroProbe confirms that the products formed are single-phase with nearby concentrations of target compositions. EPMA analysis showed the presence with majority of the "H" phase, and the traces of the Ni_3Ti phase as in controls by X-Ray.

Small variation of the enthalpy of formation that we have measured throughout the phase depending on the substitution of the Al by those of Ti atoms is not significant, it is in the order of the experimental error, but for the composition, $Al_{0.19}Ni_{0.50}Ti_{0.31}$ which is similar to the composition limits of the phase: We see a slight decrease (with absolute value) of the enthalpy of formation (see Figure 2).

Table 4: Structural control of the compositions $Al_{0.27}Ni_{0.50}Ti_{0.23}$ et $Al_{0.25}Ni_{0.50}Ti_{0.25}$ (MoK_{α1} ; λ = 0.070926 nm).

Experiment : Composition $Al_{0.27}Ni_{0.50}Ti_{0.23}$ formed at T = 1073 K			Experiment : Composition $Al_{0.25}Ni_{0.50}Ti_{0.25}$ formed at T = 1073 K			Results found by "Lazy Pulverix" [4] a = 0.585 nm Hughes [23]		
θ_{hkl} (deg)	d_{hkl} (nm)	I/I ₀	θ_{hkl} (deg)	d_{hkl} (nm)	I/I ₀	hkl	d_{hkl}	I/I ₀
6.02	0.3383	1	5.98	0.3405	2	111	0.3373	2
6.95	0.2932	10	6.92	0.2944	10	200	0.2925	9
9.55	0.2138	1	9.50	0.2148	1	(201)*		
9.82	0.2080	100	9.80	0.2084	100	220	0.2068	100
10.45	0.1956	3	10.45	0.1956	3	(202)*		
11.40	0.1795	3	11.50	0.1779	1	311	0.1763	1
12.05	0.1699	3	12.02	0.1703	3	222	0.1688	2
13.45	0.1525	2				(204)*		
13.95	0.1471	20	14.00	0.1466	15	400	0.1462	16
15.32	0.1342	<1	15.32	0.1342	<1	331	0.1342	<1
15.68	0.1312	3	15.66	0.1314	4	420	0.1308	3
16.13	0.1277	1	16.13	0.1277	1	(220)*		
17.20	0.1199	40	17.20	0.1199	35	422	0.1194	32
18.36	0.1125	<1	18.36	0.1125	<1	511	0.1125	<1
18.36	0.1125	<1	18.36	0.1125	<1	333	0.1125	<1
20.05	0.1034	10	19.97	0.1038	10	440	0.1034	9

* Reflections belonging to Ni_3Ti .

4.2. Phase "λ": $Al_{0.36}Ni_{0.28}Ti_{0.36}$

The enthalpy of formation of $Al_{0.36}Ni_{0.28}Ti_{0.36}$ after five measurements at temperature of 1073 K was:

$$\Delta H_f(Al_{0.36}Ni_{0.28}Ti_{0.36} \text{ at } T = 1073 \text{ K}) = -56\,000 \pm 2\,600 \text{ J. mol}^{-1}.$$

As can be seen, our result at T = 1073 K, is more exothermic than that reported by Kubaschewski[19] at temperature of 548 K (-50.5 kJ. mol⁻¹. at⁻¹), the authors interpolated the enthalpies of formation at temperature of 548 K while our values have been measured at high temperature. On the other hand, our experimental result for this phase, is in good agreement with the value deduced by Debski et al.[20] (-56.9 kJ mol⁻¹. at⁻¹.) and with calculated values from phase diagram optimization by Kaufman and Nesor[3] (-56.4 kJ. mol⁻¹. at⁻¹).

A diffraction pattern realized on our reaction products, (see Table 6), shows the presence of the phase (λ) with hexagonal $MgCu_2$ type structure, proposed by [24], with parameters a = 0.5003 nm, and c = 0.8041 nm, other minority lines correspond to the "H" phase.

EPMA analysis showed that both homogeneity and stoichiometry were correct.

$\langle x_{Al} \rangle = 37.0 \pm 1.3 \text{ at.}\%$, $\langle x_{Ni} \rangle = 27.1 \pm 1.1 \text{ at.}\%$, and $\langle x_{Ti} \rangle = 35.9 \pm 1.4 \text{ at.}\%$

However, small amounts of "H" phase were detected.

$\langle x_{Al} \rangle = 27.1 \pm 1.6 \text{ at.}\%$, $\langle x_{Ni} \rangle = 44.9 \pm 1.8 \text{ at.}\%$, and $\langle x_{Ti} \rangle = 28.0 \pm 1.5 \text{ at.}\%$

- the matrix "π" with average concentrations:

$\langle x_{Al} \rangle = 63.3 \pm 1.5 \text{ at.}\%$, $\langle x_{Ni} \rangle = 07.4 \pm 1.6 \text{ at.}\%$ and $\langle x_{Ti} \rangle = 29.3 \pm 1.0 \text{ at.}\%$,

- the clear phase "μ" of average concentrations:

$\langle x_{Al} \rangle = 51.6 \pm 1.8 \text{ at.}\%$, $\langle x_{Ni} \rangle = 18.3 \pm 2.7 \text{ at.}\%$ and $\langle x_{Ti} \rangle = 30.1 \pm 4.3 \text{ at.}\%$,

- the dark phase, Al_2Ti , with average concentrations:

$\langle x_{Al} \rangle = 65.3 \pm 0.2 \text{ at.}\%$, $\langle x_{Ni} \rangle = 01.4 \pm 0.5 \text{ at.}\%$ and $\langle x_{Ti} \rangle = 33.3 \pm 0.3 \text{ at.}\%$.

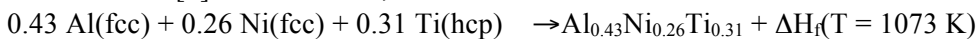
Table 5: Structural controls of the compositions $Al_{0.22}Ni_{0.50}Ti_{0.28}$ and $Al_{0.19}Ni_{0.50}Ti_{0.31}$ (MoK $_{\alpha 1}$; $\lambda = 0.070926$ nm)

Experiment : composition $Al_{0.22}Ni_{0.50}Ti_{0.28}$ formed at T = 1073 K			Experiment : composition $Al_{0.19}Ni_{0.50}Ti_{0.31}$ formed at T = 1073 K			Results found by "Lazy Pulverix"[4] a = 0.585 nm Hughes [23]		
θ_{hkl} (deg)	d_{hkl} (nm)	I/I $_0$	θ_{hkl} (deg)	d_{hkl} (nm)	I/I $_0$	hkl	d_{hkl}	I/I $_0$
5.98	0.3405	2	5.92	0.3440	2	111	0.3373	2
6.90	0.2953	10	6.87	0.2966	10	200	0.2925	9
9.20	0.2219	1				(200)*		
9.51	0.2147	2				(201)*		
9.80	0.2084	100	9.75	0.2095	100	220	0.2068	100
			9.94	0.2055	1	(004)*		
10.45	0.1956	4	10.43	0.1959	8	(202)*		
11.48	0.1782	1	11.50	0.1779	1	311	0.1763	1
			11.88	0.1723	2	(203)*		
12.02	0.1703	4	12.00	0.1706	3	222	0.1688	2
13.54	0.1515	2	13.65	0.1503	3	(204)*		
14.00	0.1466	15	13.90	0.1476	20	400	0.1462	16
15.25	0.1348	1	15.32	0.1342	<1	331	0.1342	<1
15.62	0.1317	5	15.55	0.1323	3	420	0.1308	3
			15.65	0.1315	2	(205)*		
16.12	0.1277	1	16.10	0.1279	3	(220)*		
			16.80	0.1227	1	(310)*		
17.20	0.1199	35	17.20	0.1199	35	422	0.1194	32
			17.50	0.1179	1	(312)*		
18.36	0.1125	<1				511	0.1125	<1
18.36	0.1125	<1				333	0.1125	<1
19.02	0.1088	1				(224)*		
			19.30	0.1073	1	(216)*		
			19.78	0.1048	2	(207)*		
20.00	0.1037	10	19.95	0.1039	12	440	0.1034	9

(*) Reflections belonging to Ni_3Ti .

4.3. Phase " μ ": $Al_{0.43}Ni_{0.26}Ti_{0.31}$

We have aimed the composition which is compatible with the domain plotted on the phase diagram given by Lee and Nash [6] at T = 1073 K, we obtained:



The enthalpy of formation of $Al_{0.43}Ni_{0.26}Ti_{0.31}$ after five measurements at T = 1073 K was:

$$\Delta H_f(Al_{0.43}Ni_{0.26}Ti_{0.31} \text{ at } T = 1073 \text{ K}) = -51\,600 \pm 2\,100 \text{ J. mol}^{-1}$$

As can be seen, our measured value is in good agreement with the one determined by Kubaschewski [19]. On the other hand, the optimised value by Kaufman and Nesor [3] ($-60.6 \text{ kJ. mol}^{-1} \text{. at}^{-1}$) is more exothermic than our experimental one and the value estimated by Debski et al. [20] ($-40.7 \text{ kJ mol}^{-1} \text{. at}^{-1}$. for the composition $Al_{0.50}Ni_{0.25}Ti_{0.25}$) is less exothermic.

Examination of the products by X-Rays confirmed the cubic $Mn_{23}Th_6$ [21] type structure, the resulting diffractogram (see Table 7) is comparable to that calculated by the Lazy Pulverix program [16] using data from Ma and Gjonnes [21]. Traces of the phases nearby " λ " and AlNi " $\beta 1$ " appears also, although the electronic microprobe reveals not:

- phase covered with average concentrations:
 $\langle x_{Al} \rangle = 42.4 \pm 0.3 \text{ at.}\%$, $\langle x_{Ni} \rangle = 24.2 \pm 0.1 \text{ at.}\%$, and $\langle x_{Ti} \rangle = 33.4 \pm 0.3 \text{ at.}\%$
- the minority composition of " λ " phase with average concentrations :
 $\langle x_{Al} \rangle = 42.9 \pm 0.3 \text{ at.}\%$, $\langle x_{Ni} \rangle = 32.9 \pm 0.5 \text{ at.}\%$, and $\langle x_{Ti} \rangle = 24.2 \pm 0.6 \text{ at.}\%$.

We have studied with our calorimeter at T = 1073 K, the composition $Al_{0.61}Ni_{0.10}Ti_{0.29}$, which is supposed to correspond to this phase in the ternary phases diagram proposed by Lee and Nash [6].

4.4. Ternary phase " π ": $Al_{0.61}Ni_{0.10}Ti_{0.29}$

The enthalpy of formation of this composition after five measurements at T = 1073 K was:

$$\Delta H_f(\text{Al}_{0.61}\text{Ni}_{0.10}\text{Ti}_{0.29} \text{ at } T = 1073 \text{ K}) = -49800 \pm 900 \text{ J}\cdot\text{mol}^{-1}\cdot\text{at}^{-1}$$

This result is different to the value extrapolated by Kubaschewski at temperature of 548 K.

EPMA analysis showed the existence of three phases: $\pi+\mu+\text{Al}_2\text{Ti}$ ($\text{Al}_{0.64}\text{Ni}_{0.09}\text{Ti}_{0.27}$, $\text{Al}_{0.54}\text{Ni}_{0.22}\text{Ti}_{0.23}$, and $\text{Al}_{0.65}\text{Ni}_{0.01}\text{Ti}_{0.34}$, see Figure 3, which is in contradictory with the phase diagram determined by Lee and Nash [6] but could find its place in that proposed by Schuster et al. [9]. Their alloys were melted, placed in alumina crucibles, and heat treated at $T = (1273, 1173, 1073 \text{ or } 873) \text{ K}$ for at least two weeks, sealed in evacuated quartz tubes.

After quenching, all alloys were characterized by XRD using $\text{CuK}\alpha_1$ radiation and pure Germanium as internal standard. Phase compositions were checked by Scanning Electron Microscope (EDX).

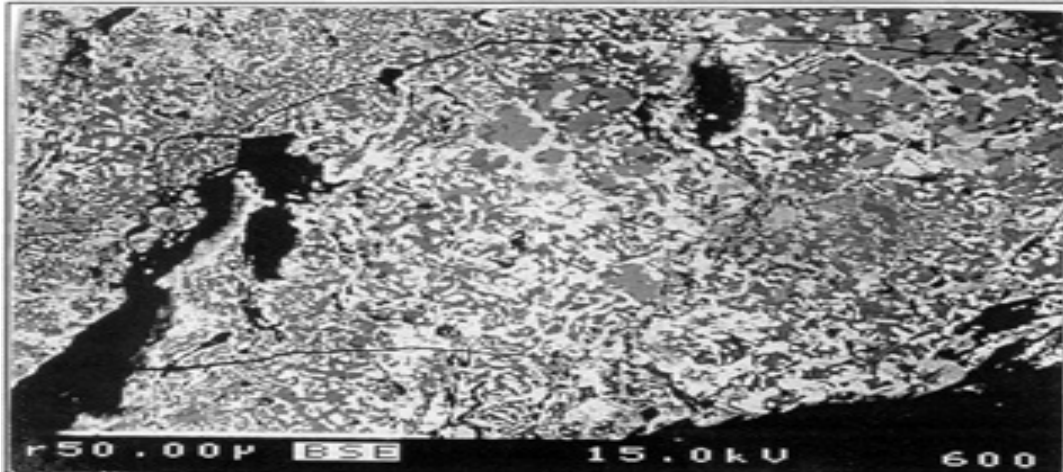


Figure 3: Micrograph of the electronic microprobe of the composition $\text{Al}_{0.61}\text{Ni}_{0.10}\text{Ti}_{0.29}$ formed at $T = 1073 \text{ K}$.

Table 6: Structural control ($\text{MoK}_{\alpha 1}$; $\lambda = 0.070926 \text{ nm}$) of the composition $\text{Al}_{0.36}\text{Ni}_{0.28}\text{Ti}_{0.36}$

Experiment : composition $\text{Al}_{0.36}\text{Ni}_{0.28}\text{Ti}_{0.36}$ formed at $T = 1073 \text{ K}$				Reference file [16] $a = 0.5003 \text{ nm}$ et $c = 0.8041 \text{ nm}$ [24]	
$\theta_{\text{hkl}} \text{ (deg)}$	$d_{\text{hkl}} \text{ (nm)}$	I/I_0	hkl	d_{hkl}	I/I_0
6.92	0.2944	5	(200)*		
8.15	0.2502	15	110	0.2502	35
8.99	0.2270	25	103	0.2284	65
9.34	0.2186	15	200	0.2164	15
9.63	0.2120	50	112	0.2124	100
9.89	0.2071	10	(220)*		
10.15	0.2013	15	004	0.2015	15
10.73	0.1905	5	202	0.1907	12
11.26	0.1817	3	113	0.1827	7
12.79	0.1601	1	211	0.1601	7
13.57	0.1511	<1	105	0.1511	2
13.92	0.1474	7	(400)*		
14.22	0.1444	1	300	0.1445	5
14.73	0.1395	7	213	0.1400	15
15.14	0.1358	7	304	0.1360	12
15.35	0.1340	6	(331)*		
16.00	0.1287	6	205	0.1294	12
16.16	0.1274	<1	214	0.1272	2
16.48	0.1250	5	220	0.1251	10
17.18	0.1201	15	312	0.1201	5
17.18	0.1201	5	(422)*		
17.23	0.1187	1	222	0.1197	1
18.20	0.1135	2	313	0.1142	5
18.90	0.1095	3	(222)*	0.1097	2

* Reflections belonging to the "H" phase.

Table 7: Structural control of the composition $\text{Al}_{0.43}\text{Ni}_{0.26}\text{Ti}_{0.31}(\text{MoK}_{-1}; \lambda = 0.070926 \text{ nm})$.

Experiment : composition $\text{Al}_{0.43}\text{Ni}_{0.26}\text{Ti}_{0.31}$ formed at T = 1073 K			Calculated results by "Lazy Pulverix"[16] : a = 1.190 nm [21]		
θ_{hkl} (deg)	d_{hkl} (nm)	I/I ₀	d_{hkl} (nm)	I/I ₀	Hkl
4.84	0.4240	4	0.4207	6	220
			0.3588	5	311
6.16	0.3306	9	0.3435	19	222
6.90	0.2953	16	0.2975	6	400
7.09	0.2874	4			(100)+
7.46	0.2732	3	0.2730	52	331
7.80	0.2614	3	0.2660	2	420
8.15	0.2502	19			(110)*
8.40	0.2428	12	0.2429	14	422
8.95	0.2280	50	0.2290	21	511
8.95	0.2280	50			(103)*
9.35	0.2183	18			(200)*
9.61	0.2125	80			(112)*
9.71	0.2103	100	0.2103	100	440
10.00	0.2043	25			(110)+
10.16	0.2011	20	0.2011	15	531
10.16	0.2011	20			(004)*
10.73	0.1905	7			(202)*
11.21	0.1825	5			(113)*
11.40	0.1795	15	0.1794	23	622
13.08	0.1567	6	0.1717	<1	444
13.23	0.1550	4	0.1666	1	553
13.60	0.1508	6	0.1487	18	800
13.92	0.1474	12	0.1453	9	733
14.22	0.1444	3			(300)*
14.70	0.1398	12			(213)*
14.70	0.1398	12	0.1402	1	822;660
15.15	0.1357	9	0.1365	17	662
15.15	0.1357	9			(302)*
15.40	0.1336	5	0.1330	<1	840
15.95	0.1291	8	0.1298	6	842
15.95	0.1291	8			(205)*
16.23	0.1269	5	0.1268	1	664
16.45	0.1252	12			(220)*
17.00	0.1213	12	0.1214	22	844
17.20	0.1199	25	0.1196	1	933
17.25	0.1196	25			(310)*;(222)*
17.50	0.1179	4	0.1190	1	862
17.60	0.1173	1			(211)+
18.04	0.1145	4	0.1145	4	10 2 2; 666
18.13	0.1140	8			(206)*

* Reflections belonging to the phase (λ),
+ Reflections belonging to the phase AlNi (β 1).

Table 8: Structural control of the composition $Al_{0.61}Ni_{0.10}Ti_{0.29}$ ($MoK_{\alpha 1}$; $\lambda = 0.070926$ nm)

Experiment : Composition $Al_{0.61}Ni_{0.10}Ti_{0.26}$ at T = 1073 K				Calculated results by Lazy Pulverix [16] a = 0.394 nm	
θ_{hkl} (deg)	d_{hkl} (nm)	I/I ₀	hkl	d_{hkl} (nm)	I/I ₀
5.10	0.3991	4	100	0.3940	5
5.19	0.3922	1	(011)+		
5.67	0.3591	1	(311)*		
5.93	0.3434	5	(222)*		
6.90	0.2953	5	(400)*		
7.35	0.2773	1	110	0.2786	4
7.37	0.2766	2	(331)*		
8.40	0.2428	5	(422)*		
8.83	0.2311	30	(116)+	0.2274	100
8.97	0.2275	100	111;(511)*		
9.71	0.2103	40	(440)*		
10.08	0.2027	5	(00 12)+		
10.16	0.2011	8	(531)*		
10.25	0.1993	8	(020)+		
10.40	0.1965	40	200	0.1970	50
10.70	0.1911	3	(204)+		
11.45	0.1787	10	(622)*		
11.60	0.1764	2	210	0.1762	2
11.95	0.1713	2	(444)*		
12.08	0.1695	1	(1 0 13)+		
13.23	0.1550	<1	(553)*		
13.60	0.1508	1	(01 15)+		
13.80	0.1487	5	(800)*		
14.58	0.1409	5	(02 12)+	0.1393	33
14.65	0.1402	10	(660)*;(220)+		
14.70	0.1398	24	220	0.1393	33
15.10	0.1362	1	(662)*		
15.60	0.1319	1	221	0.1313	1
15.70	0.1311	2	(753)*		
16.80	0.1227	1	(844)*; (1 1 18)+		
17.02	0.1212	3	(844)*		
17.25	0.1196	3	(862)*	0.1188	38
17.45	0.1183	20	311		
18.00	0.1148	1	(666)*		
18.22	0.1134	4	222	0.1137	10

* Reflections belonging to the "μ" phase,
+ Reflections belonging to the phase Al_2Ti .

Conclusion

The enthalpies of formation of the intermetallic compounds of ternary phases: "H": $Ni_{0.50}Al_{0.25+x}Ti_{0.25-x}$ ($0 \leq x \leq 0.14$), "λ": $Al_{0.36}Ni_{0.28}Ti_{0.36}$, "μ": $Al_{0.43}Ni_{0.26}Ti_{0.31}$, and "π": $Al_{0.61}Ni_{0.10}Ti_{0.29}$ in the Al-Ni-Ti system have been measured by calorimetry at high temperature.

Results were compared with the available experimental values and calculated X-Ray in used to check the crystal structure and the homogeneity of the calorimetric products.

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