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CALORIMETRIC STUDIES OF THE INTERMETALLIC COMPOUNDS FROM Al-Ti AND Al-Ni SYSTEMS

Key words:

intermetallics, calorimetry, solution, direct reaction techniques, enthalpy of formation

Abstract

Two calorimetric methods: solution and direct reaction technique were used for determination of the enthalpy of formation of advanced aluminides from Al-Ti and Al-Ni systems – candidates for high temperature application. The special construction of solution calorimeter enables to determine enthalpy of formation at various temperatures and to compare them with existing literature information and with theoretical calculations. In the case of titanium aluminates, differences between results obtained by solution method and direct reaction technique grows up with the decrease of aluminium content in the phases – this tendency was explained by mechanism of formation of phases from powders – in particular by the sequence of phases formation. In nickel aluminates,

temperature dependence of the enthalpies of formation may explain also the differences between experimental results and *ab initio* calculations at 0 K and may be attributed to the different reference state of the compound and its components. Differences between the numerical values of enthalpies of formation of these intermetallic phases are discussed in terms of structural similarities and combined with literature Gibbs energies to calculate excess entropies responsible for high temperature stability.

Streszczenie

Dwie metody kalorymetryczne: rozpuszczania i bezpośredniej reakcji użyto dla określenia entalpii tworzenia aluminidków z układów Al-Ti i Al-Ni – będących kandydatami do wysokotemperaturowych zastosowań. Specjalna konstrukcja kalorymetru typu rozpuszczania umożliwiła wyznaczenie entalpii tworzenia w różnych temperaturach i porównanie jej z informacjami z literatury oraz z obliczeniami teoretycznymi. W przypadku aluminidków tytanu różnice pomiędzy wynikami otrzymanymi metodą rozpuszczania a bezpośredniej syntezy wzrastały wraz ze zmniejszającym się udziałem aluminium w fazie – ta tendencja została wytłumaczona mechanizmem tworzenia się faz z proszków – w szczególności kolejnością tworzenia się faz. Dla aluminidków niklu, temperaturowa zależność entalpii tworzenia może tłumaczyć różnice pomiędzy wynikami eksperymentalnymi i obliczeniami *ab initio* w 0 K i może być związana z różnymi stanami odniesienia związku i jego składników. Różnice pomiędzy wynikami entalpii tworzenia aluminidków przedyskutowano w aspekcie ich strukturalnych podobieństw i powiązano z danymi resztkowych energii Gibbsa celem obliczeń resztkowych entropii odpowiedzialnych za wysoko temperaturową stabilność.

1. Introduction

In experimental thermodynamic studies of metallic alloys emf with liquid and solid electrolytes, vapour pressure measurements and calorimetric studies are used. It is shown that usually one experimental technique is not sufficient for a reliable separation of the Gibbs energy into appropriate entropy and enthalpy contributions, which is necessary if one seeks the correlation between thermodynamic properties and phase equilibria. It is particularly important for systems with intermetallic compounds. One of the recent trends in the study of thermodynamics of intermetallics is the comparison between experiment and phase diagram constructs based on theoretical predictions of the enthalpies of formation of ordered phases. To compare the results of these two approaches, enthalpies of formation are interesting to observe. This quantity may be obtained experimentally by emf methods from partial molar value along the liquidus in an indirect manner, or directly and more precisely by calorimetric techniques.

Calorimetric techniques in metallic systems were discussed in details by Kleppa [1-2], Castanet [3], while for instance calculations of enthalpies from vapour pressure measurements of Al and Ni in Al-Ni system were presented by Raj et al. [4] and Benche et al.[5].

Indirect estimates can be obtained also by the Calphad method based on the phase diagram optimization, by Miedema model and finally in recent years from first principle calculations. One limitation of the latter calculations is the fact that the theoretical enthalpies of formation are obtained at 0 K, while experimental data are mainly available at higher temperatures. Therefore, the difference sometimes observed between

experiment and theory may be attributed to the possible temperature dependence of the enthalpy of formation. In this respect since the 1995 Rindberg meeting in Germany [6] the Institute of Metallurgy and Materials Science, PAS have started co-operation with Brookhaven National Laboratory in USA. It was based on the previous co-operation with Max Planck Institute in Stuttgart, Germany from which the original construction of the calorimeter was used, and later on its modified version in our Institute in Kraków. During the recent years our results of enthalpies of formation from solution calorimetry were compared with the method based on powder products synthesis directly in the calorimeter realised within the co-operation with Nancy University in France.

Enthalpies of formation from first-principles calculations of transition metal compounds were compared [7], [8], [9] with experimental data. Similar comparison for other systems, such as Al-Ni, were made by Colinet and Pasturel [10] who reviewed their tight-binding and linear muffin tin orbital (LMTO) calculations along with other theoretical predictions and available experimental data. The Al-Ni system was also considered by Carlsson and Meschter [11] and recently by Watson [12] using mainly FLASTO calculations.

In addition, enthalpies of formations of these three intermetallic phases from Al-Ni system from experimental techniques are compared with theoretical calculations and are discussed in terms of entropies contributions. The latter discussion is possible as from solution calorimetry we have directly measured enthalpies of formation at desired

temperatures to join them with literature excess Gibbs energies on the one hand and on the other to observe how extrapolation to 0 K corresponds with first principle calculations. The mutual agreement of enthalpies of formation from experiment and theory may be a good indication for phase diagram calculations from theoretical estimates.

The phases belonging to Al-Ti system and alloys based on these phases are the object of the intensive fundamental studies and studies directed for their application. Recently, more than half of papers referring to the intermetallic phases relates to the phases of Al-Ti system [13]. Such a considerable interest in these phases is a result of their merits, which are important from application viewpoint. The property which attracts the attention is their high strength to density ratio [14] what makes it possible reduction by ca. half the weight of constructional materials like exhaust valves, turbine wheels, comparing with classical superalloys. It is also worth to note their outstanding corrosion resistance [15]. A good mechanical properties, obtained for two phase AlTi/AlTi₃ alloys [16] or by introduction of alloy additions for example niobium [17] makes interest in these materials understandable by the automotive, aircraft industry and space investigations agency.

In the case of Ti aluminates the difference between the results from solution calorimetry and direct teaction technique is connected with the mechanism of formation of these aluminates from powders, particularly by the sequence of phase foramation.

The main aim of this monograph being a part of a wide program of investigations on intermetallic phases was to summarize the calorimetric

studies of intermetallics from Al-Ti and Al-Ni systems from solution and direct reaction methods, previously published in two separate papers [18-19] which review mainly the results of both authors Z.M. and K.R. in Institute of Metallurgy and Materials Science in Kraków, Poland carried out until the recent years when K.R. completed his habilitation [20]. Results from direct reaction method were performed jointly with Prof.J.-C. Gachon from Nancy University. This monograph reviews the progress made on calorimetric studies used for determination of the formation enthalpies of AlNi, AlNi₃, Al₃Ni₂ and AlTi, Al₃Ti, AlTi₃ and Al₂Ti and compares them with first principle calculations as the source for verification of phase equilibria of Al-Ni and Al-Ti systems and phase diagram calculations from theoretical estimates. The updated information on enthalpies of formation from literature both from calorimetric studies, emf and vapour pressure measurements was added.

2. Calorimetric techniques used in this monograph

Calorimetry provides the way of the determination of the enthalpy of formation, heat capacity, heat of transformation, enthalpies of mixing, etc. by means of a suitable device since it enables a direct measurement of the heat effects. Depending on the construction the measured heat can be stored in the calorimetric vessel or the bath and / or exchanged with the surroundings shield. Due to this fact calorimetric measurements consist in general in the measurements of temperature changes.

In this study there are used two kinds of calorimeters, solution and based on the direct synthesis of the product - intermetallic phase in the calorimetric vessel, commonly named direct reaction method. In both cases the solid state of components and of the alloy was chosen as a reference state. Thermochemical data were taken from [21].

2. 1. 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 the two-component phase the following equation is applied:

$$\Delta_f H = X_A \Delta H_A^{ef,0} + X_B \Delta H_B^{ef,0} - \Delta H^{ef,0}_{X_A X_B} \quad (1)$$

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

Schematic diagram of solution method is presented in the Figure 1.

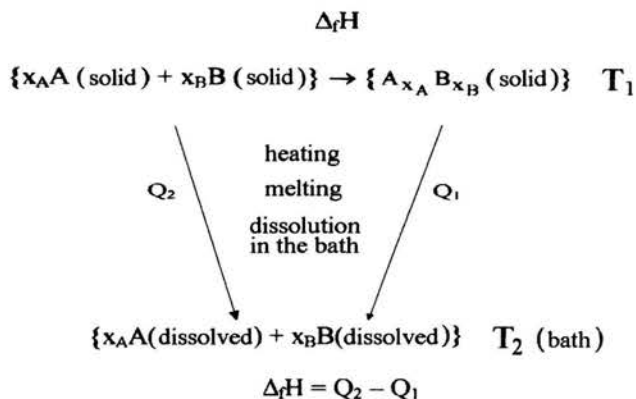


Fig. 1. Schematic diagram of calorimetric solution method

Value $\Delta H_A^{\text{ef.0}}$ and $\Delta H_B^{\text{ef.0}}$ consists of the following terms: 1/ enthalpy of heating up of the solid component from room temperature to the temperature of the calorimeter ($H_{\text{room}}^{\text{calor.}}$), 2/ heat of melting of the component (H_{melt}), 3/ limiting partial heat of solution of titanium in liquid aluminium for zero concentration of titanium (H_{Ti}^0) - this value were determined in our own measurements and is equal -128.3 kJ/gramatom at 1356K; (respective value for aluminium equals zero) 4/ $\Delta H_{\text{melting}}$ - if melting of component takes place at temperatures higher than temperature of the bath, one should add the value of enthalpy of melting of this component.

Details of the applied high-temperature calorimeter constructed at the Institute of Metallurgy and Materials Science, PAS and experimental procedure are described in [22], [23]. A previously described prototype calorimeter [24] was reconstructed at the Institute of Metallurgy and Materials Science. The main modification is an installation of intermediate rotary multiple container enabling simultaneous annealing

of several samples at any temperature from ambient up to 1300 K before dropping the samples into the liquid bath.

The calorimeter block of solution calorimeter is shown in Fig.2.

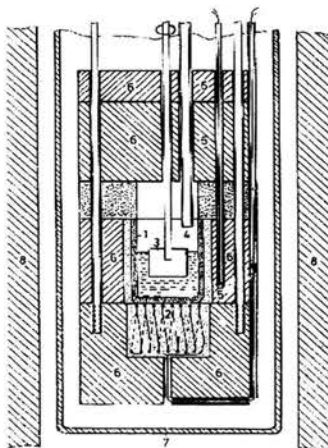


Fig. 2. Calorimeter block (solution method)

In the central part is placed crucible (1) made of sintered alumina holding about 55 grams of Al to which there are added during measurements samples of intermetallic compounds amounting from 0.3 to 0.5 grams. Due to small weight of added samples of compounds in comparison to the Al bath, extrapolation of the heat effects of separate single measurements to the limiting concentration in the bath of the investigated material requires only the averaging. Very important is also negligible change of filling of crucible during experimental series. The measurement of the heat effect is done by means of thermopile (2) composed of about 50 thermocouples AlNi-CrNi situated directly below the bottom of the bath crucible. In the figure we can also see effective ceramic stirrer (3), lower part of device facilitating delivery of the

samples crucible with the bath (4), thermocouple (5), block of calorimeter (6). All elements of block are immersed in a heat-resistant tube (7), which in turn is installed inside calorimetric furnace (8).

The front view of the calorimeter is shown in Fig. 3.

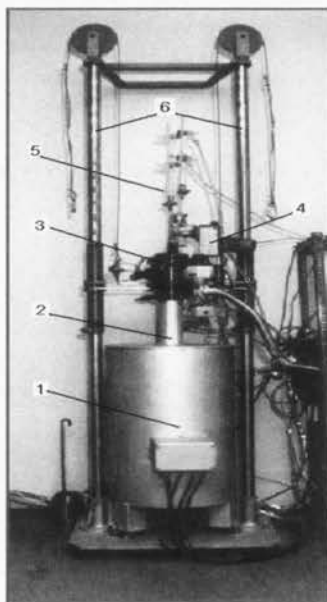


Fig. 3. The front view of solution calorimeter

At the bottom part is situated the vertical furnace (1) heated by three independent heating elements. It enables from one side to maintain the constant zone of temperature at the length of 15 centimetres, and from the other to get the temperature gradient amounting 12 K/cm along the vertical axis of the furnace. The latter enables to heat the sample in the container to any temperature between room temperature and 1200 K before dropping it into the bath. This rotary container with five seating enabled the simultaneous heating of 5 samples before dropping them into the bath and considerably decreased the time of measurements.

The other details of the Fig.3 are as follows: (2) - heat resistant holder containing the calorimetric block connected with calorimeter head (3), (4) driving gear of the stirrer, (5) - glass interconnections and (6) - pulling arrangement enabling to operate with the calorimeter block.

Before each experimental run, the calorimeter was three-fold evacuated and flushed with high purity argon. Numerous runs were done in a steady argon atmosphere with continuous stirring of the bath. Calibration was done at the beginning of a run by adding several Al samples of known enthalpy content.

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 planimetry was done automatically, and the enthalpies of formation were calculated directly from the recorded enthalpy effects.

Samples of investigated intermetallic compounds $AlTi_3$, $AlTi$, Al_3Ti and Al_2Ti were obtained from the proper amounts of 99.99 wt.%Ti and 99.99 wt.%Al by five-fold arc-melting under an Ar atmosphere. After every arc-melting the samples were turned (180°). Then, they were homogenised in the quartz tubes in a separate furnace under the same atmosphere at temperatures of range 1223 K \pm 1273 K for 72 h. Then the samples Al_3Ti , $AlTi$, $AlTi_3$ and Al_2Ti devoted for measurements of formation enthalpy at room temperature were cooled slowly with the furnace. These samples were delivered into a bath at room temperature. Another part of Al_3Ti samples devoted for the measurements of formation enthalpy at 1031 K, after homogenising annealing at 1123 K,

were annealed at 1031 K for 24 hours and then rapidly quenched in water with ice. The last stage of annealing was performed also at 1031 K for 12 hours inside intermediate container inside the calorimeter directly before dropping samples into the bath.

Samples of investigated intermetallic compounds AlNi_3 , AlNi and Al_3Ni_2 were obtained by melting the proper amounts of 99,98wt.%Ni and 99.999wt.%Al in an induction furnace under an Ar atmosphere and then homogenising in a separate furnace under the same atmosphere at 1273 K for 72 h. Next, the temperature of the furnace was lowered to 1090K and kept within 48h and the first part of samples were quenched in water with ice. The remaining part of samples were maintained at 770 K for 48h and similarly quenched. The last portion of samples was cooled down in the furnace to room temperature within 48h. Finally, 4h of additional heating for each sample took place in the calorimeter container at temperatures planned for measurements before dropping the samples into the bath. For instance, in the case of Al_3Ni_2 , samples were heated respectively at 770 K and 1090 K. The alloys were tested by X-ray analysis to confirm the existence of the desired intermetallic phase for intermetallic compounds both from Al-Ti and Al-Ni systems.

2. 2. Direct reaction method

In this method, the basis of determination of formation enthalpy is the measurement of the heat effect accompanying the direct reaction of

powder components at elevated temperature in the calorimeter accordingly to the scheme in Fig. 4.

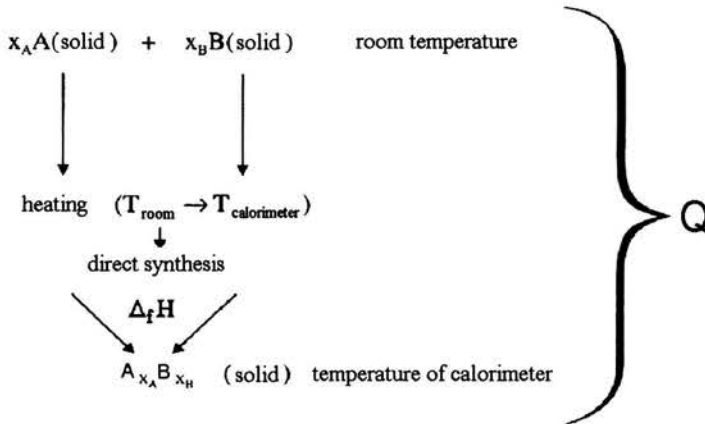
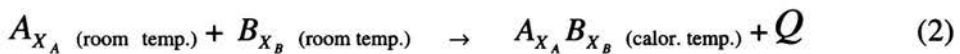


Fig. 4. Schematic diagram of calorimetric direct reaction method

Calibration and reaction samples are dropped from the room temperature to the elevated temperature of the reaction crucible. The desired synthesis of binary alloy can be presented using the following form:



The amount of heat measured calorimetrically (Q) is the algebraic sum of formation enthalpy $\Delta_f H_{A_{x_A} B_{x_B}}$ and the heating effects $\Delta H_{\text{room}}^{\text{calor.}}(A)$, $\Delta H_{\text{room}}^{\text{calor.}}(B)$ of the alloy components from room temperature to the temperature of the reaction crucible.

The enthalpy of formation is calculated from the equation: $\Delta_f H_{A_{x_A}} = Q - [X_A \Delta H_{\text{room}}^{\text{calor.}}(A) + X_B \Delta H_{\text{room}}^{\text{calor.}}(B)] \quad (3)$

In the solution method and in the direct reaction technique, the solid state of components and phase was chosen as a reference state. Due to this, it is necessary to add to the value calculated from Eq.3, a portion proportional to the concentration of the component of the enthalpy accompanying the change of the state of aggregation or other change of conversion of the component. The latter remark is valid for the conversions taking place between ambient temperature and the temperature of the reaction crucible of the calorimeter.

Calorimeter for the direct reaction method used at the University of Nancy was described in details in Ref [25] and in Ref [18].

The preparation of the samples has been done in a separate glove-box where the powders of Al, Ni and Ti produced by Cerac of the 99.5 weight % purity were weighted and pressed to get samples of about 0.5 g. In the same glove-box were weighted the α -alumina samples (99.7 weight %, produced by Haldenwanger) used for calibration.

In the course of the calorimeter run, the samples for measurement and for calibration are falling down directly to the reaction crucible. The heating of the furnace enables to maintain the zone of the constant temperature (± 1 K) amounting 10 centimetres. To the side walls of both crucibles: reaction and for calibration are mounted the NiCr-NiAl thermocouples forming the pile to measure the heat effect of the synthesis reaction.

During the experimental run the heat effect is visible on the monitor screen of the computer due to coupling with the thermocouples file. Integration of the resulting heat effect and the calculation of the enthalpy of formation is facilitated by the computer program as reported in [25].

3. Phase Diagram of the Al-Ti system

Phase diagram of the Al-Ti system is reproduced from Massalski [26]. Due to practical application of intermetallics from Al-Ti system, the precise determination of phase equilibria is of very importance, however up till now there are significant discrepancies between various authors [27], [28], [29], [30], [31], [32]. There is although a concordant opinion that one of main reasons of dimness of determination of phase equilibrium of Al-Ti system is inconsiderable (in some temperature extent) difference between values of Gibbs energy of liquid phase and other phases being in equilibrium with each other. In this situation impurities of phases may play an important role in difficulties in precise determination of phase equilibria.

The equilibrium phase diagram of Al-Ti system [26] is presented in Fig.5.

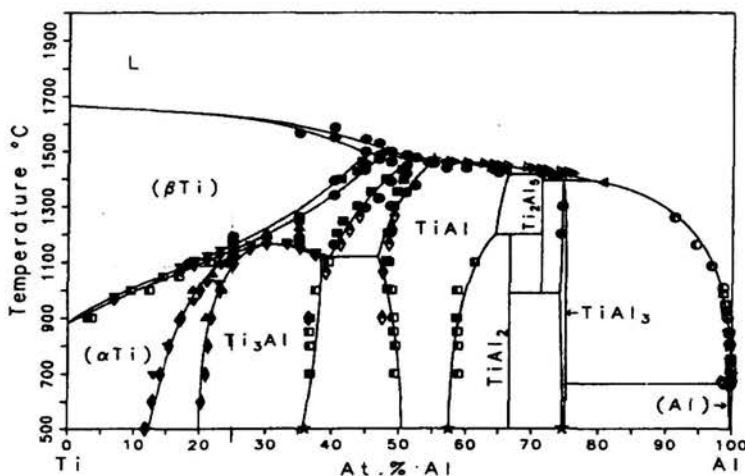


Fig. 5. Phase diagram of the Al – Ti system [26]

4. Experimental results of the enthalpies of formation for aluminates from Al-Ti system

Apart our own experimental results of the enthalpies of formation obtained by solution and direct reaction methods, the values of formation enthalpy determined experimentally and theoretically by other authors are also included.

4.1. Data for Al₃Ti

Table 4.1.1 Results obtained by calorimetric solution method for Al₃Ti intermetallic compound; samples were delivered into the bath at room temperature=303K; temperature of the bath = 1335 K

The temperature of intermediate container [K]	Temperature of Al bath [K]	Meas. no.	Heat effects accompanying the dissolution of Al ₃ Ti intermetallic compound in liquid aluminium [kJ/mole of atoms]
303	1335	1	47.8
		2	50.1
		3	48.4
		4	48.4
		5	48.5
			Average value: 48.7±1.0
Formation enthalpy = -37.8±2.3			

Table 4.1.2 Results obtained by calorimetric solution method for Al₃Ti intermetallic compound; samples were delivered into the bath at temperature=1031K; temperature of the bath = 1335 K)

The temperature of intermediate container [K]	Temperature of Al bath [K]0	Meas. no.	Heat effects accompanying the dissolution of Al ₃ Ti intermetallic compound in liquid aluminium [kJ/mole of atoms]
1031	1335	1	27.9
		2	27.5
		3	28.4
		4	26.4
		5	27.8
			Average value: 27.8±0.8
Formation enthalpy = -37.3±2.3 kJ/ mole of atoms			

Table 4.1.3 The values of formation enthalpy of Al₃Ti determined experimentally and theoretically by other authors

Method	Formation enthalpy of Al ₃ Ti [kJ/mole of atoms]	Temperature [K]	References
Experimental methods			
Calorimetric method of direct synthesis	-37	1073	[33] cit. [34]
As above	-37	298	[35]
As above	-39.6	298	[36]
As above	-35.7	298	[37]
EMF measurements	-36	960	[38]
Optimization of experimental data	-36.6	298	[39] cit. [40], [41]
As above	-36	298	[42], [43]

Theoretical estimations			
Miedema's method	-39		[44]
CALPHAD estimation	-39.0	298	[27]
Theoretical calculations of <i>ab initio</i> type	-41.5	0	[45]
	-41.5	0	[46]
	-39.6	0	[47]

4.2. Data for Al₂Ti

Table 4.2.1 Results obtained by calorimetric solution method for Al₂Ti intermetallic compound; samples were delivered into the bath at temperature=306K; temperature of the bath = 1337 K

The temperature of intermediate container [K]	Temperature of Al bath [K]	Meas. no.	Heat effects accompanying the dissolution of Al ₂ Ti intermetallic compound in liquid aluminium [kJ/mole of atoms]
306	1337	1	39.8
		2	41.6
		3	38.8
		4	39.0
		5	36.9
			Average value: 39.2±1.9
Formation enthalpy = -38.6±2.6 [kJ/mole of atoms]			

Table 4.2.2 The values of formation enthalpy of Al₂Ti determined experimentally and theoretically by other authors

Method	Formation enthalpy of Al ₂ Ti [kJ/mole of atoms]	Temperature [K]	References
Experimental methods			
Calorimetric method of direct synthesis	-38.4	298	[41]
Theoretical estimations			
CALPHAD estimation	-36	298	[48]
As above	-42	298	[27]

4.3. Data for AlTi

Table 4.3.1 Results obtained by calorimetric solution method for AlTi intermetallic compound; samples were delivered into the bath at temperature=300K; temperature of the bath = 1360 K

The temperature of intermediate container [K]	Temperature of Al bath [K]	Meas. no.	Heat effects accompanying the dissolution of AlTi intermetallic compound in liquid aluminium [kJ/mole of atoms]
300	1360	1	-23.6
		2	-24.1
		3	-21.7
		4	-22.4
		Average value: -23.0±1.1	
Formation enthalpy = -41.9±3.1 kJ/ mole of atoms			

Table 4.3.2 Formation enthalpy of AlTi determined by the method of direct synthesis; room temperature = 300K; temperature of reaction crucible = 1306 K

Measurement no.	Formation enthalpy of AlTi [kJ/mol of atoms]
1	-37.3
2	-36.9
3	-37.9
4	-36.0
5	-37.6
Average value	-37.1±1.0

Table 4.3.3 The values of formation enthalpy of AlTi determined experimentally and theoretically by other authors

Method	Enthalpy of formation of AlTi [kJ/mole of atoms]	Temperature [K]	References
Experimental methods			
Calorimetric method of direct reaction	-38	298	[39] cit. [40] and [41]
EMF measurements	-36	960	[38]
Optimisation of experimental data	-36	298	[42], [43]
Theoretical estimations			
Miedema's method	-61		[44]
CALPHAD estimation	-38.4	298	[27]
Theoretical calculations of <i>ab</i> <i>initio</i> type	-42.4	0	[46]
	-39.6	0	[47]

4.4. Data for AlTi₃

Table 4.4.1 Results obtained by calorimetric solution method for AlTi₃ intermetallic compound; samples were delivered into the bath at temperature=300K; temperature of the bath = 1356 K

The temperature of intermediate container [K]	Temperature of Al bath [K]	Meas. no.		Heat effects accompanying the dissolution of AlTi ₃ intermetallic compound in liquid aluminium [kJ/mole of atoms]		
300	1356	Se-ries 1	1	-17.7		
			2	-19.1		
			3	-21.6		
		Se-ries 2	1	-21.6		
			2	-18.2		
			3	-21.6		
						Average value: 19.7.0±1.9
		Formation enthalpy = -41.9±3.1 kJ/ mole of atoms				

Table 4.4.2 Formation enthalpy of AlTi₃ determined by the method of direct synthesis; room temperature = 299K; temperature of rection crucible = 1306 K

Measurement no.	Formation enthalpy of AlTi [kJ/mol of atoms]
1	-18.3
2	-21.1
3	-21.6
Average value	-20.3±1.9

Table 4.4.3 The values of formation enthalpy of $AlTi_3$ determined experimentally and theoretically by other authors

Method	Formation enthalpy of $AlTi_3$ [kJ/mole of atoms]	Temperature [K]	References
Experimental methods			
Calorimetric method of direct synthesis	-25	298	[40]
EMF measurements	-24	960	[38]
Theoretical estimations			
Miedema's method	-39		[44]
CALPHAD estimation	-28.6	298	[27]
Theoretical calculations of <i>ab initio</i> type	-27.0	0	[48]
	-28.9	0	[46]
	-27.0	0	[47]

5. Discussion and final remarks for Al-Ti aluminates

Analysing results obtained by solution method and by direct reaction method obtained both at University of Nancy and by Kubaschewski [40], [41] the considerable difference between results obtained by two calorimetric methods for compounds $AlTi$ and $AlTi_3$ focus the attention. Simultaneously, very similar results obtained for Al_3Ti obtained by both methods were noted. Also similar values of formation enthalpy of Al_3Ti obtained by solution method for room temperature ($\Delta_f H = -37.8 \pm 2.3$ kJ/mole of atoms) and 1031 K ($\Delta_f H = -37.3 \pm 2.3$ kJ/mole of atoms).

To recognise the sources of differences between results obtained by both methods in the case of $AlTi$ and $AlTi_3$ and their accordance in the case of Al_3Ti , it is worth to recall results of studies concerning the recognition of the mechanism of formation of phases in the Al-Ti system.

The results of numerous works where powders were used as the initial material [49], [50], [33], [51], [52], [53], [54], [55] indicate, that irrespectively on the proportions of the amount of introduced powders of aluminium and titanium, first obtained product is phase Al_3Ti . An important factor is melting of aluminium, which coats the particles of titanium. This reaction dominates up to exhausting of metallic aluminium. If quantitative proportion of titanium to aluminium is higher than 1:3 (at.%), the particles of titanium which did not react, start to react with Al_3Ti phase, forming the layer of $AlTi$ and Al_2Ti directly around metallic titanium. It is worth to notice, that after melting and reacting of aluminium to mainly Al_3Ti , the further reactions take place between solid substances much slower. This reflects the change of temperature during reaction between initial powder materials in a ratio 3:1 of Ti:Al [49], [50]. In the first moments of process temperature considerably increases although majority of titanium remains non-reacted. The further reactions occur quicker at temperatures higher than 1165K. At this temperature titanium allotropic form (β), of high diffusivity appears, contrary to the (α) titanium existing at lower temperatures. Much slower reaction between solid substances causes distinct decrease of temperature. In other works structural analysis indicate also existence of phases like $AlTi$, Al_2Ti , Al_3Ti . $Ti(Al)$ among the products.

It is interesting to analyse the results of enthalpy of formation, comparing data obtained by solution and direct reaction calorimetry. In the case of solution method, problems connected to mechanism of

formation of desired phase are focused on the stage of formation of the compound of demanded composition. It takes place before application the sample to the calorimetric measurements, that is before dropping the sample into metallic bath. Considering compound AlTi, in the case direct synthesis we noted that similar values were obtained in Nancy University (-37.1 ± 1.0 kJ/mol of atoms) and by Kubaschewski (37.7 ± 2.1 kJ/mol of atoms) [40]. For other compounds the difference is bigger what was discussed in detail in [20]. The basic problem which needs to be emphasised is the distinct difference between results obtained in solution and direct reaction methods in the case of AlTi and AlTi₃ and good agreement of results obtained for Al₃Ti. We noted a great rate of formation of Al₃Ti first in the presence of liquid Al; comparing with the rate of formation of other phase of this system, where reaction occur between solid substances. Basing on the work of [56] one can conclude that at the first stage of mechanical milling process, particles form long strips being in tight contact. Apart from it the oxides are teared off from the particles.

Two kinds of the powder materials were studied in our work : 1) one directly after direct synthesis in calorimeter (Fig 6-left side) after direct synthesis in calorimeter + 2 hours of mechanical alloying + one more synthesis in calorimeter (Fig.6-right side). In the latter figure AlTi₃ phase is dominating.

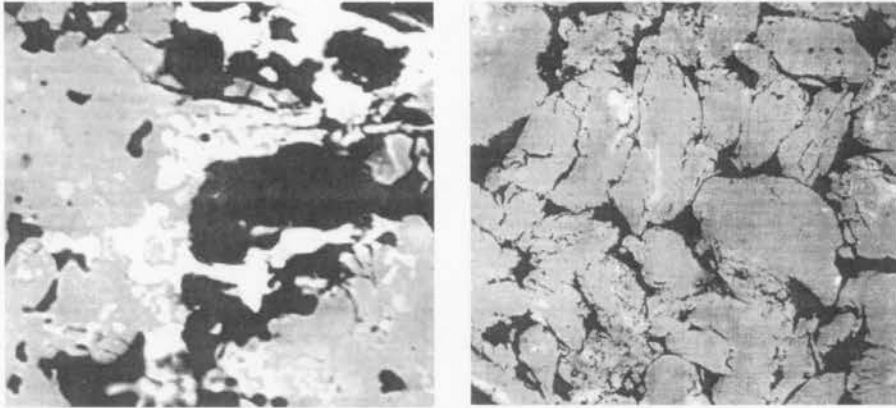


Fig. 6. The BSE microstructures of the phases achieved by direct synthesis performed in calorimeter: left side – the synthesis non-preceded by the mechanical alloying process, right side – synthesis preceded by the mechanical alloying process

Obtained result indicates an interesting technological path: in initial stage of application mechanical alloying, then spontaneous synthesis or synthesis with assistance of external source of heat.

6. Phase diagram of the Al-Ni system and phase diagram calculations

Okamoto [57] updated the Al-Ni phase diagram from [26] which was reported by [58]. This updated phase diagram is shown in Fig.7 and in addition to the liquid phase has five intermetallic phases: Al_3Ni (orthorombic), Al_3Ni_2 (trigonal), AlNi (bcc), Al_3Ni_5 (orthorombic) and AlNi_3 (fcc)

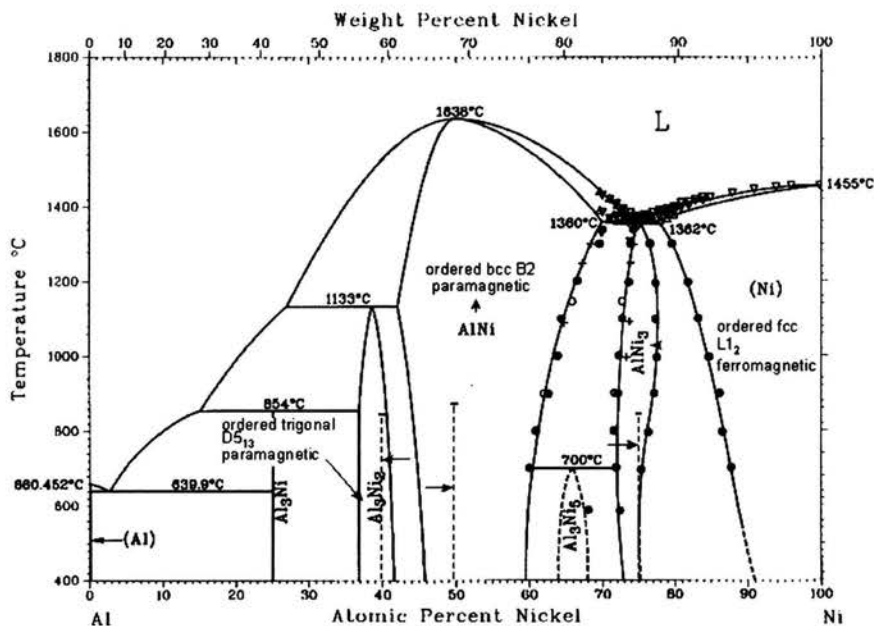


Fig. 7. Al-Ni phase diagram updated by Okamoto [57]. Dotted lines for each stoichiometric intermediate phase: AlNi [19] and AlNi₃ [19] and Al₃Ni₂ [19], denote the range of temperature in which calorimetric studies were undertaken

The solid solubility of Ni in Al is very small and increases with temperature from 0.01 at.% (773 K) to 0.11 at.% at the eutectic temperature (913 K). Ni has a wide γ solid solution range with significant solubility of Al up to 21.1 at.% at the eutectic temperature (1658 K). The decrease of the terminal solubility of Al in the γ - solid solution with decrease of the temperature results in precipitation of the γ' AlNi₃ phase and strengthening of these alloys. The presence of a congruently melting compound, AlNi, suggests a strong interaction in the liquid Al-Ni system

and hence high absolute values of both enthalpies of mixing and formation.

Several attempts have been made to describe the phase diagram of the Al-Ni system by means of a thermodynamic approach with various modelling of the existing phases. Ansara et al. [59], [60] and Du et al. [61] used the CALPHAD approach in which Gibbs energies for all the phases are expressed in terms of phenomenological models based on existing thermodynamic and phase diagram data (for instance the compound energy model with two sublattices). Huang and Chang [62] treated the liquid and fcc (γ) phases as disordered solutions and γ' AlNi₃-based ordered phase as the intermetallic compounds with appreciable ranges of homogeneity.

AlNi (B2) and Al₃Ni₂ phases are described by energy models, while the other intermetallic phases are assumed to be the line compounds.

In the subsequent analysis, enthalpies of formation of this study from solution and direct reaction calorimetry will be compared with other experimental data from literature sources, based on modeling in [59], [60], [61], [62] and as well on first principal calculations.

7. Experimental results of the enthalpies of formation of aluminates from Al-Ni system from solution and direct method

Advanced aluminides, including the ordered phases AlNi_3 and AlNi , are potential candidates for practical applications. AlNi_3 is the principal phase exhibiting interesting high-temperature properties, AlNi with a high melting temperature is very attractive due to its low density, good corrosion resistance, high thermal conductivity, and low raw material cost; however, the main limitation is the fact that, contrary to single crystals, polycrystalline material is brittle [63]

7.1. Data of AlNi

Heat effects accompanying the dissolution of AlNi in liquid Al bath are summarised in Table 7.1.1, and in Table 7.1.2 there are presented the enthalpies of formation at the investigated range of temperature. In Table 7.1.3 there are given enthalpies of formation from the direct reaction method.

Table 7.1.1 Heat effects accompanying the dissolution of AlNi intermetallic compound in liquid aluminium

The temperature of intermediate rotary container [K]	Temperature of Al bath [K]	Measurement No.	Heat effects accompanying the dissolution of AlNi compound in liquid aluminium [kJ/mole of atoms]
298	1181	1	31.6
		2	31.0
		3	30.0
		4	31.6
		5	30.4
545	1181	1	24.2
		2	25.5
		3	25.5
		4	25.2
779	1123	1	14.6
		2	15.5
		3	15.5
		4	14.8
939	1181	1	13.0
		2	13.9
		3	13.2
1140	1140	1	5.1
		2	4.6
		3	4.7
		4	4.1

Table 7.1.2 Formation enthalpy $\Delta_f H$ of intermetallic compound AlNi determined at various temperatures by calorimetric solution method

Temperature [K]	Formation enthalpy of AlNi intermetallic compound [kJ/mole of atoms]
298	-66.1±1.3
545	-67.0±1.2
779	-66.9±1.1
939	-67.5±0.9
1140	-67.3±0.8

Table 7.1.3 Formation enthalpy $\Delta_f H$ of AlNi intermetallic compound determined by direct reaction method; room temperature = 296K; temperature of reaction crucible = 1136 K

Measurement No.	Formation enthalpy of AlNi [kJ/mole of atoms]
1	-65.6
2	-64.9
3	-65.1
4	-67.2
Average value	-65.7±1.1

In the next Table 7.1.4 the summary is given of the experimental data of the enthalpy of formation from various references from literature and compared with theoretical calculations.

Table 7.1.4 The values of formation enthalpy of AlNi determined experimentally and theoretically by other authors

Method	Formation enthalpy [kJ/mole of atoms]	References	Remarks
Experimental results			
Calorimetric solution method	-66.4±2.0	[64]	Measurement conducted in a wide concentration range of B2 phase
As above	-67.0	[65]	
Calorimetric direct reaction method	-58.8	[66]	
EMF measurements	-62.0	[67]	
Calorimetric direct reaction method	-58.3±1.1	[68]	Measurement conducted for stoichiometric AlNi
EMF measurements	-67.4±2.6	[69]	
Calorimetric solution method	-66.0	[70]	
Theoretical results			
Miedema model	-48	[71]	
CALPHAD estimation	-66.8	[60]	Two sublattice model used as in [21].
<i>Ab initio</i> calculations	-71	[72]	
	-80	[73]	
	-76	[74]	
	-71	[75], [76]	
	-76	[77]	

	-79	[78]	
	-63	[79]	
	-67.5±1	[19] – calculations conducted by Watson	Ferromagnetism of nickel not taken into account
	-66.0	[19] – calculations conducted by Watson	Ferromagnetism of nickel taken into account

7.2. Data of Al₃Ni₂

This compound is not important from the practical point of view, but its enthalpies of formation will be used for phase diagram verification. Similarly as for AlNi, in a tabular form there are presented for Al₃Ni₂ the heat effects of the dissolution in liquid Al bath (Table 7.2.1), the enthalpy of formation values (Table 7.2.2), and next in Table 7.2.3 the data from direct reaction method and finally in Table 7.2.4, a comparison with calorimetric data of Kubaschewski [80] and with theoretical calculations.

Table 7.2.1 Heat effects accompanying the dissolution of Al₃Ni₂ intermetallic compound in liquid aluminium

Temperature of intermediate rotary container [K]	Temperature of Al bath [K]	Measurement No.	Heat effects accompanying the dissolution of Al ₃ Ni ₂ compound in liquid aluminium [kJ/mole of atoms]
301	1123	1	-40.7
		2	-40.5
		3	-38.5
		4	-40.9
			Average value: -40.2±1.1
767	1113	1	-26.0
		2	-27.1
		3	-28.7
		4	-27.0
			Average value: -27.2±1.1
1093	1172	1	-20.2
		2	-18.8
		3	-17.4
		4	-19.0
		5	-19.5
			Average value: -19.0±1.0

Table 7.2.2 Formation enthalpy $\Delta_f H$ of the compound Al_3Ni_2 determined at various temperatures by calorimetric solution method

Temperature [K]	Formation enthalpy of compound Al_3Ni_2 [kJ/mole of atoms]
301	-63.5±1.7
767	-64.3±1.6
1093	-64.5±1.6

Table 7.2.3 Formation enthalpy $\Delta_f H$ of Al_3Ni_2 compound determined by direct reaction method; series 1: room temperature = 297 K; temperature of reaction crucible = 1093 K; series 2: room temperature = 296 K; temperature of reaction crucible = 1175 K

Series	Measurement No.	Formation enthalpy of compound Al_3Ni_2 [kJ/mole of atoms]
1	1	-62.8
	2	-63.9
	3	-63.6
	Average value	-63.4±0.8
2	1	-62.8
	2	-62.9
	3	-61.5
	Average value	-62.4±1.0

Table 7.2.4 The values of formation enthalpy of Al_3Ni_2 determined experimentally and theoretically by other authors

Method	Formation enthalpy [kJ/mole of atoms]	References	Remarks
Experimental results			
Calorimetric direct reaction method	-56.5	[80]	Determined at 298K
Theoretical results			
Miedema model	-43	[71]	
CALPHAD estimation	-61.6	[59]	Two sublattice model applied
<i>Ab initio</i> calculations	-61.8	[77]	
	-62.9	[12]	
	-52.1	[10]	

7.3. Data of $AlNi_3$

In Table 7.3.1 there are summarised the enthalpy effects accompanying the dissolution of $AlNi_3$ at various temperatures and in Table 7.3.2 the resulting enthalpies of formation are listed. In Table 7.3.3 there are given the enthalpies of formation from the direct reaction method and in Table 7.3.4 a comparison with other literature data.

Table 7.3.1 Heat effects accompanying the dissolution of $AlNi_3$ compound in liquid aluminium. Temperature of bath = 1123 K

Temperature of intermediate rotary container [K]	Measurement No.	Heat effects accompanying the dissolution of $AlNi_3$ compound in liquid aluminium. [kJ/mole of atoms]
300	1	-34.4
	2	-32.2
	3	-33.0
	4	-32.7
	5	-33.6
	6	-32.8
	7	-32.0
	8	-33.1
	9	-32.3
		Average value: -32.9±0.7
521	1	-37.9
	2	-38.6
	3	-37.8
	4	-38.6
	5	-38.5
		Average value: -38.3 ±0.7
756	1	-46.4
	2	-45.8
		Average value: -46. ±0.8
947	1	-51.0
	2	-51.8
	3	-51.7
	4	-51.6
		Average value: -51. ±0.6
1123	1	-57.7
	2	-57.3
	3	-56.8
	4	-58.6
	5	-57.6
	6	-56.0
	7	-59.2
		Average value: -57. ±1.1

Table 7.3.2 Formation enthalpy $\Delta_f H$ of the compound $AlNi_3$ determined at various temperatures by calorimetric solution method

Temperature [K]	Formation enthalpy of compound $AlNi_3$
	[kJ/mole of atoms]
300	-41.3±1.3
521	-42.0±1.1
756	-41.6±1.2
947	-42.2±1.0
1123	-42.3±1.6

Table 7.3.3 Formation enthalpy $\Delta_f H$ of $AlNi_3$ compound determined by direct reaction method: room temperature = 297 K; temperature of reaction crucible = 1116 K

Measurement No.	Formation enthalpy of intermetallic compound $AlNi_3$
	[kJ/mole of atoms]
1	-39.4
2	-39.1
3	-39.0
4	-39.8
Average value	-39.4±0.6

Table 7.3.4 The values of formation enthalpy of AlNi₃ determined experimentally and theoretically by other authors

Method	Formation enthalpy [kJ/mole of atoms]	References
Experimental results		
Calorimetric solution method	-40.6±1	[81]
Calorimetric direct reaction method	-40.2	[82]
As above	-37.6	[80]
Vapour pressure measurements	-38.2±5.0	[83]
Theoretical results		
Miedema model	-33	[71]
CALPHAD estimation	-38.0	[61]
<i>Ab initio</i> calculations	- 49	[74]
	-48	[77]
	-47	[84]
	-45	[85]
	-44.4	[12]

8. Discussions and final remarks for Al-Ni aluminates

The experimental data of enthalpies of formation of AlNi₃, AlNi and Al₃Ni₂ obtained by solution and direct reaction calorimetry were obtained in the range from ambient temperature to about 1140 K.

Data for AlNi₃ indicating slight temperature dependence of the enthalpy of formation were discussed in 1995 during the Rindberg meeting in

Germany [6] with Watson from Brookhaven National Laboratory. Some joint attempts were undertaken to correlate theoretical calculations (first principle) of formation enthalpies of intermetallic phases obtained for 0 K with experimental data mainly available at higher temperatures. The difference observed between experiment and theory may be attributed to a possible temperature dependence of the enthalpy of formation and to the different reference states of the compound and its components. As a reference state we do not mean in this case the state of aggregation, because solid state was chosen as the reference state in the case of all substances, but the state considered from the point of view of magnetic properties.

The first to be studied in this venture was AlNi_3 compound [86]. The enthalpy of formation of AlNi_3 extrapolated to 0 K from results of measurements by solution calorimeter, showed only a slight temperature dependence and was in reasonable agreement with calculations by the FLASTO method. In the case of AlNi_3 there is no significant complication from the point of view of the reference state, as this intermetallic phase is a weak ferromagnet and Ni is also ferromagnetic.

Another situation was in the studies of the stoichiometric AlNi phase, which is paramagnetic, and discrepancies between theoretical calculations and experimentally determined enthalpies of formation showed differences between results of experiments and theoretical calculations as is also the case for AlFe , FeTi , FeV [87]. As a result, it was concluded that magnetic properties of constituents and alloy have influence on the enthalpies of formation of intermetallic phases, which

has been proved for AlFe [88]. The bottom part of Table 7.3.4 summarises the calculations of enthalpy of formation by *ab initio* [87] when the correction for magnetic energy for Ni has been taken into account.

The obtained absolute values of the enthalpies of formation for AlNi are higher than the similar data for other compounds crystallising also in B2 structure (see table 8.1).

Table 8.1 The values of formation enthalpy of some B2 intermetallic compounds and the highest range of their existence

Intermetallic compound	Formation enthalpy [kJ/mole of atoms]	Temperature of determination of formation enthalpy [K]	References	Upper temperature range of existence [K]	References
AlFe	-26.7±1.7	296	[89]	1520	[26]
	-22.9±1.9	791			
	-31.2±0.8	1248			
AlNi	-65.7±0.9	939	[19]	1911	[26]
AlCo	-60.7±0.5	1073	[70]	1913	[26]

The present results of enthalpies of formation of AlNi, taken together with the published data of the excess Gibbs energies [90] (-54.0 kJ/ mole of atoms at 1273 K) let one evaluate the excess entropies of formation. Assuming entalpies of formation of this study as -67.7 kJ/ mole of atoms at 1273 K, enabled the calculations of excess entropies of formation equal to -16.53 J/K.mole of atoms. The absolute value of this excess

entropy of formation is much higher than the values for other compounds, for instance equal to -11.5 , 0.0 and -9.5 J/K.mole of atoms in the case of AlNi_3 , AlFe_3 , and AlTi_3 , respectively [86].

This pronounced negative value of excess entropy of formation for AlNi contributes to the stability and the ordering of AlNi even at temperatures of the order of 1200 K. It is also interesting to compare the concentration dependence of enthalpy of formation over the entire range of homogeneity of AlNi (B2). Measurements of [91] were carried out at 1100 K at concentration range $X_{\text{Al}} = 0.40$ to 0.55 molar fractions (see Fig.8).

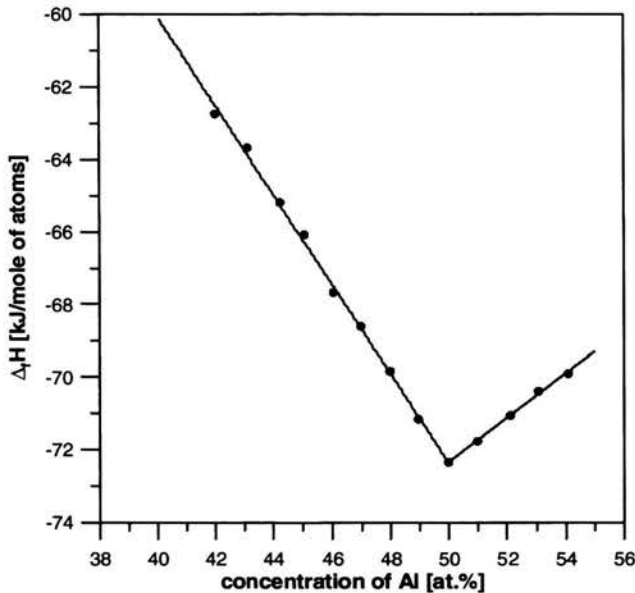


Fig.8. Formation enthalpy of AlNi (B2) phase as a function of concentration of Al according to [91]. Al liquid state of aluminium was chosen as a reference state

For the equimolar concentration, the value -72.2 kJ/mole of atoms was obtained, standing in good agreement with the value from our studies, taking into account the differences of the assumed reference states (in this study-solid Al and for [91]- liquid Al). Accepting for the value presented in Ref. [91] and as the reference state - solid Al, one can obtain, $\Delta_f H = -66.8$ kJ/mole of atoms being very close to $\Delta_f H = -67.5$ kJ/mole of atoms of our study.

Results of enthalpies of formation performed at the considerable range of B2 phase [91] enable to confirm the linear decrease of the enthalpy of formation when leaving the equimolar composition. The decrease in enthalpy of formation of AlNi on both sides of stoichiometry is connected with an increase in disordering in these alloys, which is indicated by x-ray studies [92], by lattice parameter and density measurements [93].

The latter two properties were taken from ref. [93] for AlNi. For Ni-rich alloys, Al sites are occupied by the smaller atoms of Ni, resulting in a decrease of the lattice parameter and an increase in the density in these alloys ($r_{Ni} = 0.124$ nm, $r_{Al} = 143$ nm [94]).

On the other hand, for the Al-rich AlNi phase, we note the decrease of the absolute value of formation enthalpy when compared with stoichiometric AlNi (Fig. 8). Because of considerable difference in the size of aluminium and nickel atoms [95] substituting of Ni atoms by Al atoms is not possible, but the extension of existence of AlNi phase towards Al-rich range is possible thanks to the formation of vacancies and this fact is responsible for decrease of the absolute value of

formation enthalpy mentioned above. It is reflected also in the decrease of lattice parameter and density of the considered alloys [96]. According to [97] as much as 25 at. % of Ni positions may be not occupied in B2 Al-rich alloys. These phenomena also result in the extensive homogeneity range of B2 phase (42 to 69 at.%Ni).

The resulting data of enthalpies of formation of this study for AlNi, together with the excess Gibbs energies, the pronounced negative of excess entropy of formation calculated on their basis, contributes to the stability and the ordering of AlNi even at temperatures of the order of 1200 K.

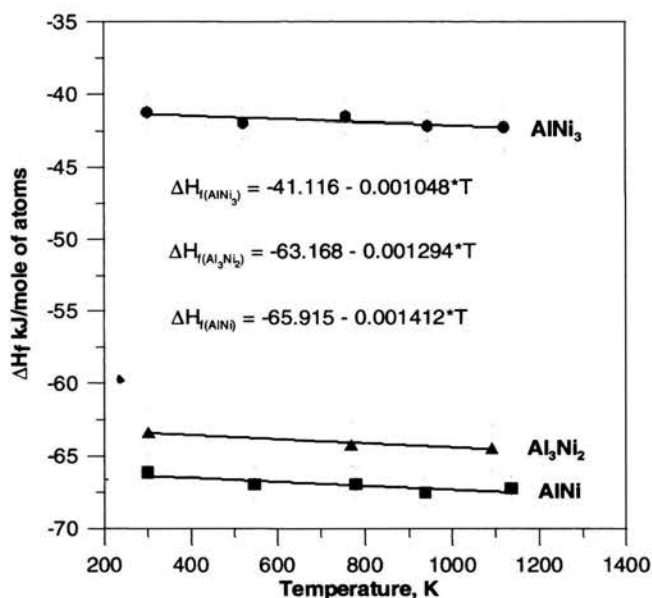
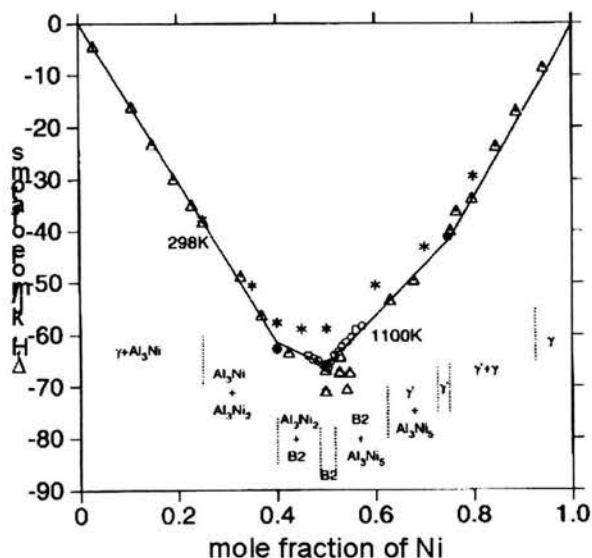


Fig. 9. Formation enthalpy of Al₃Ni₂ [19] AlNi [19], AlNi₃ [19] compounds as a function of temperature

In Fig.9 there are presented the temperature dependencies of enthalpies of formation of all three intermetallic phases: AlNi, Al₃Ni₂ and AlNi₃.

The present experimental results indicate a slight temperature dependence of the enthalpy of formation of Al₃Ni₂, which however is within experimental uncertainties. It is observed that numerical values of the enthalpies of formation of Al₃Ni₂ are close to those of AlNi with an approximate difference of about 3kJ/mole. It is understandable due to the similar structure of both intermetallic compounds. The structure of Al₃Ni₂ may be considered as a modification of AlNi with every third diagonal plane of nickel atoms missing [98].

It seems particularly interesting, when the compositions of the considered AlNi and Al₃Ni₂ phases come nearer to each other. Thus, on the Ni-rich side of stoichiometric Al₃Ni₂, it would be possible for the excess Ni atoms to be accommodated in the lattice vacancies [96] and this leads to the increase of the absolute value of formation enthalpy of these alloys in comparison with the stoichiometric Al₃Ni₂, as it can be seen in the Fig. 10.



*Fig.10. The calculated enthalpies of formation at 298 K [62], solid line, compared with experimental data: * [80], Δ [82], o [65]. For Al_3Ni_2 • this study -63.5 kJ/mole of atoms, 301 K, for $AlNi$ • [19] -66.1 kJ/mole of atoms, 298K, and for $AlNi_3$ • [86] -41.3 kJ/mole of atoms, 300 K. Data of this study from solution method [19]*

The full points in this figure are the data of our work, values obtained by other authors in previous calorimetric measurements are also marked, and the solid curve refers to the recent thermodynamic analysis of Al-Ni system [62]. Accommodation of Ni atoms in the lattice vacancies leads also to lattice expansion and the increase of density, what was confirmed by [96].

One can observe the interesting phenomena connected with the change of enthalpy of formation with composition changes in both Al_3Ni_2 and $AlNi$. It was discussed previously, that in B2 phase it is

possible to replace the Al atoms by Ni atoms for alloys rich in Ni in relation to stoichiometric AlNi, but due to considerable size of Al atoms, the reverse case, i.e. replacing of Ni atoms by Al is not possible, and the extension of existence of the range of B2 phase in Al-rich alloys is by formation of vacancies. This results in the increase of the energy of the alloy and is reflected in decreasing of the absolute value of enthalpy of formation. For instance, for the limiting alloy close to B2: Ni₄₆Al₅₄, this decrease amounts to 2.4 kJ/mole of atoms (temperature 1100 K) from [91]. The composition of the analysed alloy is still belonging to the B2 phase, however most close to Al₃Ni₂. Contrary to AlNi, where it was not possible to replace Ni atoms by Al, in the structure of the phase Al₃Ni₂ (due to removing of Ni atoms in each third plane, in relation to AlNi) it is possible to accommodate the big Al atoms in non-occupied sites “reserved” for nickel [96].

However, in the case of increasing content of nickel (when compared with stoichiometric Al₃Ni₂), the empty sites are filled gradually by nickel atoms, making the structure more and more like that of AlNi.

In the case of Al₃Ni₂ compound the value of formation enthalpy calculated by FLASTO method [12] equals – 62.9 kJ/mol of atoms, which is close to the value obtained experimentally in this work –63.2 kJ/mol of atoms.

Using Al solution calorimetry, the enthalpies of formation of AlNi₃ in the L1₂ structure ranging from –41.3 to –42.3 kJ/mol of atoms were determined at temperatures from 300 to 1123 K [56]. Slightly lower absolute values were obtained in this study by the direct method $\Delta_f H = -$

39.4 ± 0.8 kJ/mole of atoms (Table 7.2.3). The obtained results of this study are in good agreement with data from solution calorimetry : -40.6 ± 1 kJ/mol of atoms [81] as well as with -40.2 ± 1 kJ/mole of atoms from direct synthesis method [82]. Kubaschewski et al. [80] by the direct method reported slightly lower absolute values: $\Delta_f H = -37.6$ kJ/mol of atoms. From vapor pressure studies [83] it was possible to evaluate the enthalpy of formation equal to: $\Delta_f H = -38.2$ kJ/mol of atoms. As noted in Table 7.2.4, higher discrepancies in the absolute values of enthalpies of formation were observed when comparing experimental results with theoretical calculations. These considerable negative values of the enthalpy of formation of $AlNi_3$, both experimental and theoretical, are related to the lack of any transformation of the compound, which remains ordered up to the melting temperature amounting to 1635 K. This lack of transformation is reflected by nearly constant, at the range of experimental error, values of enthalpy of formation versus temperature. $AlNi_3$ crystallizes in the close-packed, face-centered cubic lattice of the Cu_3Au structure as do other transition metal aluminides including the transition metals such as Sc, Ti, and Ni. In this structure, the minority Al constituents has 12 unlike neighbours, thus enhancing the opportunity for alloy bonding. Each Al atom is surrounded by 12 Ni atoms, and each Ni atom is surrounded by 8 Ni atoms and by 4 Al atoms. Such arrangement is energetically profitable [99] and is reflected also in the values of excess entropy of formation. The value of excess entropy equal to -12.9 J/K.mol of atoms was calculated using $\Delta_f H = -42.2$ kJ/mol of atoms of this study and the excess Gibbs energy: $\Delta_f G^{ex} = -33.6$ kJ/mol of atoms at

1045 K from the emf method [100]. A similar considerable, negative value is obtained from excess Gibbs energy [101] at 1273 K for the composition of the alloy Al_{25.8}Ni_{74.2} equal to -27.89 kJ/mol of atoms, which simultaneously with data of our study of enthalpy of formation from solution calorimetry extrapolated to 1273 K, results finally in excess entropy of formation equal -11.5 J/K.mole of atoms. This negative value of excess entropy reflects the high degree of the ordered structure L₁₂ in which AlNi₃ crystallises.

When comparing the differences between formation enthalpy values obtained by solution and by the direct reaction method it is worth to notice that these differences are higher in the case of AlNi₃ than in the case of the two other studied compounds (1.6; 1.6; 2.9 kJ /mole of atoms for Al₂Ni₃, AlNi, AlNi₃, respectively). It is due to the low melting temperature of aluminium and low temperature of eutectics containing 97.3% at. of Al. As a consequence, the phases with the richest Al-content appear at the first stage of the reaction proceeding [102], [103], [104], [105]. Such tendency of a growing difference in the values of formation enthalpy, obtained by two methods mentioned above, for decreasing content of Al was very clearly visible in the Al-Ti system, as discussed in the first part of this monograph.

References

1. Kleppa O.J., J. Phase Equilibria, 15, 240, (1994).
2. Kleppa O.J., Journal of Alloys and Compounds, 321, 153, (2001).
3. Castanet R, J. Phase Equilibria, 15, 339 (1994).

4. Raj D, Bencze L, Kath D, Oates W.A, Herrmann J, Singheiser L, Hilpert K, *Intermetallics*,11, 1119 (2003).
5. Bencze L, Raj D, Kath D, Oates W.A, Singheiser L, Hilpert K, *Metallurgical Materials Transactions* (in print)
6. Chang A, Colinet C, Hillert M, Moser Z, Sanchez J.M., Saunders N, Watson RE, Kussmaul A, *CALPHAD*, 1995; 19:481. Workshop on Thermodynamic Models and Data of Pure Elements and other End-Members of Solutions, Schloss Rindberg Germany (Feb-March 1995) org. by F. Aldiger and B. Sundman.
7. Watson R.E., Weinert M, Davenport J. and Fernando D.W. *Phys Rev B* 1989;39:10761
8. Watson R.E., Fernando D., Weinert M., and Davenport J.W., *J. Phase Equilibria*, 1992;13: 244
9. Watson R.E., Weinert M. And Davenport, J. *Phase Equilibria*, 1994;15:330
10. Colinet C, Pasturel, J. *Phase Equilibria*, 1994;15:338
11. Carlsson A.E. and Meschter, *Intermetallic Compound* Westbrook J.H. and Fleischer R.L. Ed., John Wiley & Sons, New York, 1994:55
12. Watson R.E. and Weinert M., *Physical Review B*, 1998; 58,(10):5981
13. Bystrzycki J, Garbacz H, Przetakiewicz W, Kurzydłowski K.J., *Inżynieria Materiałowa*, 1,8 (2001)
14. Faller K., Froes F.H., *JOM*, 53, 27 (2001).
15. Froes F.H, Friedrich H., Kiese J., Bergoint D., *JOM*, 56, 40 (2004).
16. Eckert M., Bencze L., Kath D., Nickel H., Hilpert K., *Ber.Bunsenges Phys.Chem.*, 100, 418, (1996).
17. Banerjee D, *Ti₃Al and its alloys, Intermetallic Compounds*, 2, Practice, Edited by Westbrook J.H. and Fleischer, John Wiley and Sons Ltd, 91-131 (1994).
18. Rzyman K., Moser Z., Gachon J.C., *Archives of Metallurgy and Materials*, 49, 3, 545-563, (2004).
19. Rzyman K., Moser Z., *Progres in Materials Science*, 49, 3-4, 581-606, (2004).

20. Rzyman K., Habilitation work: "Energy effects accompanying the formation of intermetallic phases", pp.1-110, Kraków, (2002)
21. SGTE Substance Data Base, Royal Institute of Technology, Sweden, (1994).
22. Rzyman K., Moser Z. and Kiecka B., Archives of Metallurgy, 38,(4), 393-396, (1993),
23. Rzyman K., Moser Z., XII Konferencja Sprawozdawcza „Metalurgia 98”, Polska Akademia Nauk, Komitet Metalurgii, Krynica 1998, 626÷631
24. Sommer F., Lee J.J., Predel B., Z. Metallkde, 71, 818, (1980)
25. Gachon J.C., Notin M., Hertz J., Journees de Calorimetrie et Analyse Thermique de l'Association Francaise de Calorimetrie et Analyse Chimique, Marseille, HT.2, 1÷11, (1979),
26. Massalski T.B., *Binary Alloy Phase Diagrams*, ed.2, ASM International Materials Information Society, (1990)
27. Kattner U. R., Lin J. C., Chang Y. A., , Met. Trans.A, 23A, 2081÷2090 (1992),
28. Gros J.P., Sundman, B., Ansara I., Scripta Metall. 22, 1587, (1988)
29. Hellwig A., Inden G., Palm M., Scripta Metall., 27, 143, (1992)
30. Anderson C.D., Hofmeister W.H., Bayuzick R. J, Met. Trans.A, 24A, 61, (1993)
31. Kainuma R., Palm M., Inden G., Intermetallics, 2, 321, (1994)
32. Okamoto H., J. Phase Equilibria, 21, No 3, 311, (2000),
33. Jean-Francois Javel, Thesis, Universyté Henri Poincaré, Nancy, (France), (1997).
34. Chrifi-Alaoui Nassik , F.A., Thesis , Université Henri Poincaré, Nancy, (France), (1997)
35. Liang W.W., Calphad 7, 13, (1983),
36. Kleppa O.J., J.Phase Equilibria, 15, (1994), 240
37. Smithels Metals Reference Book, ed. By E.A. Brandes i G. B. Brook (Butterworth, Oxford,1992)
38. Samokhval V.V., Poleshchuk P.A., Veher A.A., Russ. J. Phys. Chem. 45, 1174,(1971)

39. Hultgren R., Desai P.D., Hawkins D.T., Gleser M., Kelley K.K., ASM, Metals Park, Ohio, (1973)
40. Kubaschewski O., Dench W.A., *Acta Metall.*, 3, 339÷346 (1955),
41. Kubaschewski O., Heymer G., *Trans. Faraday Soc.* 56, 473÷478, (1960),
42. Barin I., Knacke O., Kubaschewski O., *Thermochemical Properties of Inorganic Substances, Supplement* (Springer Verlag, Berlin, Heilderberg, New York, and Verlag Stahleisen, Düsseldorf, 1977.
43. Kubaschewski O., Alcock C.B., *Metallurgical Thermochemistry* (Pergamon Press, Oxford, New York, Toronto, Sidney, Paris, Frankfurt, 1979.
44. F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, *Cohesion in Metals, Transition Metal Alloys*, ed. North-Holland, 1988.
45. Fu C.L., *J. Mater.Res.*, 5, 971, (1990)
46. Asta M., D.de Fontaine, M. van Schilfgaarde, Sluiter M., Methfessel M., *Phys. Rev. B*, 46, 5055, (1992),
47. Watson R.E., Weinert M., *Phys. Rev. B.*, 58, (10), 5981÷5988,(1998),
48. Hong T., J.Watson –Yung, X .Q. Guo, A.J. Freeman, T. Oguchi and J.H.X u, *Phys. Rev.B*, 43, 1940, (1991)
49. Orrú R., Cao G., Munir Z.A., *Metall and Mater. Trans. A*, 30A, 1101÷1108 (1999),
50. Orrú R., Cao G., Munir Z.A., *Chemical Engineering Science*, 54, 3349÷3355,(1999)
51. H.C.Y i, A. Petric, Moore J.J., *J. Mater. Sci.* 27, (1992), 6797÷6806
52. W. Y.Yang, Baker, *Scripta Metall. Mater.*, 34, 803 (1996),
53. M. Ho-Yi, Y. Hong-Yu, M. Shu-Xia, Y. Sheng, *Int..J. SHS*, 1, 6797÷6806 (1992)
54. Dahms M., Jewett T.J., Michaeln C., *Z. Metallkde*, 88, 125-130 (1997)

55. Sujata M., Bhargava S., Sangal S., J.Mater.Sci. Lett., 16, 1175÷1178 (1997),
56. Olivier Held, Thesis, Université Henri Poincarè Nancy (France), (1998)
57. Okamoto H, J. Phase Equil., 1993;14:257
58. Nash P, Singleton MF, Murray JL, Phase Diagrams of Binary Nickel Alloys, Nash P. ed. ASM International, Materials Park,OH, 1991:3
59. Ansara I, Dupin N, Lukas HL, Sundman B, Journal of Alloys and Compounds, 1997; 247:20
60. Ansara I, Sundman B, Willemin P, Acta metall, 1998; 36;(40): 977
61. Du Y, Clavaguera N, Journal of Alloys and Compounds, 1996;237:20
62. Huang W, Chang YA, Intermetallics, 1998;6:499
63. Stoloff NS, In High-Temperature Ordered Intermetallic Alloys, ed.Koch CC. Liu CT and Stoloff N.S. Materials Research Soc. Pittsburgh PA, 1985: p.3
64. Dannohl H.D., Lukas H.L, Z. Metallkde, 1974; 65:642
65. Henig E. Th., Lukas H.L, Z. Metallkde , 1975;66:98
66. Kubaschewski O, Dench W.A, Acta Metall, 1955;3:339
67. Wang J., Engell H.J., Steel Research, 1992; 27:620
68. Meschel SV, Kleppa OJ, Metallic Alloys: Experimental and Theoretical Perspectives, Faulkner J.S. ed. Kluwer Academic Publishers, Dordrecht, Holandia, (in press)
69. Eskov V.M, Samokhval V.V., Veher A.A, Russ. Metall, 1974;2:118
70. Grün Alex, Dissertation: Kalorimetrische Untersuchungen der Bildungsenthalpie von Überstrukturphasen in der Systemen Nickel-Aluminium-Kobalt, Institut für Metallkunde der Universität Stuttgart, 1966.

71. de Boer F.R., Boom R, Mattens WCM, Miedema A.R., Niessen A.K., Cohesion in Metals, Transition Metal Alloys, ed. North-Holland, 1988
72. Min B.I, Oguchi T., Jansen H.J.F., Freeman, J. Magn.Magn. Mater., 1986; 54:1091
73. Burton B.P., Osborn J.E., Pasturel A., High Temperature Ordered Intermetallic Alloys IV, Johnson LA, et al. Ed. Materials Research Society, Pittsburg, PA, 1991:107
74. Lu Z.W., Wei S.H., Zunger A., Frota-Pessoa S., Ferreira L.G., Phys. Rev. B, 1991;44:512
75. Lin W., Xu J.H., Freeman A.J., J. Mater. Res.1992;7:592
76. Lin W., Freeman AJ, Phys.Rev. B, 1992;45:61
77. Pasturel A., Colinet C., Paxton A.T., Van Schilfgearde M., J., Phys. Condens. Matter, 1992; 4:945
78. Burton B.P., Osborn J.E., Pasturel A., Phys. Rev.B, 1991; 45:7677
79. Schultz P.A., Davenport J.W., Scripta Metall. Mater. 1992; 27:620
80. Kubaschewski O., Trans. Faraday Soc.,1958; 54:814
81. Kek S, Rzyman K., Sommer F, Anales de Fizika, 1990;B86:31
82. Oelsen W., Middell W., Mitt. Kaiser Wilhelm Inst. Eisenforsch.Düsseldorf, 1937;19:1
83. Hilpert O., Miller M., Gerade H., Nickel H., Ber. Bunsenges. Phys. Chem, 1990; 94:40
84. Xu J-H, Min B.I., Freeman A.J., Oguchi T, Phys.Rev.B, 1990;41:5010
85. Hackenbracht D., Kübler J., J.Phys.F., 1980;10: 427
86. Rzyman K., Moser Z., Watson R.E., Weinert M., J.Phase Equilibria, 1996; 17:173.
87. Rzyman K., Moser Z., Watson R.E., Weinert M., J.Phase Equilibria, 1998; 19:106.

88. Rzyman K., Moser Z., Miodownik P., Kaufman L., Watson R.E., Weinert M., CALPHAD, 2000;24:309
89. Rzyman K., Moser Z., Gachon J.C., Inżynieria Materiałowa, 2001;1:19
90. Wang J, Engell H-J, Steel research, 1992; 63:320
91. Henig E. Th., Lukas H.L, Z. Metallkde, 1975;66:118
92. Bradley A.J., Taylor A., Proc. R. Soc, (London), A, 1955; 159:56
93. Noebe R.D., Bowman R.R, Nathal M.V., Int Met, Rev, 1993; 159:56
94. Chemical Courier, Periodical Tables of Elements, Warsaw, 1991
95. Pearson W.B., The Crystal Chemistry and Physics of Metals and Alloys (New York: Wiley), 1972
96. Taylor A., Doyle N.J, J. Appl. Cryst., 1972; 5:201
97. Nash P., Singleton M.F., Murray J.L., Phase Diagrams of Binary Nickel Alloys, Nash P, ed. ASM International, Materials Park, OH, 1991:3
98. Delavignette P., Richel H., Amelinckx S., Phys. Status Solidi,1972;A13:545
99. Schubert K., Kristallstrukturen zweikomponenten Phasen, Springer-Verlaf, Berlin, 1964
100. Malkin V.J., Pokidishev, Izvest. Akad. Nauk SSSR, Metally, 1966;2:166
101. Desai P.D., J. Phys. Chem. Ref. Data, 1998;16:109
102. Colgan E., Nastasi M., Mayer J.W, J.appl.Physics,1985;58:4125
103. Houghton D.D. Materials RES.,Soc. Proc. Symp.1984;25:149
104. Olszówka-Myalska A., Formanek B., Maciejny A., Szopiński K.; Müller G. editor, Ceramics- Processing, Reliability, Tribology and Wear; Euromat vol. 13. Wiley-VCH, 1992: (94pp)
105. Olszówka-Myalska A., Materials Chemistry and Physics, 2003; 81:333