W. GĄSIOR*, A. DĘBSKI*

ENTHALPY OF FORMATION OF INTERMETALLIC PHASES FROM Fe-Ni-Ti SYSTEM. COMPARATIVE STUDIES

ENTALPIA TWORZENIA FAZ MIĘDZYMETALICZNYCH Z UKŁADU Fe-Ni-Ti. STUDIA PORÓWNAWCZE

The solution calorimetric method was used for the measurement of the formation enthalpy of the binary FeTi and Fe_2Ti intermetallic phases and of the $FeNiTi_2$ phase from the region of the ternary B2 one.

The FeNi and $FeNiTi_2$ phases were prepared by levitation melting and the Fe_2Ti phase – by melting the metals in a glove-box under high purity argon. The alloys obtained were identified by the X-ray diffraction analysis. The structural study of the alloys with the composition equal to the FeTi and Fe_2Ti phase confirmed the mentioned phases mainly in the samples. In the case of the ternary alloy of the composition of the $FeNiTi_2$ phase, a slight amount of iron was also found. The obtained values of the formation enthalpy equal as follows: -27.2±1.3 kJ/mole of atoms, -22.5±1.4 kJ/mole of atoms and -34.2±1.3 kJ/mole of atoms for the Fe_2Ti, FeTi and $FeNiTi_2$ phase, respectively.

Keywords: intermetallics, phase diagrams, thermodynamic and thermochemical properties, phase identification, calorimetry

Stosując kalorymetryczną metodę rozpuszczania zostały zmierzone entalpie tworzenia dwóch dwuskładnikowych faz międzymetalicznych FeTi i Fe_2Ti oraz z obszaru fazy trójskładnikowej B2.

Fazy FeTi i $FeNiTi_2$ zostały przygotowane metodą lewitacyjnego topienia a faza Fe_2Ti metodą metalurgiczną przez stopienie metali w komorze manipulacyjnej z atmosferą ochronną argonu wysokiej czystości. Otrzymane stopy były poddane identyfikacji metodą analizy dyfrakcji promieniowania rentgenowskiego. Badania te potwierdziły występowanie w próbkach dwuskładnikowych głównie faz FeTi i Fe_2Ti. W przypadku stopu trójskładnikowego oprócz fazy $FeNiTi_2$ została wykryta niewielka ilość żelaza. Zmierzone wartości entalpii tworzenia faz wynoszą: -27.2±1.3 kJ/mol atomów dla Fe_2Ti, -22.5±1.4 kJ/mol atomów dla FeTi oraz -34.2±1.3 kJ/mol atomów dla $FeNiTi_2$.

1. Introduction

The ternary Fe-Ni-Ti alloys belong to the group of superalloys, which are characterized by a high corrosion resistance and good mechanical properties, both at low or elevated temperatures. The mentioned alloys are very interesting for the power industry because of the financial profits which result from a longer time of utilization of the electric turbines, as well as other elements of the power plants which work under very destructive conditions (for example, high temperature corrosion), in comparison to the traditional materials used.

Therefore, the great interest of research institutions to characterize the mechanical, thermodynamic, physicochemical properties and the modeling phase equilibria in these alloys is fully justified.

Kaufman and Nesor [1] were the first to present the assessment of the Fe-Ti system in 1978. In the following

years, also Dinsdale et al. [2], Murray [3], Balasubramanian [4] (report Dep. Mater. Sci. & Eng., KTH), Kumar et al. [5], Okamoto [6] and Jonsson [7] presented the studies on the equilibria in the Fe-Ti system, applying the experimental data available in literature.

The comparison analysis of the mentioned assessments of the Fe-Ti system was carried out by Dumitrescu et al. [8]. The last report of the phase equilibria in the discussed system was shown in the SGTE data base [9]. In the Fe-Ti system, two intermetallic phases, FeTi and Fe_2Ti, were found. The FeTi phase is of the bulk cubic structure (Space group Pm3m) with the lattice parameters equaling a = 0.29789 nm, and the other one, Fe_2Ti, is characterized by the hexagonal structure (Space group P63/mmc) with the lattice parameters equaling a= 0.4785 nm, b= 0.4785 nm, c = 0.7799 nm, respectively. The assessment of the Fe-Ti system by Kaufman and Nesor [1] is presented in Fig. 1 and the last one

*   ALEKSANDER KRUPKOWSKI INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, 30-059 KRAKÓW, 25 REYMONTA STR., POLAND

proposed in the SGTE data base – in Fig. 2. The main differences concern the homogenous ranges of the FeTi and Fe$_2$Ti intermetallic phases. Other deviations between the Fe-Ti phase diagrams proposed by the cited above authors concern also the transition temperatures and the equilibrium lines.

The thermodynamic investigations of the Fe-Ti system were focused mainly on the calorimetric measurements of the formation enthalpy of the intermetallic phases and they were carried out by Gachon and Hertz [10, 11] for both the FeTi and Fe$_2$Ti phase as well as by Kubaschewski and Dench [12] for the FeTi phase, by the direct synthesis method. In the work of [10, 11] the formation enthalpy measured by Dinsdale [2] was cited, however, the experimental method was not mentioned. The measurement for the Fe$_2$Ti phase was also conducted by Kubaschewski and Dench [12]; however, the structural investigations did not confirm its structure and the experimental results were not given in their publication. The studies of the phase transitions were conducted by different methods (thermal analysis by Hellawell and Hume-Rothery [13], resistance heating of specimens in He by Booker [14], DTA by Kivilahti and Tarasova [15]).

The measurements of the component activity for the solid and liquid alloys have not been performed up till now, either for the Fe-Ti or the Fe-Ni-Ti system.

The phase equilibria in the Fe-Ni-Ti system were studied by [16-23] by means of the differential thermal analysis and a differential scanning calorimeter. Figs. 3-4 show the isothermal intersections at 1273 K and the liquidus line's projection developed by Duarte et al. [23]. They are in good agreement with those earlier proposed by Keyzer et al. [22].
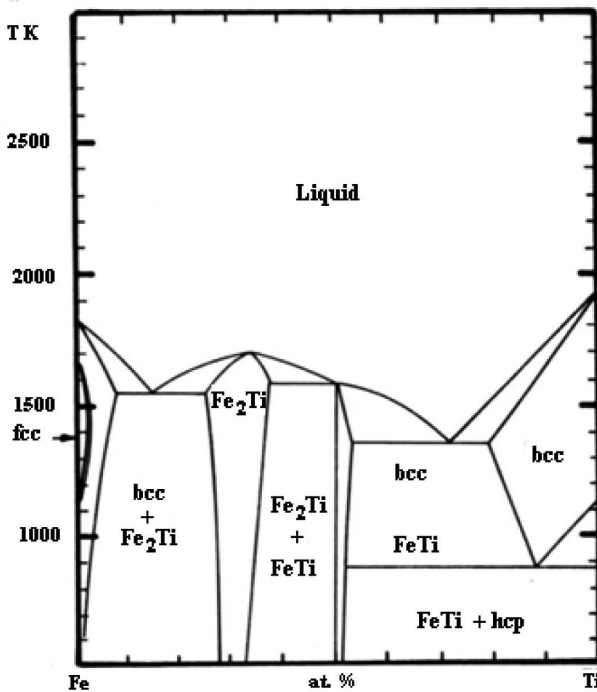

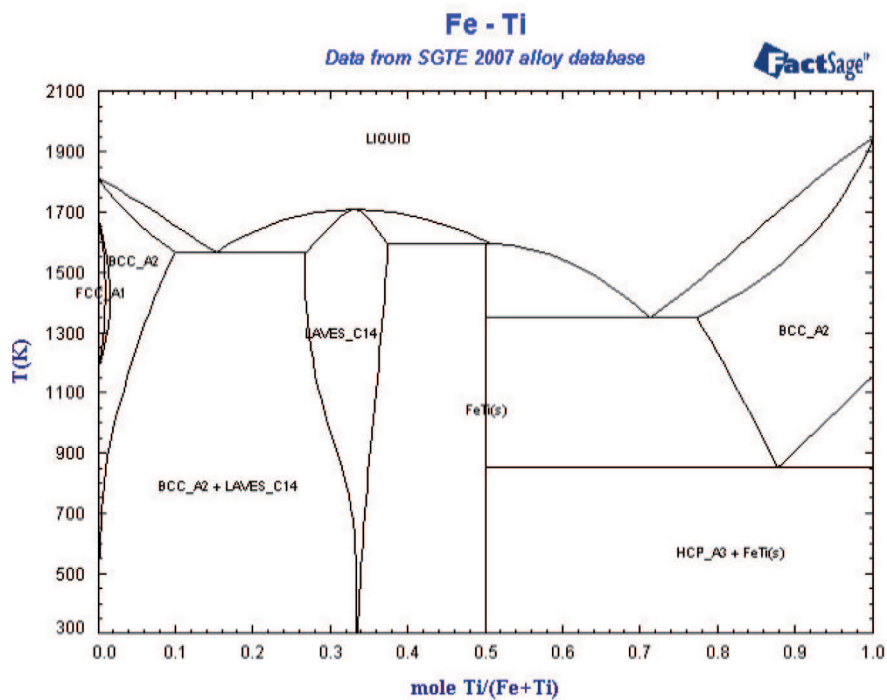Fig. 1. Phase diagram of Fe-Ti system proposed by Kaufman and Nesor [1]

Fig. 2. Phase diagram of the Fe-Ti system proposed in the SGTE alloy database [9]
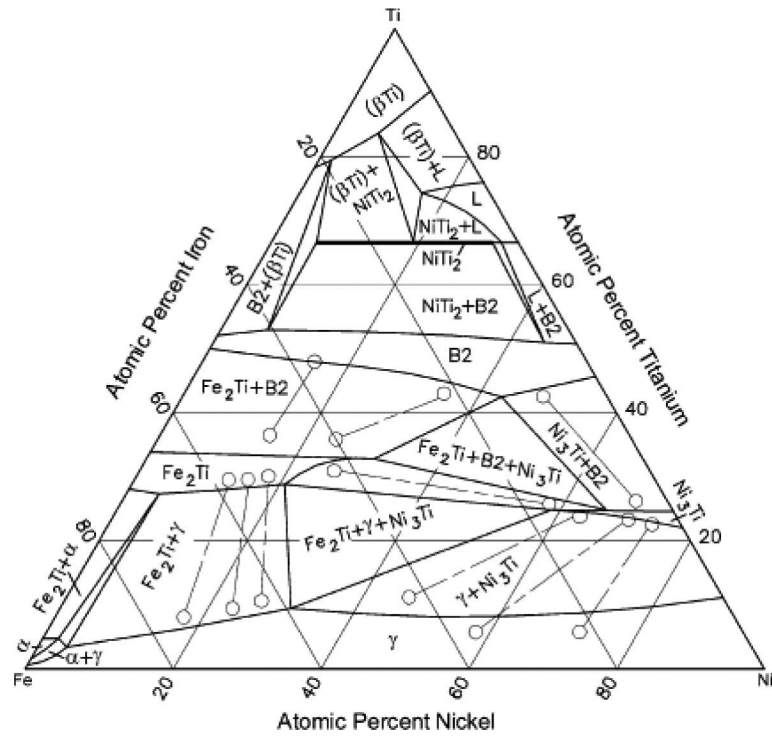
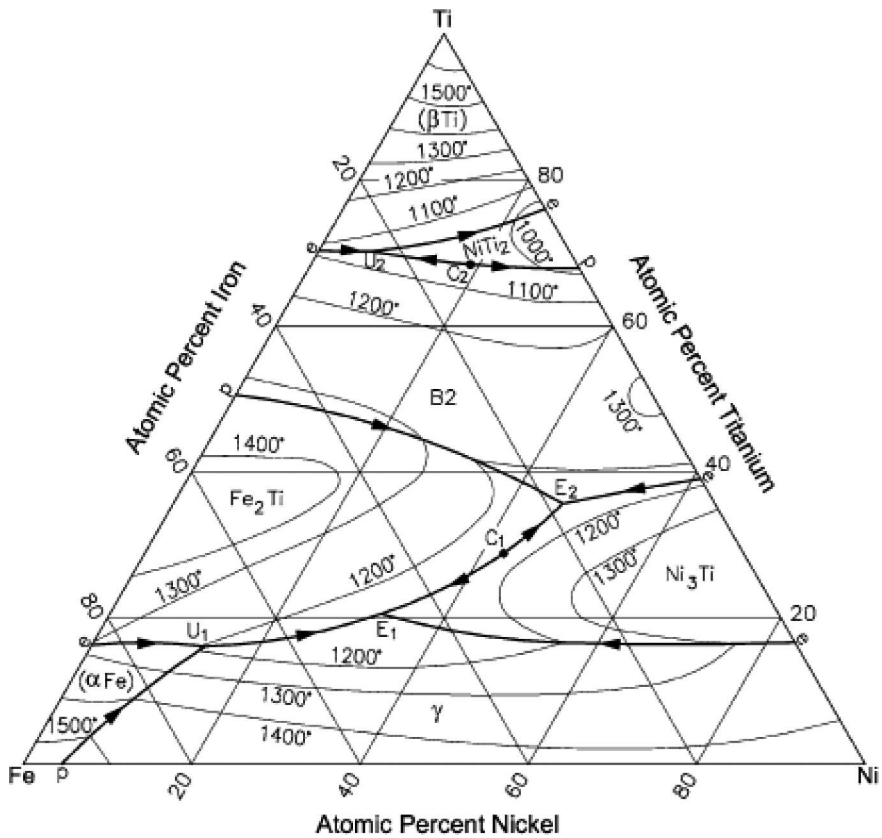Fig. 3. Isothermal section of the Fe-Ni-Ti system at 1273 K by [18]

Fig. 4. The Fe-Ni-Ti liquidus projection by [23]

2. Measurement of the formation enthalpy

The determination of the formation enthalpy of intermetallic phases is based on the usage of energetic effects of the solution of the phase and its components in the solvent, which is very often aluminium. The thermodynamic analysis of the solution process of the metals and the phase shows that the formation enthalpy determined in such a case concerns the temperature at which the samples were thrown into the bath (solvent) and it is independent of the bath temperature. From the measured heat (energetic) effects mentioned above, the formation enthalpy of the binary and ternary intermetallic phase can be calculated with the use of the following equations:

binary intermetallic phase:

$$\Delta_f H = X_A \Delta H^{ef}_{A_{X_A}} + X_B \Delta H^{ef}_{B_{X_B}} - \Delta H^{ef}_{A_{X_A} B_{X_B}} \qquad (1)$$

and ternary intermetallic phase:

$$\Delta_f H = X_A \Delta H^{ef}_{A_{X_A}} + X_B \Delta H^{ef}_{B_{X_B}} + X_C \Delta H^{ef}_{C_{X_C}} - \Delta H^{ef}_{A_{X_A} B_{X_B} C_{X_C}} \qquad (2)$$

where:

$A_f H$ is the formation enthalpy of the mole of atoms of the intermetallic phase at the temperature in which the sample was inserted into the solvent (Al bath), X_A, X_B, X_C are the mole fractions of the components in the phase $A_{X_A} B_{X_B} C_{X_C}$ and $\Delta H^{ef}_{A_{X_A}}$, $\Delta H^{ef}_{B_{X_B}}$, $\Delta H^{ef}_{C_{X_C}}$, $\Delta H^{ef}_{A_{X_A} B_{X_B} C_{X_C}}$ $\Delta H^{ef}_{A_{X_A} B_{X_B} C_{X_C}}$ are heat effects of the solution of one mole of the components and the phase in the Al bath at temperature T.

In this study, the heat effect of the dissolution of the binary and ternary phases $\Delta H^{ef}_{A_{X_A} B_{X_B} C_{X_C}}$ and $\Delta H^{ef}_{A_{X_A} B_{X_B}}$ were measured. The heat effects of the solution of the components $\Delta H^{ef}_{A_{X_A}}$, $\Delta H^{ef}_{B_{X_B}}$, $\Delta H^{ef}_{C_{X_C}}$ were taken from our earlier works [24, 25]. They were determined by the same calorimeter and at the same temperature. In this work, solid iron, nickel and titanium at room temperature was assumed as the reference state. The experiments were carried out with the use of a high temperature calorimeter, whose scheme was shown in [24, 25].

The Fe_2Ti phase was obtained by means of melting high purity metals (min. 99.99 wt. %) delivered by Alfa Aesar in MgO crucibles, in a glove-box with a protective atmosphere of high purity argon, in which the amounts of impurities of O_2 and H_2O were much lower than 1 ppm and N_2 was removed in a high temperature reactor, filled with a Ti-sponge. After melting the metals, the liquid alloy was thoroughly mixed and next it was cooled together with the oven.

The binary FeTi and the ternary $FeNiTi_2$ phase were prepared by levitation melting of the metals.

The phase samples were studied by X-ray and scanning electron microscopy. The electron diffraction study of the FeTi phase showed the presence of very small amounts of a Ti-rich phase in the sample. The latter was so small that it was impossible to identify it by the X-ray study. It means that the amounts of the mentioned phase were really very low and they should not considerably influence the results of the calorimetric investigations. The X-ray diffraction patterns of the Fe_2Ti and FeTi phases are shown in Figs. 5 and 6.

The X-ray structural study of the $FeNiT_2$ phase (Fig. 7) confirmed its presence mainly in the sample. Also 7 wt. % of iron what was considered in the calculations of the formation enthalpy of this intermetallic phase.
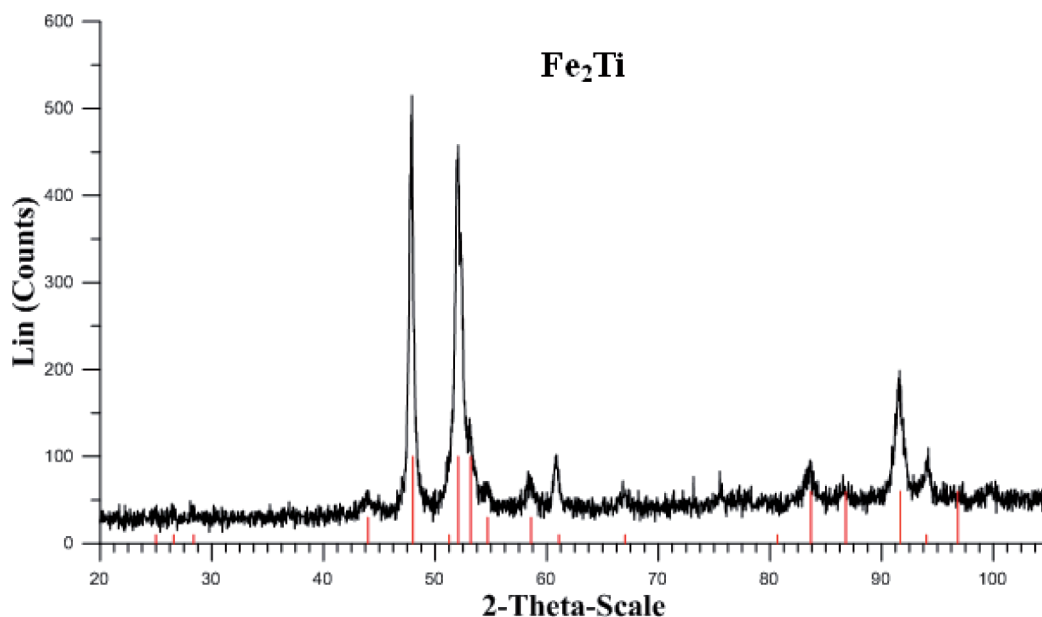

Fig. 5. X-ray diffraction pattern of the Fe_2Ti phase (black line) with the standard pattern (red line)
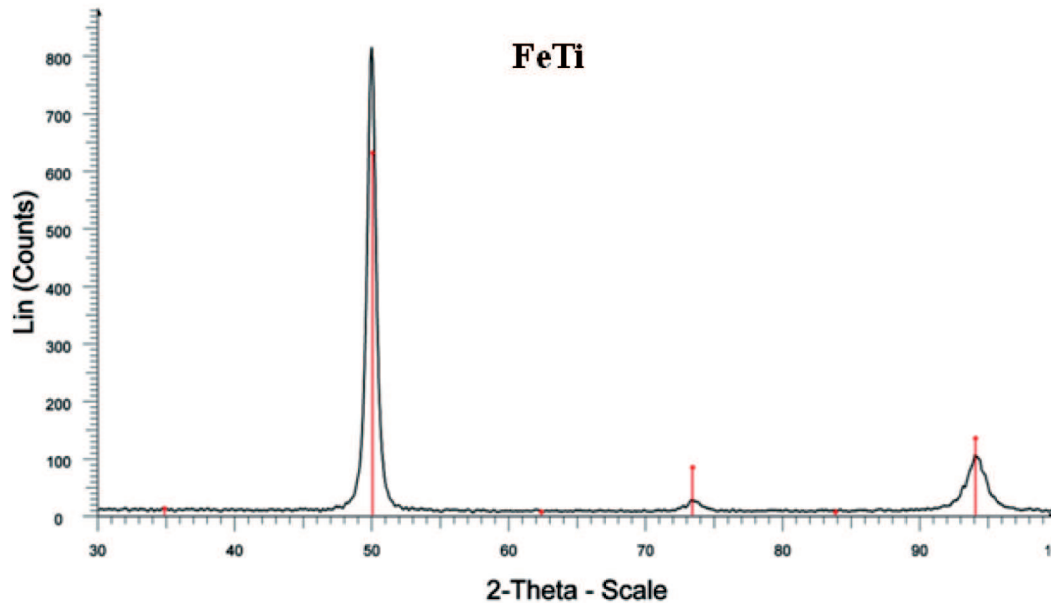
Fig. 6. X-ray diffraction pattern of the FeTi phase (black line) with the standard pattern (red line)
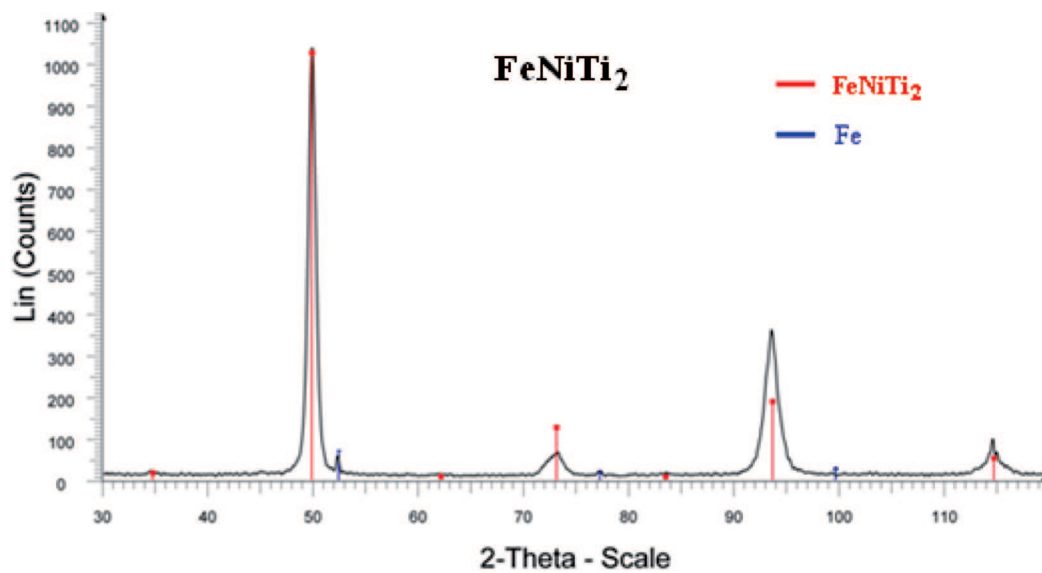
Fig. 7. X-ray diffraction pattern of the FeNiTi$_2$ phase (~7 wt. % Fe. Red line – FeNiTi$_2$ standard, blue lines – Fe standard)

TABLE 1

Comparison of the lattice parameter for the Fe-Ni-Ti intermetallic phases obtained in this work and from the literature

Phase	Lattice parameter nm			
	a	b	c	References
FeTi	0.299255	0.299255	0.299255	[This study]
	0.29789	0.29789	0.29789	[26]
Fe$_2$Ti	0.4785	0.4785	0.7799	[This study]
	0.4785	0.4785	0.7799	[27]
FeNiTi$_2$	0.300366	0.300366	0.300366	[This study]
	0.2985	0.2985	0.2985	[28]

3. Results of calorimetric study

The measurement of the formation enthalpy by the solution calorimetric method is a comparative one and it is based on the assumption that the area under the line of the measured calorimetric signal is the same for the same heat effect. And so, the calibration of the calorimeter is a very important procedure having a considerable influence on the measurement result. It allows to determine the calibration constant used in the calculation of the heat effect of the dissolution of the samples in the bath. In this study, the calorimetric constant was obtained with the application of aluminium samples in every experimental run.

The thermochemical data of the intermetallic phase components used in the calculation of the formation enthalpy and the calorimetric constant were taken from the SGTE Substances Database of 2001, update: March 1, 2002 applied in Thermo-Calc Software.

The results of the limiting heat of the solution of nickel, iron and titanium in the liquid aluminium used in the calculations of the formation enthalpy of the studied binary and ternary phases are presented in Table 2. They were measured in the same calorimeter at the time of on the occasion of determining the formation enthalpy of the intermetallic phases from the Ni-Ti and Fe-Ni systems [24, 25].

The formation enthalpy of the FeTi and Fe_2Ti phases are presented in Table 3 and 4, respectively, and in Table 5 and in Fig. 8 there are shown all available in the literature experimental values and these calculated using the optimized thermodynamic parameters obtained in the course of the critical evaluation of the Fe-Ti phase diagram.

TABLE 2

Heat of solution of Fe, Ni and Ti in liquid aluminium

Metal	Melting point K	Temperature K	ΔH_i^0 kJ/g · atom	References
Fe	1811	1158±2	-123.1±2.3	[25]
		1273±2	-120.0±0.7	
		1383±2	-113.9±2.5	
Ni	1728	1273±2	-150±0.4	[24]
Ti	1943	1273±2	-128.8±0.7	

TABLE 3

Heat effects of the solution of the Fe_2Ti phase in an Al bath at 1270±2K
and formation enthalpy of the Fe_2Ti phase at 298 K

Phase	Temperature K	Measurement number	Heat effect ΔH^{ef} kJ/mole of atoms	Formation enthalpy $\Delta_f H$ kJ/mole of atoms
Fe_2Ti	298	1	-49.0	-27.2±1.3
		2	-49.2	
		3	-50.0	
		4	-49.1	
		5	-47.4	
		Average	-48.9	
		Standard Dev.	0.9	

TABLE 4

Heat effects of the solution of the FeTi phase in an Al bath at 1270±2K and formation enthalpy the of Fe_2Ti phase at 298 K

Phase	Temperature K	Measurement Nr	Heat effect ΔH^{ef} kJ/mole of atoms	Formation enthalpy $\Delta_f H$ kJ/mole of atoms
FeTi	298	1	-54.4	-22.5±1.4
		2	-55.9	
		3	-54.7	
		Average	-55.0	
		Standard Dev.	0.8	

TABLE 5

Experimental and calculated data of the formation enthalpy of FeTi and Fe_2Ti available in the literature

Phase	$\Delta_f H$ kJ/mol of atoms	T K	Ref.	$\Delta_f H$ kJ/mol of atoms	T K	Ref.
	Experiment			Calculation		
FeTi	-22.5±1.4	298	This study	-22.2	298	[5]
	-20.3±0.6	298	[12]	-27.5	1450	
	-31.0±1.0	1450	[10]	-27.3	1513	
	-31.0±1.3	1440	[11]	-24.4	298	[7]
	-27.8±4	1513	[2]	-31.7	1450	
	Calculation			-31.6	1513	
	-19.2	298	[4]	-22.6	298	[8]
	-24.5	1450		-29.9	1450	
	-24.3	1513		-29.8	1513	
	-18.4	298	[29]	-20.3	298	[1]
	-25.7	1450		-24.8	298	[30]
	-25.7	1513		-26.8	0	[31]
Fe_2Ti	Experiment			Calculation		
	-27.2±1.3	298	This study	-31.8	1514	[5]
	-27.6±1	1514	[10, 11]	-34.5	1413	
	-25.4±2	1413	[2]	-31.5	1514	[7]
	Calculation			-33.9	1413	
	-25.7	298	[1]	-26.9	1514	[8]
	-34.2	1413	[4]	-29.3	1413	
	-29.8	1514	[29]	-21.9	298	[30]
	-31.8	1413				

Analyzing the data in Table 5, one can notice that the values measured by solution calorimetric method (this study) and the direct reaction method by Gachon et al. [10, 11] for the Fe_2Ti phase are almost the same and about -2 kJ/mole of atoms more exothermic than the value determined by Dinsdale et al. [2]. However, taking in to account the experimental errors, one can conclude that this mentioned data are in good agreement.

From all the shown values of the formation enthalpy of the Fe_2Ti phase obtained in the process of the optimization the thermodynamic properties for the phase equilibria calculations, only these cited in [1] and [8] as

well as the values calculated with the use of the Miedema's model [30] are different of less than 3 kJ/mole of atoms from those determined by the experimental calorimetric methods [this study, 10, 11]. The other ones are much more exothermic – from 3 to 6 kJ/mole of atoms.

In the case of the FeTi phase, only the formation enthalpy measured by Kubaschewski and Dench [12] is comparable with that obtained in this work, and the difference between the cited data is a bit higher than 2 kJ/mole of atoms. However, taking into consideration the cited experimental errors, one can state that they are in excellent agreement, similarly to those estimated by [1, 5, 8]. The other experimental data obtained by [2, 10, 11] by the direct reaction technique and at high temperatures are much more exothermic – by about 5-9 kJ/mole of atoms. The analyses of the calculated formation enthalpy data also shows considerable discrepancies between them, both at low and high temperatures, and the differences reach the values from about 4 to 7 kJ/mole of atoms. The formation enthalpy calculated from the Miedema model at room temperature equals -24.8 kJ/mole of atoms and it is more exothermic than that determined in this work, – by about 2 kJ/mole of atoms and also, by about 0.4-6.4 kJ/mole of atoms when compared with the values given by [4, 5, 7, 8, 29].

The determined heat effects of the solution for the FeNiTi$_2$ phase and the formation enthalpy $\Delta_f H$ of this phase calculated from equation 1 are presented in Table 6, while Fig. 9 shows the comparison between the data of the NiTi, FeTi and FeNiTi$_2$ phase. Tables 7 and 8 present the formation enthalpy of the phases from the Ni-Ti [24] and Fe-Ni [25] systems, for comparison's sake. These data were obtained with the use of the same apparatus, operating at IMIM PAS in Kraków. As it can be seen, the formation enthalpy of the ternary FeNiTi$_2$ phase is more exothermic than that of the binary NiTi and FeTi phases, and its value is about 3 kJ/mole of atoms lower than that for NiTi (Table 6).
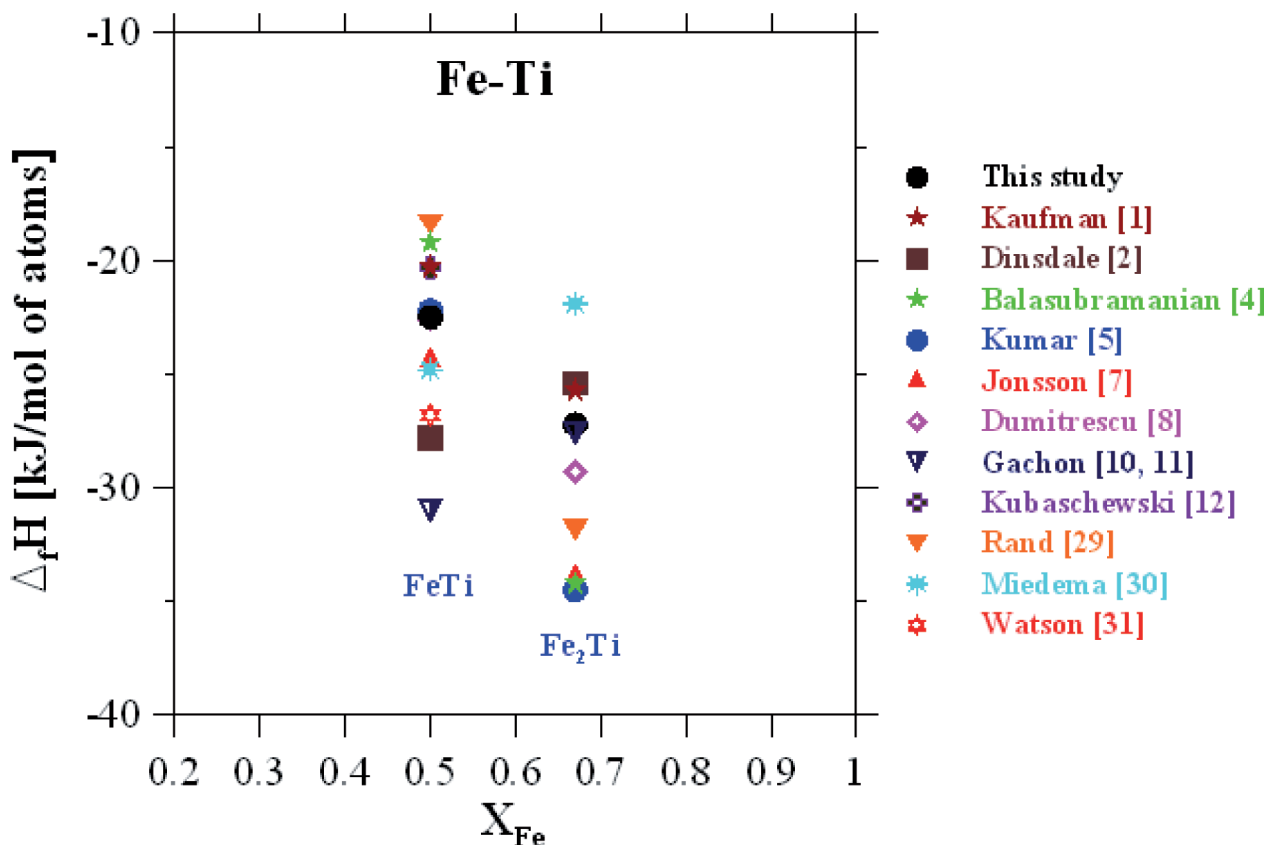

Fig. 8. Formation enthalpy data of the FeTi and Fe$_2$Ti intermetallic phases obtained by the calorimetric experimental technique, calculated from the model and obtained as a result of the calculations of the Fe-Ti phase diagram [1, 2, 4, 5, 7, 8, 10-12, 29-31]

TABLE 6

Formation enthalpy of the FeNiTi$_2$ intermetallic phase at 300 K. The Al bath temperature equalled 1277±2K

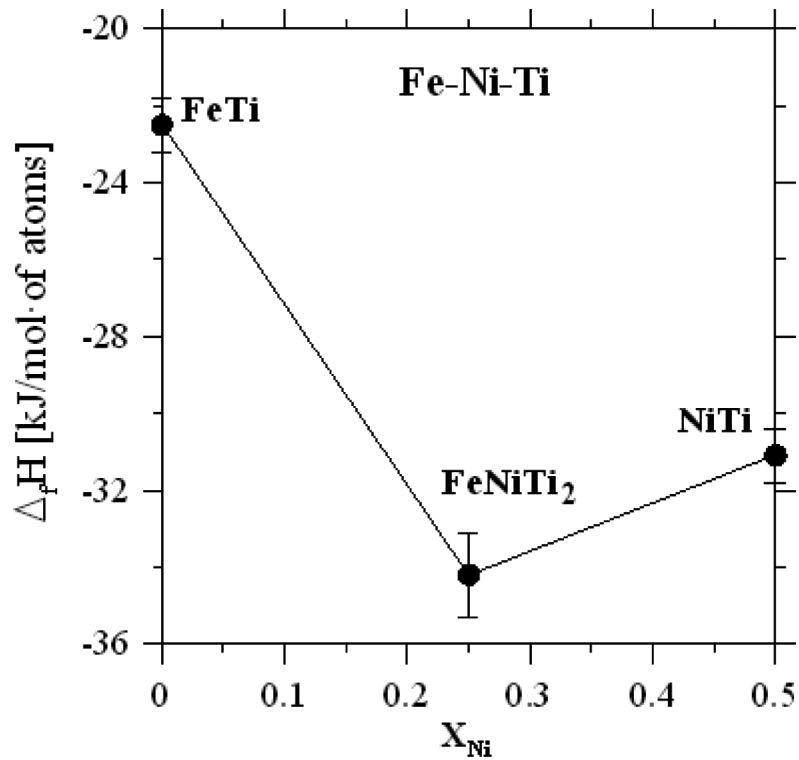| Phase	Temperature K	Measurement Number	Heat effect ΔH^{ef} kJ/mole of atoms	Formation enthalpy $\Delta_f H$ kJ/mole of atoms
FeNiTi$_2$	300	1	-51.94	-34.2±1.3
		2	-50.83	
		3	-52.18	
		Average	-51.6	
		Standard Dev.	0.7	

Fig. 9. Composition dependence of the formation enthalpy of the Fe-Ni-Ti (B2) intermetallic phase

TABLE 7

Formation enthalpy of the intermetallic phases from the Ni-Ti system [24]

System	Phase	$\Delta_f H$ kJ/mol of atoms
Ni-Ti	Ni$_3$Ti	-43.8±1.6
	NiTi	-31.1±1.1
	NiTi$_2$	-25.3±1.7

TABLE 8

Formation enthalpy of the intermetallic phases from the Fe-Ni system [25]

System	Phase	$\Delta_f H$ kJ/mol of atoms		
		FeNi$_{80}$	FeNi$_{73.5}$	FeNi$_{70}$
Fe-Ni	FeNi$_3$	-6.9±1.9	-7.2±1.2	-7.5±1.5

4. Summary

Two methods were applied for the preparation of the phases from the Fe-Ti and Fe-Ni-Ti systems. The phases $FeNiTi_2$ and FeTi were prepared by levitation melting and the preparation of the Fe_2Ti phase was carried out by melting the metals in a resistant oven, in a MgO crucible and in a glove-box with a protective atmosphere of high purity argon. In the case of the first method, the liquid alloy was cooled very fast in a metallic mould and in the case of the other one, the alloys were cooled to the room temperature for many hours together with the oven.

The X-ray diffraction study of the FeTi and Fe_2Ti phases showed that the phases were characterized by a suitable structure; therefore they were not annealed and they were used for the preparation of the samples for the calorimetric investigations. In the case of the ternary $FeNiTi_2$ phase, 7 wt. % of Fe was found and this was taken into account in the calculation of the formation enthalpy of the cited phase.

The solution calorimetric method was applied for the determination of the formation enthalpy of the intermetallic phases from the binary Fe-Ti and ternary Fe-Ni-Ti systems. The heat effects of the Fe, Ni and Ti solution in the aluminium measured earlier with the use of the same calorimeter were applied in the calculations of the formation enthalpy of the studied phases, and they are equal to: -27.2±1.3 kJ/mole atoms for Fe_2Ti, -22.5 ±1.4 kJ/mole atoms for FeTi and -34.2±1.3 kJ/mole atoms for $FeNiTi_2$.

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