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NEW FEATURES OF ENTALL DATABASE: COMPARISON OF EXPERIMENTAL AND MODEL FORMATION ENTHALPIES

NOWE FUNKCJE BAZY DANYCH ENTALL: PORÓWNANIE DOŚWIADCZALNYCH I MODELOWYCH ENTALPII TWORZENIA

This paper presents a new version of the Entall database of the thermodynamic properties of metals and their alloys. The changes are related to the thermodynamic data of new binary and ternary systems as well as the integration of the database with an application for the modeling of the formation enthalpies of intermetallic phases with the use of the Miedema model. Using this tool, calculations of the enthalpies of formation of 38 intermetallic phases from 12 binary systems were performed and a comparative analysis conducted. The results of the analysis clearly showed a weak correlation between the model and experimental data. To improve this correlation, an intermediate method of proportional change was proposed, on the basis of the measurement of the enthalpy of formation for one of the phases. The values for the other phases obtained from this indirect method should not deviate much from the experimental ones provided that before the measurements (dissolving or pulping) or after them (direct synthesis), the phase being examined should undergo structural tests, in order to confirm its dominating amount in the samples.

Keywords: COST 535, database, thermodynamic properties, Miedema model

W pracy przedstawiona została nowa wersja bazy właściwości termodynamicznych metali i stopów Entall. Modyfikacja dotyczyła z jednej strony danych termodynamicznych nowych układów dwu i trójskładnikowych a z drugiej zaadaptowania do niej opracowanego programu (kalkulatora) do modelowania entalpii tworzenia faz międzymetalicznych modelem Miedemy. Korzystając z tego nowego narzędzia wykonane zostały obliczenia entalpii tworzenia dla 38 faz międzymetalicznych z 12 układów dwuskładnikowych oraz przeprowadzona została analiza porównawcza. Wyniki analizy pokazały jednoznacznie słabą korelację między danymi modelowymi i doświadczalnymi. Dla poprawienia tej korelacji zaproponowana została pośrednia metoda proporcjonalnej zmiany w oparciu o pomiar entalpii tworzenia dla jednej z faz. Uzyskane z tej pośredniej metody wartości dla innych faz powinny niewiele odbiegać od eksperymentalnych przy spełnieniu warunku, że faza dla której wykonywane były badania została przed pomiarami (rozpuszczanie lub roztwarzanie) lub po nich (bezpośrednia synteza) poddana badaniom strukturalnym, w celu potwierdzenia jej dominującej ilości w próbkach.

1. Introduction

The significant interest in materials with an intermetallic phase matrix, where one of the metals is aluminium, contributed to the establishment of the COST 535 program (Thermodynamics of Alloyed Aluminides THALU), which was finalized in November 2007. The program was directed to the development of new alloys based on intermetallic compounds from the Al-Fe-Ni-Ti system. Its basis was the modeling of the thermodynamic properties of aluminides by way of evaluating the existing data as well as obtaining new data by experimental tests. As enthalpy of formation constitutes one of the most important thermodynamic quantities used in the calculations of phase diagrams and the most accurate way of its determination is its calorimetric measurement, IMIM PAS, within the frames of the COST 535 program, performed calorimetric and microcalorimetric tests for the alloys from the Al-Fe-Ni-Ti type system. Other research programs involving investigations

of the enthalpy of formation realized at IMIM PAS include the COST 531 and COST MP0602 program. They were concentrated on tests of low- and high-melting soldering materials. However, calorimetric tests, contrary to those implemented in COST 535, constituted a very minor part of the whole research program.

The application of alloys with the matrix of intermetallic phases from binary and ternary Al-Fe-Ni-Ti systems is presented in Fig. 1. The alloys based on the Al-Fe-Ni-Ti type system are marked in blue.

The enthalpies of formation of the intermetallic phases from the Al-Ni and Al-Ti systems were examined by Rzyman et al. [1-3] by the methods of dissolution and a direct synthesis. Only in the case of the Al₃Ti phase, the results obtained from both calorimetric methods were in agreement, while for the remaining phases from the Al-Ti system, the differences were ~5 kJ/mol atom for the AlTi phase and ~10 kJ/mol atom for the AlTi₃ phase. It was proven that, during the reaction of

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titanium and aluminium powders, regardless of the applied proportion, the first obtained product was the Al_3Ti phase [4, 5]. This is why the data for the enthalpy of formation for the Al_3Ti phase obtained from both methods are similar, whereas for the $AlTi$ and $AlTi_3$ phases, we can observe differences in the enthalpy of formation values, which points to the fact that the reaction of the phase formation was not finalized in the calorimeter, this being the reason for the difference in the results obtained from these two methods.

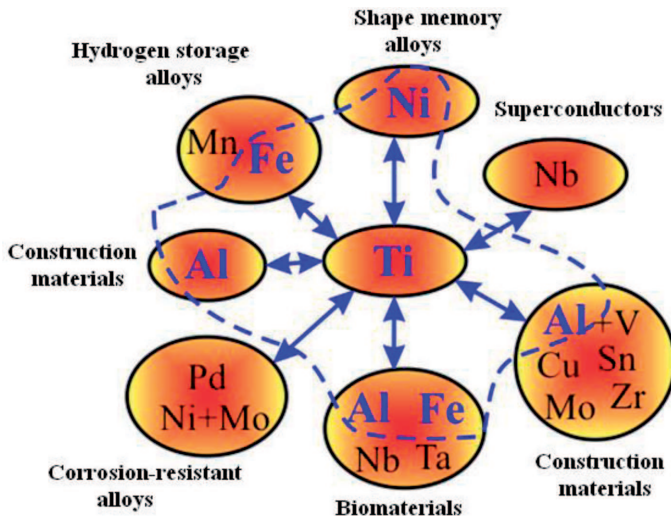


Fig. 1. Application of titanium-based alloys

The calorimetric data of the enthalpy of formation of the intermetallic phases from the Al-Fe-Ni-Ti type systems obtained by Rzyman et al. [1-3] as well as in our own studies [6-10] was introduced into the Entall database [11], which is available at www.entall.imim.pl.

The aim of this work is an analysis of the agreement of the model and experimental values of the enthalpy of formation of the intermetallic phases present in the binary alloys for which IMIM PAS performed the preparation, phase analysis and calorimetric measurements as well as a presentation of a new tool, that is a calculator of the Miedema model of the enthalpies of formation, and finally, a demonstration of the operation of the Entall database and the technique of data acquisition.

2. Description of the new Entall database

The main assumption made while developing the web application which makes available the content of the Entall database was the creation of a high-interactive and intuitive user interface. Its central element is a chart with four input parameters:

- system U,
- thermodynamic property W,
- independent variable for which the thermodynamic property is determined X (e.g. mole fraction or temperature),
- source materials from which the data originates A.

On defining the query to the database, the user sees an empty diagram with missing values of the parameters: U, W, X and A. The Entall application (Fig. 2) guides the user through the consecutive steps and when, in a certain context, only one

value of the parameter is available, the application selects it automatically.

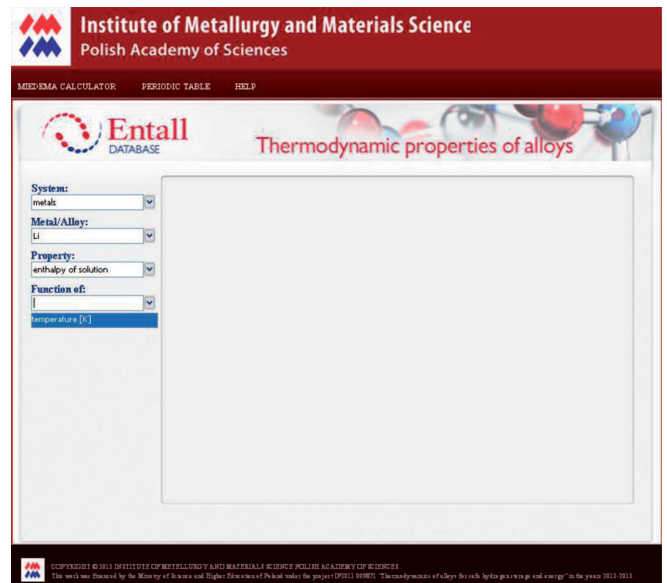


Fig. 2. Presentation of the selection window for the values of the parameters: U, W, X and A (system, property, independent variable, author)

The database does not include figures. Each point which can occur in a particular diagram is represented as a separate entry (record). This allows the user to compose diagrams which precisely meet their expectations (e.g. combining several data sources in one diagram, displaying the points which meet the assigned criterion).

The original Entall database published in 2013 [11] contained thermodynamic data for 5 binary systems: Li-Si, Ag-Ca, B-Li, Ca-Li and Al-Li. Figures 3 and 4 present (for Li-Si system) the way of identifying the values visible in the diagram and the existing possibility to calculate other thermodynamic functions on the basis of measurement of the electromotive forces included in the Entall database [11], respectively.

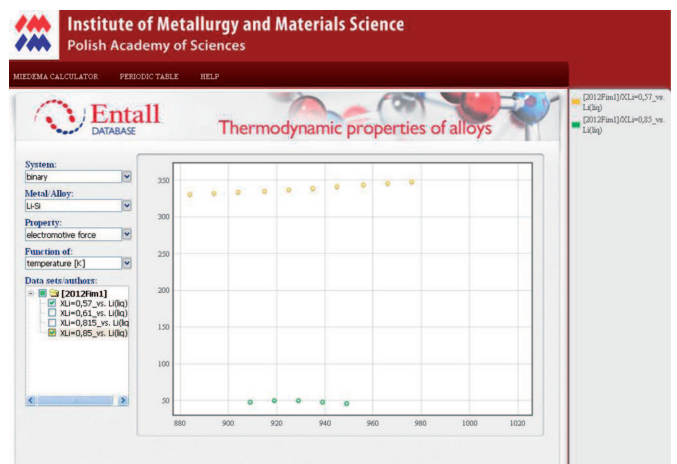


Fig. 3. Presentation of the electromotive forces for selected mole fractions of lithium in the Li-Si system [12]

Currently, the database contains data for 12 metals, 16 binary systems and 7 ternary systems presented in Table 1. It also provides information on the data source, which is pre-

sented on the example of the enthalpy of formation of the intermetallic phases from the Al-Ni system (Fig. 5).

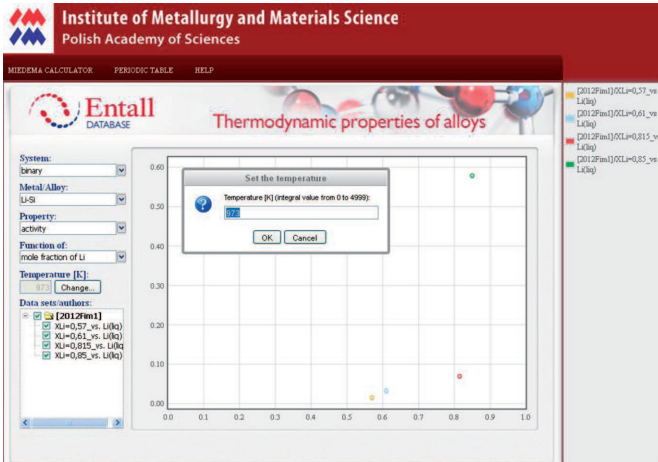


Fig. 4. Method of introducing temperature values with the objective of calculating Li activity in Li-Si system on the basis of electromotive force data [12] in Entall database

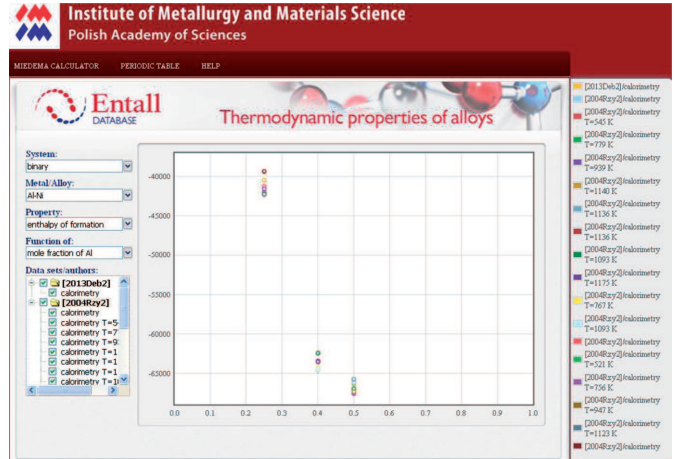


Fig. 5. Entall – enthalpy of formation of intermetallic phases from Al-Ni [1, 3, 10]

3. Miedema Model

In the case when we do not have at our disposal the experimental data of the enthalpy of formation of the intermetallic phases, we can apply modeling. One of the semi-empiric models allowing for the calculation of the value of the enthalpy of formation in binary systems is the Miedema model. The history of this model goes back to the 1970s, when Miedema and his co-workers presented a model allowing for the prediction of the enthalpies of formation for binary alloys [13-19], which can be calculated by applying equation (1).

$$\Delta_f H_{X_A X_B} = \frac{x_A V_{A(\text{alloy})}^{\frac{2}{3}} \cdot f_B^A [-P(\Delta\Phi^*)^2 + Q(\Delta n_{ws}^{\frac{1}{3}})^2 - R]}{[(n_{ws}^A)^{\frac{-1}{3}} + (n_{ws}^B)^{\frac{-1}{3}}]} + x_A \Delta H_A^{\text{trans}} + x_B \Delta H_B^{\text{trans}} \quad (1)$$

In the case of the enthalpy of formation of the intermetallic phases in binary systems, the particular terms of equation (1) can be calculated by way of application of equations 2-5.

$$f_B^A = c_B^S \cdot [1 + 8 \cdot (c_A^S \cdot c_B^S)^2] \quad (2)$$

$$c_A^S = \frac{x_A V_A^{\frac{2}{3}}}{x_A V_A^{\frac{2}{3}} + (1-x_A) V_B^{\frac{2}{3}}} \quad (3)$$

$$c_B^S = 1 - c_A^S \quad (4)$$

$$V_{A(\text{alloy})}^{\frac{2}{3}} = V_A^{\frac{2}{3}} \cdot [1 + a \cdot c_A^S \cdot f_B^A \cdot (\phi_A^* - \phi_B^*)] \quad (5)$$

where:

ϕ_A^*, ϕ_B^* – electronegativity of elements „A” and „B”,
 n_{ws}^A, n_{ws}^B – densities of electrons at Wigner-Seitz cell boundary,

V_A, V_B – molar volume of components „A” and „B”,
 P, Q, R, α, a, cf – empiric constants determined by Miedema et al. [19],

$$\frac{Q}{P} = 9.4,$$

$\alpha = 0.73$ for liquid alloys, whereas $\alpha = 1$ for solid alloys,
 $a, cf = 0.14$ for alkaline metals, $a, cf = 0.1$ for 2-valence metals,

TABLE 1

Metals and alloys whose thermodynamic properties are included in the Entall database

Metals	Binary systems	Ternary systems
Ag	Ag-Ca	Al-Co-Ni
Au	Ag-Sn	Al-Cr-Ni
Ca	Al-Fe	Al-Cu-Ni
Co	Al-Li	Al-Fe-Ni
Cr	Al-Ni	Al-Ni-Ti
Cu	Al-Ti	Al-Ni-V
Fe	Au-Sn	Fe-Ni-Ti
Li	B-Li	
Ni	Ca-Li	
Si	Fe-Ni	
Ti	Fe-Ti	
V	Li-Bi	
	Li-Pb	
	Li-Si	
	Li-Sn	
	Ni-Ti	

We should point out one more aspect connected with access to the numerical values. In order to obtain a numerical value for a given point (measuring value), it is enough to place the cursor on the point in the diagram to display the corresponding experimental value next to it. Thus we can see that the Entall database not only shows the location of the experimental values between the axes but also provides the user with the experimental numerical data.

a.cf = 0.07 for 3-valence metals 3 and for Ag, Au, and Cu. In other cases, a.cf = 0.04.

P – depends on whether „A” and „B” are transition or non-transition metals,

P = 12.3, when „A” is a transition metal and „B” is a non-transition metal,

P = 14.1, when „A” and „B” are transition metals,

P = 10.6, when „A” and „B” are non-transition metals.

R/P = 0 in the case when both „A” and „B” are transition or non-transition metals. In the case when one is a transition metal and the other is a non-transition metal, R is determined with the use of the following formula:

$$R = R.cf_{(A)} \cdot R.cf_{(B)} \quad (6)$$

ΔH_A^{trans} , ΔH_B^{trans} – compounds whose one component is a semiconductor or a non-metal, requiring a special treatment of the Miedema model. For these elements, enthalpies of transformation, ΔH_A^{trans} or ΔH_B^{trans} , are introduced. This type of enthalpy describes the energy which is required to transform the element from its standard state into a hypothetical metallic state.

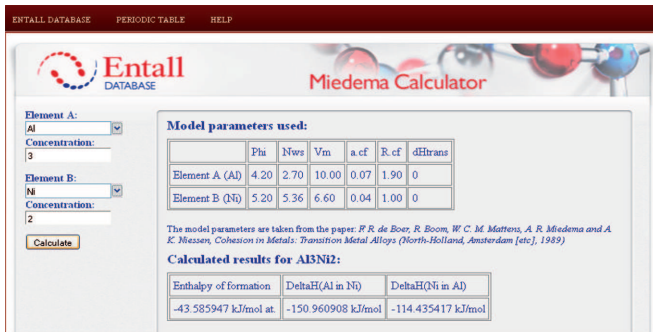


Fig. 6. The Miedema calculator in the Entall database. The calculated value for the Al_3Ni_2 intermetallic phase is shown in the bottom table and the model parameters [19] used in the calculations are presented in the upper table. <http://www.entall.imim.pl/calculator>

The above equations and assumptions of the Mediema model constitute the basis for the modeling module (calculator) created by the authors of this work, which expands the potential of applications of Entall [11]. The application window shown in Fig. 6 presents the values of the enthalpy of formation of the Al_3Ni_2 phase, the heat of solution of Ni in Al and Al in Ni, which are calculated by means of equations (7-8), as well as the parameters of the Mediema model which were used in the calculation of the values of the enthalpy of formation of intermetallic phases belonging to the Al-Ni system.

$$\Delta H_{A \text{ in } B} = \frac{2V_{B(\text{alloy})}^{\frac{2}{3}} \cdot [-P(\Delta\Phi^*)^2 + Q(\Delta n_{ws}^{\frac{1}{3}})^2 - R_{(1)}]}{[(n_{ws}^A)^{-\frac{1}{3}} + (n_{ws}^B)^{-\frac{1}{3}}]} \quad (7)$$

$$\Delta H_{B \text{ in } A} = \frac{2V_{B(\text{alloy})}^{\frac{2}{3}} \cdot [-P(\Delta\Phi^*)^2 + Q(\Delta n_{ws}^{\frac{1}{3}})^2 - R_{(1)}]}{[(n_{ws}^A)^{-\frac{1}{3}} + (n_{ws}^B)^{-\frac{1}{3}}]} \quad (8)$$

where: $R_{(1)} = 0.73R$.

4. Discussion

The values of the enthalpy of formation of intermetallic phases calculated by means of the Mediema model (Eq. 1-8) and those measured in our own studies with the use of 3 different calorimetric methods, i.e. the method of dissolving, pulping and direct synthesis, for 12 different binary systems are compiled in Table 2. In all the cases, one can observe significant absolute or percentage differences between the calculated and measured values of the enthalpy of formation, which is always connected with one of the phases. This discrepancy is visible in the case of the three analyzed systems: Al-Fe, Fe-Ti and Ni-Ti, for which the minimal values of the enthalpy of formation from the model calculations are observed for phases $Al_{38}Fe_{62}$, FeTi and NiTi, whereas the measured minimal values of the enthalpy of formation are observed for phases Al_5Fe_2 , Fe_2Ti and Ni_3Ti .

In the analysis of the differences between the model and experimental values of the enthalpy of formation in Table 2, we can see that they vary between a few and a few tens of kJ/mol atoms, and the biggest difference is observed for the Li-Si system, where, for phase $Li_{13}Si_4$, the absolute value of the difference equals 27.3 kJ/mol atom.

The presented comparative analysis of the model and experimental values of the enthalpy of formation of intermetallic phases confirms that very often the Mediema model predicts both the values of the enthalpy of formation and the phase for which its value is minimal, with a very low accuracy. That is why the application of model values of the enthalpy of formation of intermetallic phases in other thermodynamic calculations should take place only in the case where there is absolutely no available experimental data. We can, however, propose an intermediate procedure consisting in correcting the model values by way of an experimental test of one of the phases, e.g. that of the lowest enthalpy of formation, and proportionally increasing or decreasing the values of the remaining phases from the analyzed system. This procedure will be explained in the next paper.

TABLE 2

Values of enthalpy of formation of intermetallic phases – experimental and calculated by the Miedema model – presented with the calculated absolute values of the differences

System	Phase	Enthalpy of formation [kJ/mol of atoms]		Experimental method	Absolute value of difference [kJ/mol of atoms]	References
		Miedema model [17]	Experiment			
Ag-Ca	Ag ₉ Ca ₂	-23.7	-14.7	Solution calorimetry	9	[20]
	Ag ₇ Ca ₂	-28.8	-18.8		10	[21]
	Ag ₂ Ca	-39.9	-24.1		15.8	
	AgCa	-43.0	-28.0		15	
	Ag ₃ Ca ₅	-35.1	-26.7		8.4	
	AgCa ₃	-23.6	-11.8		11.8	[20]
Al-Fe	Al ₂ Fe	-25.2	-27.8	Solution calorimetry	2.6	[8]
	Al ₅ Fe ₂	-21.9	-30.5		8.6	
	Al ₃₈ Fe ₆₂	-30.3	-27.1		3.2	This work
Al-Li	AlLi	-4.9	-20.7; -20.4	Solution calorimetry	15.8; 15.5	[22]
	Al ₂ Li ₃	-4.7	-19.1		14.4	
	Al ₄ Li ₉	-3.9	-15.1		11.2	
Al-Ni	AlNi	-48.4	-66.3	Solution calorimetry	17.9	[10]
			-66.1		17.7	[3]
			-67.0 (at 545 K)		18.6	
			-66.9 (at 779 K)		18.5	
			-67.5 (at 939 K)		19.1	
			-67.3 (at 1140 K)		18.9	
			-65.7 (at 1136 K)	17.3	Direct synthesis	
	Al ₃ Ni ₂	-43.6	-63.5	Solution calorimetry	19.9	[3]
			-64.3 (at 767 K)		20.7	
			-64.5 (at 1093 K)		20.9	
			-63.4 (at 1093 K)	19.8	Direct synthesis	
			-62.4 (at 1175 K)	18.8		
	AlNi ₃	-33.5	-41.3	Solution calorimetry	7.8	[3]
			-42.0 (at 521 K)		8.5	
			-41.6 (at 756 K)		8.1	
-42.2 (at 947 K)			8.7			
-42.3 (at 1123 K)			8.8			
-39.4 (at 1123 K)			5.9		Direct synthesis	
-40.5			7	Solution calorimetry	[10]	

Al-Ti	AlTi ₃	-39.2	-29.9	Solution calorimetry	9.3	[2]
			-20.3	Direct synthesis	18.9	
	AlTi	-61.0	-41.9	Solution calorimetry	19.1	
			-37.1	Direct synthesis	23.9	
	Al ₂ Ti	-50.3	-38.6	Solution calorimetry	11.7	
	Al ₃ Ti	-39.0	-37.8		1.2	
-37.3 (at 1031 K)			1.7			
Ag-Sn	Ag ₃ Sn	-5.2	-3.0	Solution calorimetry	2.2	[23]
Au-Sn	Au ₅ Sn (Au ₈₉ Sn ₁₁)	-6.7	-1.3	Solution calorimetry	5.4	[24]
	Au ₅ Sn	-10.1	-5.8		4.3	
	AuSn	-21.1	-15.4		5.7	
	AuSn ₂	-16.3	-14.2		2.1	[25]
	AuSn ₄	-9.9	-7.9		2	
Ca-Li	CaLi ₂	-1.0	-2.9; -2.7	Solution calorimetry	1.9; 1.7	[24]
Fe-Ni	FeNi ₇₀	-1.8	-7.5	Solution calorimetry	5.7	[7]
	FeNi _{73.5}	-1.6	-7.2		5.6	
	FeNi ₈₀	-1.2	-6.9		5.7	
Fe-Ti	Fe ₂ Ti	-21.9	-27.2	Solution calorimetry	5.3	[9]
	FeTi	-24.8	-22.5		2.3	
Li-Si	Li ₂₂ Si ₅	-2.4	-24.4	Reaction calorimetry	22	[27]
	Li ₁₃ Si ₄	-3.1	-30.4		27.3	[28]
	Li ₇ Si ₃	-3.9	-29.4		25.5	
	Li ₁₂ Si ₇	-4.1	-25.6		21.5	
Ni-Ti	Ni ₃ Ti	-36.2	-43.8	Solution calorimetry	7.6	[6]
	NiTi	-51.2	-31.1		20.1	
	NiTi ₂	-39.5	-25.3		14.2	

5. Conclusions

The proposed modification of the thermodynamics database Entall concerns both an expansion of the number of available systems and the possibility of modeling enthalpies of formation of intermetallic phases by means of the Mediema model. The performed analysis of the agreement of the model and experimental values of the enthalpy of formation of 12 binary systems showed significant discrepancies between those groups of data, which reach even a few dozen of kJ/mol atoms or a few hundred percent. This conclusion is drawn from the comparative analysis of the phases from the binary systems belonging to the Al-Fe-Ni-Ti system, four systems applied in energy storage (Ag-Ca, Al-Li, Li-Si, Ca-Li) and two systems (Ag-Sn, Au-Sn) from the group of lead-free solders.

In the authors' opinion, an improvement of the predictability of the enthalpy of formation of phases by way of modeling requires a continuation of the works on the modification of the Mediema model based mainly on those experimental tests in which the samples – before or after the tests – were structurally characterized and they confirmed the structure of the examined phase.

The proposed method of correcting the model data by way of experimental determination of the enthalpy of formation of one of the phases of the given binary system will make the corrected model values significantly closer to the experimental ones and thus to the actual values as well.

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