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**THERMODYNAMIC ANALYSIS OF BINARY METAL SYSTEMS
USING DIFFERENTIAL THERMAL ANALYSIS**

**ANALIZA TERMODYNAMICZNA PODWÓJNYCH UKŁADÓW METALICZNYCH
PRZY POMOCY RÓŻNICOWEJ ANALIZY CIEPLNEJ**

Brief review on history and development of DTA as thermal analysis method; with special aspect to the application of quantitative thermodynamic analysis for binary metal systems, are presented in this paper. Importance of the calibration constant determination is pointed out, as well as its changeable value depending on composition of the investigated system. Results obtained using DTA method in thermodynamic analysis of some binary systems are also given and compared with data measured by other experimental techniques (calorimetry, EMF measurements) or calculated by thermodynamic predicting methods. Good agreement reached between these results enables to the correctness of application of quantitative DTA.

W pracy przedstawiono krótki przegląd historii i rozwoju DTA jako metody analizy cieplnej ze specjalnym uwzględnieniem zastosowania do ilościowej analizy termodynamicznej podwójnych układów metalicznych.

Podkreślono wagę poprawnego wyznaczenia wartości stałej kalibracyjnej oraz jej zależności od składu badanego układu. Przedstawiono wyniki uzyskane metodą DTA w odniesieniu do kilku układów podwójnych w porównaniu z wynikami pomiarów innymi metodami (kalorymetrycznymi; EMF) lub obliczonymi metodami termodynamicznymi. Dolna zgodność wyników uzasadnia poprawność zastosowania ilościowej, różnicowej analizy cieplnej.

Key words: thermal analysis, quantitative DTA, thermodynamics, binary metal systems

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1. Introduction

Although H. le Chatelier is considered to be the creator of thermal analysis [1, 2], early development of differential thermal analysis, DTA, in the sense as it is used nowadays, is connected with R. Austin's work [3] in 1989, while Russian school N.C. Kurnakov [4] and L.G. Berg, [5] did further steps in DTA development.

During sixties, ICTA (International Confederation on Thermal Analysis) has been founded and international journals, such as *Thermochimica Acta*, *Journal of Thermal Analysis* and *Thermal Analysis Abstracts*, were started. In the last decade of the twentieth century, ICTA transforms to ICTAC (International Confederation on Thermal Analysis and Calorimetry).

Industry of TA apparatus production (Mettler, Netzch, Setram, MOM, etc.) follows the development of these methods and numerous modern, usually simultaneous apparatus, which include more different TA methods at the same time (DTA is mostly presented), are produced.

2. Theoretical principles

Theoretical principles of DTA application in quantitative calorimetric determination are given in literature [6, 7], while further experimental accomplishments were presented by different authors [8–29]. The basic analytical expression of the quantitative DTA is given as

$$m\Delta H_T^\circ = gK_s \int Tdt, \quad (1)$$

where are: m — mass of the sample, ΔH_T° — reaction enthalpy, gK_s — calibration constant of the apparatus and $\int Tdt$ — area of DTA peak. It should be pointed out that calibration constant consists of two constants: g — geometric constant and K_s — heat conductivity of the sample, as was pointed out in Refs. [20, 30]. Both have influence to the correlation between endothermic or exothermic effects, which occur during the investigated process, and area of DTA peak, and this correlation plays the most important role in quantitative determination by using DTA. Dependence of calibration constant gK_s on sample mass, in the example of pure indium melting [31], is shown in Fig.1.

Commercial DTA apparatus could not be directly used for quantitative measurements of binary and ternary metal systems. For that reason, special DTA apparatus (Fig. 2) adequate for these purposes has been made [17–19, 21–29]. The sample of metals with chosen binary composition is put in the quartz tube: metal Me_1 , with lower melting temperature is positioned at the bottom of a tube, while the metal Me_2 , with higher melting temperature has to be put in a shape of a ring above metal Me_1 and attached to a quartz tube in which thermocouple is fixed. In the other tube of the same geometry, another thermocouple is put in a referent sample. Both tubes are heated in the furnace according to a appropriate program, so T and DTA curves could be obtained. Sample mass ($m_{Me_1} + m_{Me_2}$) should be lower than maximum mass up to which linear dependence $m\Delta H_T^\circ = f(S)$ (S is an area of DTA peak) is valid, so constant influence of geometrical factor g in calibration constant gK_s is still kept.

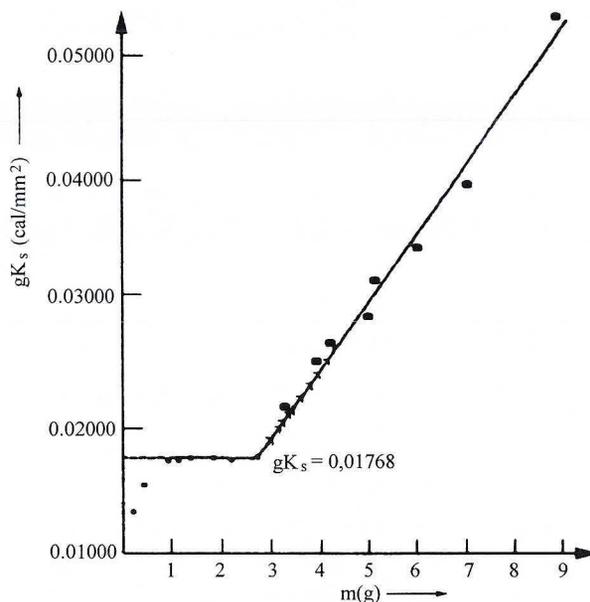


Fig. 1. gK_s dependence on sample mass for pure indium melting [31]

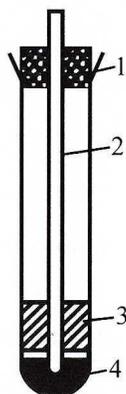


Fig. 2. Sample holder for quantitative DTA

(1 – gasket of the reaction area, 2 – protective tube for thermocouple; 3 – Me_1 , 4 – Me_2)

During the heating, metal Me_1 with lower melting temperature is firstly melted, which is recorded by the first peak at the obtained DTA curve. Further, as heating process goes on, Me_2 metal is melting at its melting temperature and at the same time, Me_2 drops into the Me_1 melt. They mix and $(Me_1 + Me_2)$ melt is formed, which is recorded by the second peak at obtained DTA curve. So, during the first melting (I), obtained DTA peak areas are proportional to the enthalpy of the process. Enthalpy of the first melting can be expressed as:

$$\Delta H_I = x_1 \Delta H_1 + x_2 (\Delta H_2 + \Delta H_{liq}), \quad (2)$$

where are: ΔH_i — melting enthalpy for the component i ; x_i — molar content of component i ; and ΔH_{liq} — enthalpy of mixing in liquid state.

After the homogenization of such formed alloy ($Me_1 + Me_2$), it solidifies up to the room temperature. Then, heating is repeated during the second melting (II). Phase transformations occurring in the solid state, as well as the alloy melting, are recorded at DTA curve. The peak areas are proportional to the following enthalpy of the second melting:

$$\Delta H_{II} = x_1 \Delta H_1 + x_2 \Delta H_2 + \Delta H_{liq} - \Delta H_{sol}, \quad (3)$$

where ΔH_{sol} presents the mixing enthalpy in the solid state, which could be obtained as a difference between Eqs. (3) and (2):

$$\Delta H_{sol} = \Delta H_I - \Delta H_{II}. \quad (4)$$

In the case of formation of an intermetallic compound from metals Me_1 and Me_2 , DTA peak is obtained during the second melting, which presents the melting of the compound. The enthalpy of the intermetallic compound, ΔH_i , is proportional to the total enthalpy of the second melting, as follows:

$$\Delta H_{II} = x_1 \Delta H_1 + x_2 \Delta H_2 + \Delta H_{liq} - \Delta H_{sol} - x_i \Delta H_i. \quad (5)$$

Determination of ΔH_i is done for the sample which responds by composition to the intermetallic compound, where $\Delta H_{sol} = 0$, and $x_i = 1$, so Eq. (5) becomes

$$\Delta H_i = \Delta H_{liq} + x_1 \Delta H_1 + x_2 \Delta H_2 - \Delta H_{II}, \quad (6)$$

while, in such a system, determination of (H_{sol} term is done as follows:

$$\Delta H_{sol} = \Delta H_{liq} + x_1 \Delta H_1 + x_2 \Delta H_2 - x_i \Delta H_i - \Delta H_{II}. \quad (7)$$

Based on the dependence: $\Delta G^m = RT \ln a_i = \Delta H_{i,liq} - T \Delta S_{i,liq}$, values of the component activities in the system could be determined. In the case of ideal solutions, expression

$$\Delta S_{id}^m = -R(x_1 \ln x_1 + x_2 \ln x_2 + \dots) \quad (8)$$

is valid. Further, Planck potential value can be expressed as follows

$$P_{x,T} = \Delta S_{x,T} - \Delta H_{x,T}/T. \quad (9)$$

Values for $R \ln a_1$ and $R \ln a_2$ at certain temperature could be determined by graphical interpretation of $P_{x,T} = f(x_i)$ and tangent construction at the Planck potential curve for different binary system compositions.

DTA is mostly considered as qualitative method, for some limitations, such as poor repeatability of the effects or causing troubles in interpretation. But, this method can be used as quantitative one, also. Investigations of N. S m a j i ć [20] and Ž. Ž i v k o v i ć [21] show that control of experimental conditions (sample mass and granulation, mass and granulation of the referent material, heat conductivity, etc.), as well as correct deter-

mination of the calibration constant, positively influence and contribute to the reproducibility of the results, which has already been proved [23, 26, 27, 30, 31]. Therefore application of DTA as quantitative method in thermodynamic analysis of binary systems is presented in this paper.

3. Results and discussion

Changes occur during the heating of alloys in binary and ternary metal systems, and can be recorded in DTA curve, if accompanied by measurable heat effects (according to the sensitivity of the used apparatus). Shape of DTA curves for the hypotetic binary system is shown in Fig. 3. according to Ref.[32]. As can be seen, shape of the curve depends on the characteristics of the transformation registered.

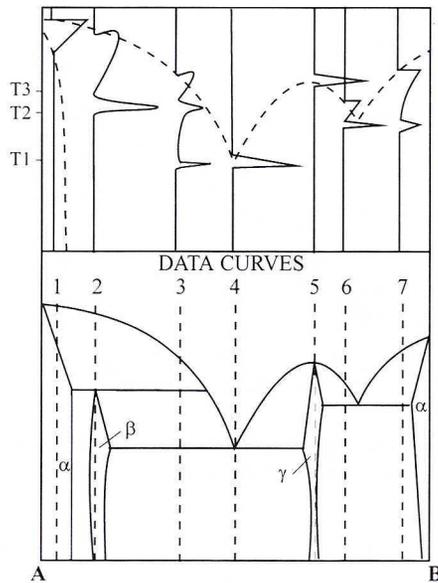
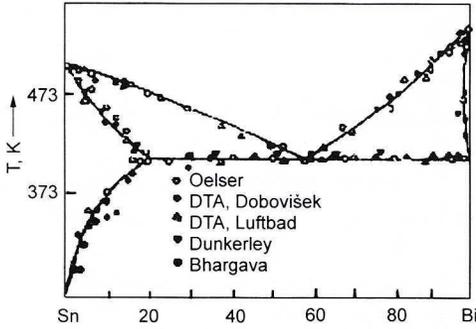


Fig. 3. Hypotetic binary system and responding DTA curves for the characteristic compositions [32]

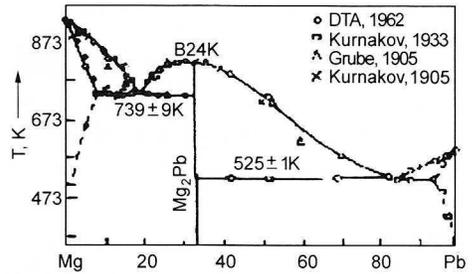
Based on DTA measurements done as described, comparative results for some phase diagrams of binary systems obtained by DTA and other methods [27, 33] are presented in Fig. 4. These results show that phase diagrams could be successfully determined by DTA.

First step in quantitative determination by DTA method for binary metal systems is a determination of calibration constant, gK_s , which is done by DTA curves recording for different masses of pure metals — constituents of the investigated system. A linear dependence of $gK_s = f(x_i)$ for all binary systems has been pointed out in literature [30]. Dependence of $gK_s = f(x_i)$ for binary eutectic systems (Pb-Sn) [30] and binary systems with coexisting liquid and solid solutions (Bi-Sb) [33] is given in Fig. 5.

a)



b)



c)

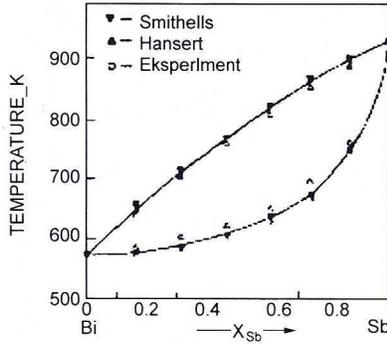


Fig. 4. Comparative results of phase diagrams determination by DTA and other methods [27, 33] (a – Sn-Bi system; b – Mg-Bi system; c – Sb-Bi system)

Characteristic DTA curves for first and second melting [30], for alloy with $x_{pb} = 0.7$ and for alloy of eutectic composition, in example of binary system Pb-Sn, are shown in Fig. 6. Using the procedure described before, and by correction of gK_s for all investigated compositions, values for ΔH_{liq} and ΔH_{sol} were obtained [30] (Fig. 7). Further, the application of Planck potential diagram enabled determination of activity values for both components in Pb-Sn system at 773 K [30], which were compared with literature data [34] obtained by emf measurements (Fig. 8). These results show good agreement, which suggest DTA method as a correct one for the quantitative determination. Similar results were obtained by using DTA for other binary systems, such as: Pb-Mg [26], Bi-Sb [33], Cd-In [31], etc.

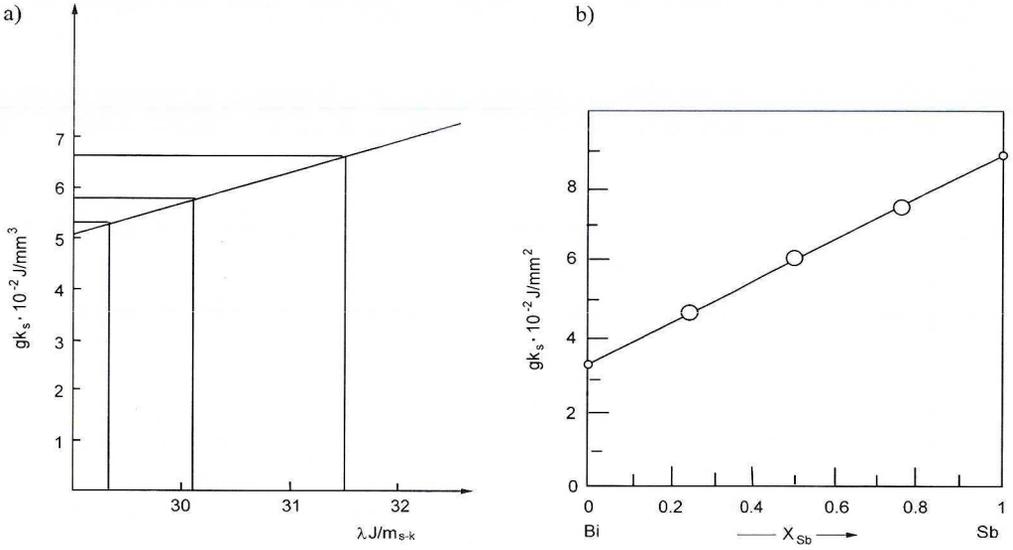


Fig. 5. Dependence of gK_s on composition of the system [30, 33]
 a) eutectic system; b) system with coexisting liquid and solid solutions

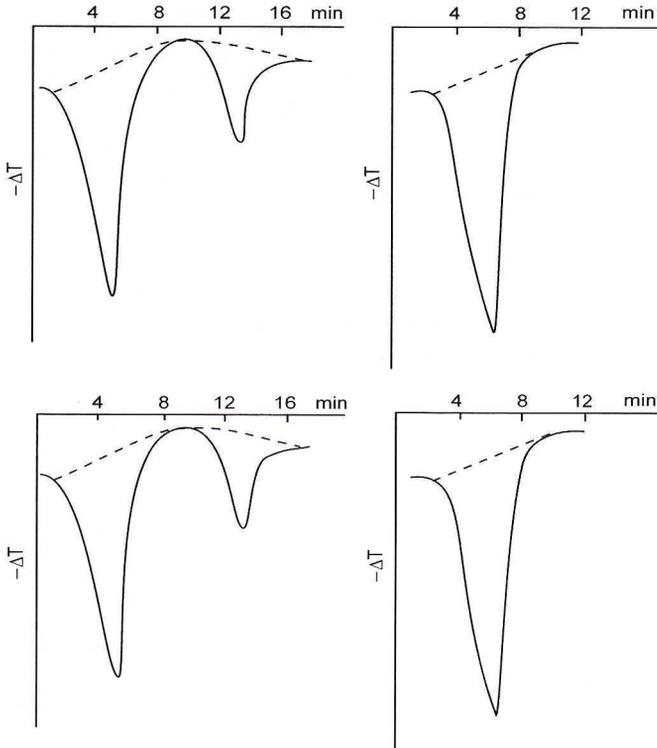


Fig. 6. DTA curves for alloys in Pb-Sn system [30]: (I) — first melting, (II) second melting
 a) alloy with eutectic composition; b) alloy with $x_{Pb} = 0.7$

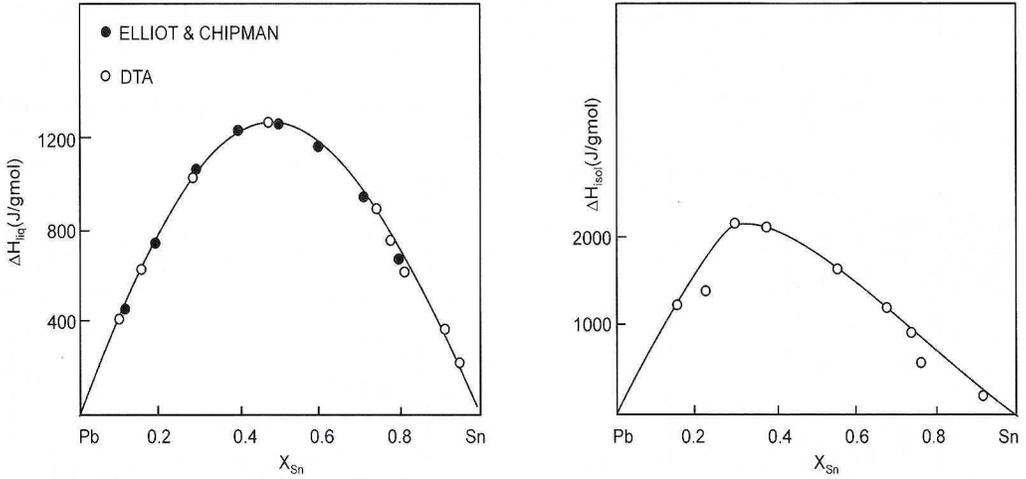


Fig. 7. Enthalpies of mixing in liquid and solid state for Pb-Sn system [30] (a - ΔH_{liq} ; b - ΔH_{sol})

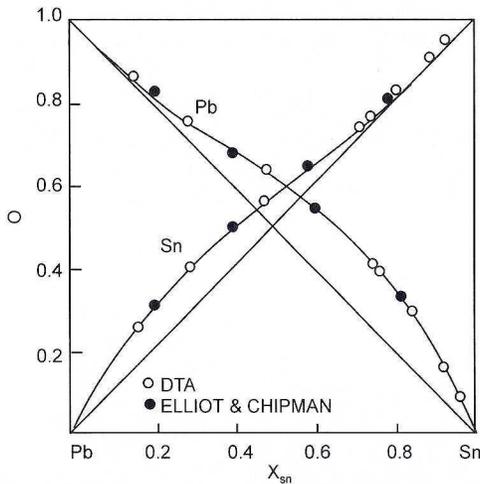


Fig. 8. Activities of components in Pb-Sn system at 773 K [30]

4. Conclusions

Values for thermodynamic quantities obtained experimentally by DTA method are in a good agreement with results obtained by different, numerous methods, like: thermodynamic predicting [35–49], calorimetric measurements [50, 51] or emf measurements [34, 52, 53]. This fact points out to a correctness of DTA method application in quantitative determination of thermodynamic values. But, it should be stated that some simplifications existing in the calculation procedure, such as the application of ideal mixing entropy, could be a limiting factor, which can cause errors.

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