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THE STUDIES OF ASSUMPTIONS ACCOMPANYING THE CALIBRATION OF HIGH-TEMPERATURE SOLUTION CALORIMETER

BADANIE ZAŁOŻEŃ TOWARZYSZĄCYCH KALIBRACJI WYSOKOTEMPERATUROWEGO KALORYMETRU TYPU ROZPUSZCZANIA

The main thesis of the research was the problem concerning calibration of high-temperature solution calorimeter with aluminum. The important assumptions applied at calibration of a device with aluminum were verified. Enthalpy values determined during the experiment clearly suggest that the level of deformation and diameters of aluminum samples used for calibration are negligible. The assumption that the temperature of the samples at the moment they reach the bath level is very close to room temperature, is appropriate.

Keywords: high-temperature solution calorimeter, calibration, aluminum, enthalpy

W pracy badano problemy dotyczące istotnych zagadnień związanych z kalibracją wysokotemperaturowego kalorymetru typu rozpuszczania za pomocą aluminium. Sprawdzono założenia wprowadzane przy kalibracji przyrządu z wykorzystaniem tego metalu. Wyznaczone podczas eksperymentów wartości entalpii świadczą, że nie ma znaczenia stopień odkształcenia oraz średnica użytych do kalibracji próbek aluminiowych. W tym ostatnim przypadku potwierdza to słuszność istotnego założenia, że próbki w momencie osiągania poziomu kąpieli mają temperaturę bardzo zbliżoną do temperatury pokojowej.

1. Introduction

One of the most crucial problems in metallurgical research is determining thermodynamic properties of alloys. Determination of thermodynamic potential with electrochemical and vapour pressure method is frequently used. One of the targets for this research is optimization of thermodynamic data and a phase diagram calculation. Equality of thermodynamic potentials is the condition of phase coexistence in equilibrium state. In order to determine the phase equilibria the option given by division of thermodynamic potential into enthalpy part and entropy part can be used. The most precise method determining the enthalpy is a direct calorimetric measurement. Another advantage resulting from determining the enthalpy with calorimetric method is the fact that it is possible to determine directly the molar enthalpy of formation. This quantity is one of the most important data used in optimization of thermodynamic data and calculations of phase equilibria.

Moreover, enthalpy of formation reflects a bond strength difference in an alloy and its components, which corresponds to their specific structure. Therefore the changes in the structure of an alloy and its properties under the influence of an alloying element are connected with enthalpy of formation changes. Apart from the advantages of calorimetric measurement mentioned above, the experimentally determined enthalpy of formation allows to verify its theoretical calculation for example by ab initio calculation.

This research concerns the measurements performed on two high-temperature solution calorimeters. Enthalpy of formation is the basic value determined with these devices. In this case the measurement method is based on comparison of thermal effects accompanying the process of dissolving the tested alloy and its components in the same metallic bath.

Calibration of calorimeter performs very important role in calorimetric measurements. Thermal effect accompanying the introduction of material with specified

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heat capacity into a bath is recorded at calibration. Various metals are used for calibration of the device. However, because aluminum bath was used in both devices, it is suggested that aluminum should be used for calibration of the calorimeter. From thermodynamic point of view it is the most precise solution because heat of solution is equal zero in this case, enthalpy of heating and melting of Al are well defined and the bath doesn't change its composition. Moreover, it is only slightly probable that a stirrer immersed in the bath is destroyed (this problem occurs when the metal which is insoluble in bath, e.g. molybdenum in aluminum bath is used for calibration).

The aim of this research was to answer two crucial questions connected with calibration of calorimeter by aluminum.

The first problem was to examine the influence of deformation upon energy state of samples used for calibration. The experiment was based on dissolving thin rods of aluminum in bath and determining the occurring thermal effects. Samples in three deformation states: soft state (after recrystallization), single deformation (deformation degree q = 38%) and twofold deformation (deformation degree q = 49%) were used. This procedure allows to verify whether the deformation state of the calibrating material might influence the obtained results.

The second problem concerning calorimeter calibration was to verify the assumption that the samples dropped into a bath from room temperature, still remain in the temperature close to room temperature in the very moment of reaching the bath. The series of tests were performed during the experiment on cylindrical samples with 3 different diameters. The applied propriety was the fact that due to good thermal conductivity from outside to inside of the material, thin samples heat faster than those of a greater diameter.

The whole experiment was carried out using the calorimeter working at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in Cracow (IMMS PAS). Precise description of the device can be found in the paper [1, 2]. The second part of the experiment was repeated on a solution calorimeter recently constructed at Department of Metallurgy of Silesian University of Technology (DM SUT).

2. Method

2.1. Sample preparation

Samples with 99.99% Al (EN AW-1199) were prepared. The aluminum comes from the material after heating extrusion, and its chemical composition based on PN-EN 573-3 standards is presented in Table 1.

Starting material used for samples preparing was ϕ=7,4mm diameter wire, drawn and, when necessary subjected to recrystallizing annealing in order to recover its soft stage material structure. Drawing was performed in a chain drawbench with 40kN load. Drawing speed was selected according to material behaviour. Carbide drawing bide of angle $2\alpha = 12°$ was used. The material was annealed in temperature of 500°C for 30 min in a laboratory muffle furnace FCF 7 SM.

In the first stage of the research, the following drawing scheme was performed (ϕ – drawing die diameter, HT – heat treatment) to obtain the samples.

1. Aluminum wire ϕ=2,94 mm soft stage (after annealing): ϕ=7,4mm HT→ ϕ=6,0mm → ϕ=5,0mm → ϕ=4,2mm HT→ ϕ=3,8mm → ϕ=3,0mm HT
2. Aluminum wire ϕ 2,94 mm medium stage (once drawn): [(...) – sequence as in point 1] (...) → ϕ=4,2mm HT→ ϕ=3,8mm HT→ ϕ=3,0mm
3. Aluminum wire ϕ=2,94 mm significant deformation (twice drawn): [(...) – sequence as in point 1] (...) → ϕ=4,2mm HT→ ϕ=3,8mm → ϕ=3,0mm

The wire prepared in the same way as above was used for the second stage of research, whereas drawing and heat treatment was additionally performed: (...) → ϕ2,2mm HT → ϕ1,5mm HT. In this way the wire was obtained in annealed state with a diameter of ϕ2,94mm, ϕ2,15mm and ϕ1,46mm, respectively.

In both cases the samples were obtained by cutting the wire into 12mm long pieces.

TABLE 1

Chemical composition of aluminum EN AW-1199 according to PN-EN 573-3 [3]

Component	Al	Zn	Si	Mg	Mn	Cu	Ti	V	Fe
Mass fraction (%)	>= 99,99	<= 0,006	<= 0,006	<= 0,006	<= 0,002	<= 0,006	<= 0,002	<= 0,005	<= 0,006

2.2. Experimental procedures

Before the experiment started the material of metallic bath was introduced into the calorimeter. Aluminum cylinder of a diameter similar to internal dimension of a crucible was placed in the reaction vessel. Three containers with titanium plates were placed close to calorimetric block in order to additionally prevent the bath oxidation and to absorb the moisture. After closing the device the air was pumped out with a rotary pump and diffusion pump. After reaching the vacuum of 10^{-4}Pa the whole system was filled with argon. All actions were performed three times before the temperature in calorimetric block exceeded 300°C. Subsequently the temperature was raised up to approximately 850°C and then the stirrer was installed and started to operate. The moment the calorimetric signal reached the stable base line the experiment began.

In case of the first calorimeter the samples were dropped into bath each time in the following order:

1. Aluminum sample of diameter 2,94mm with twofold plastic strain in the process of drawing – ϕ=4,2mm → ϕ=3,8mm → ϕ=3,0mm, deformation degree q=49%.
2. Aluminum sample of diameter 2,94mm with single plastic strain in the process of drawing – ϕ=3,8mm → ϕ=3,0mm, deformation degree q = 38%;
3. Aluminum sample of diameter 2,94mm after recrystallization;
4. Aluminum sample of diameter 2,15mm after recrystallization;
5. Aluminum sample of diameter 1,46mm after recrystallization.

8 series of measurements were performed on 40 aluminum rods.

In the second calorimeter the samples were dissolved in the following order:

1) Aluminum sample of diameter 2,94mm after recrystallization;

2) Aluminum sample of diameter 2,15mm after recrystallization;

3) Aluminum sample of diameter 1,46mm after recrystallization;

8 tests were performed on 24 aluminum rods.

A single sample was introduced into the calorimeter lock which was closed with two valves. Then the air was pumped out and the lock was blown with argon. Each time this action was repeated three times. After releasing the bottom valve, the sample fell into aluminum bath, where it was dissolved. The accompanying thermal effect could be observed on the screen as the deviation from the base line level. After dissolution of the sample, the base line stabilized and the next experiment was conducted. In every single measurement the room temperature, temperature of a calorimetric block, the dissolving time and the thermal effect were recorded.

2.3. Result elaboration

Calorimeter calibration allows determining the calibration coefficient which informs about the amount of energy which falls on conventional units registered on computer. Each experimental measurement was accompanied by a graph record illustrating thermal effect in conventional units in the function of time. Figure 1 presents typical calorimetric signal obtained at solution process.
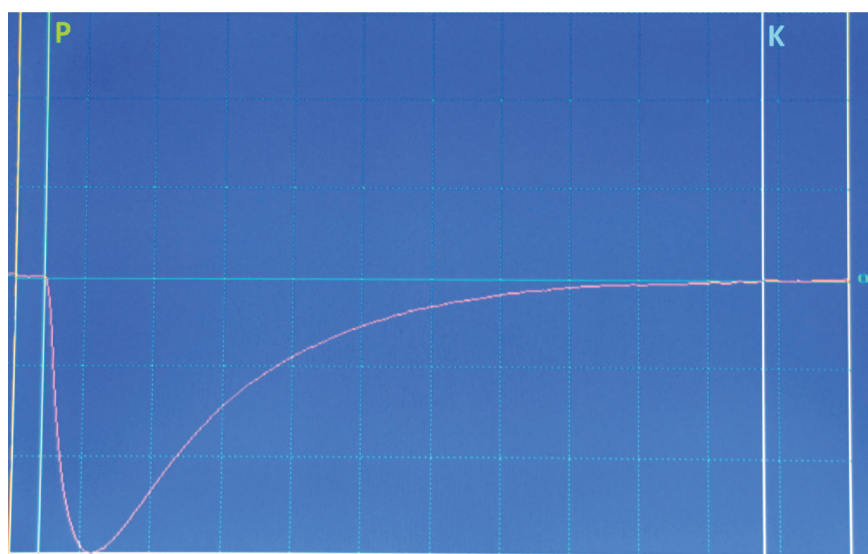

Fig. 1. Typical calorimetric signal registered for sample of Φ=2,94mm once deformed. Vertical lines P and K define boundaries within which the area over the curve was calculated

The obtained courses of thermal effect were used for calculating the surface between the curve and the straight line connecting the beginning and end of a given course. The computer program, created for the purpose of experiments with high-temperature solution calorimeter was used. Surfaces, masses of samples and other necessary data as temperature of calorimetric block and its corresponding enthalpy value for aluminum (taken from thermochemical database [4]) applied for the calculation of calibration coefficient K [kJ/c.u.] (c.u. – conventional unit) according with the following formula:

$$K = \frac{\Delta H \cdot \frac{m}{A}}{M_A} \qquad (1)$$

where:
ΔH – enthalpy change of the substance (Al), being the sum of heating the sample from room temperature to bath temperature including melting, kJ/mole of atoms
m – mass of the Al sample dropped into calorimeter, g

A – area between the calorimetric signal curve and the base line, c.u.
M_A – atomic mass of the element (Al) used in experiment, g/mole

In case of calculating enthalpy ΔH, formula 1.1. was used after converting it into the following form:

$$\Delta H = \frac{K \cdot M_A \cdot A}{m} \qquad (2)$$

2.4. Results and discussion the influence of a sample diameter and sample deformation on the calibration coefficient

At the first stage of study the influence of Al samples deformation was examined on the calibration coefficient in the solution calorimetric method. The results obtained are presented in Table 2 and they concern to the experiments performed at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences (IMMS PAS).

TABLE 2

Heat effect data and values of calibration coefficient obtained (IMMS PAS), where:
1) Samples after recrystallization,
2) Samples once deformed (deformation degree q=38%)
3) Samples twice deformed (deformation degree q= 49%). Denotations as in formula (1.1.)

Sample		A, [c.u.]	m, [g]	T, [K]	ΔH, [kJ/mole of atoms]	K, [kJ/c.u.]	Average value K, [kJ/c.u.]
1)	1	-3969	0,206	1124	34,89	$-6,72 \cdot 10^{-5}$	$-6,94 \cdot 10^{-5} \pm 1,88 \cdot 10^{-6}$
	2	-3729	0,206	1123	34,86	$-7,13 \cdot 10^{-5}$	
	3	-3596	0,198	1122	34,83	$-7,12 \cdot 10^{-5}$	
	4	-4228	0,222	1122	34,83	$-6,78 \cdot 10^{-5}$	
	5	-3750	0,202	1124	34,89	$-6,95 \cdot 10^{-5}$	
2)	1	-4465	0,238	1123	34,86	$-6,89 \cdot 10^{-5}$	$-6,89 \cdot 10^{-5} \pm 3,04 \cdot 10^{-6}$
	2	-4338	0,219	1122	34,83	$-6,52 \cdot 10^{-5}$	
	3	-4251	0,243	1122	34,83	$-7,37 \cdot 10^{-5}$	
	4	-4431	0,234	1122	34,83	$-6,81 \cdot 10^{-5}$	
	5	-4142	0,220	1123	34,86	$-6,87 \cdot 10^{-5}$	
3)	1	-4403	0,232	1124	34,89	$-6,78 \cdot 10^{-5}$	$-6,85 \cdot 10^{-5} \pm 3,08 \cdot 10^{-6}$
	2	-3784	0,215	1122	34,83	$-7,34 \cdot 10^{-5}$	
	3	-4838	0,247	1122	34,83	$-6,59 \cdot 10^{-5}$	
	4	-4319	0,221	1122	34,83	$-6,61 \cdot 10^{-5}$	
	5	-4180	0,223	1123	34,86	$-6,91 \cdot 10^{-5}$	

As it is seen in Table 2 all calibration coefficients are comparable what means a negligible differences in the amount of energy accumulated in samples. In order to confirm this fact, the following approach to the presented problem was suggested. The value of calibration coefficient for a sample of diameter ϕ=2,94mm in an annealed state was the reference point since such a material does not posses additional energy accumulated during deformation. The coefficient was the basis of calculating of the enthalpy for the remaining samples and it was used in formula 1.2. Such an approach helped to find out whether differences in energy amount accumulated in aluminum with various degree of deformation exist. All the obtained values are presented in Table 3.

TABLE 3

Enthalpy values obtained at IMMS PAS for samples of Φ=2,94mm diameter with various deformation degree according to comments in subsection 2.3, where:
1) samples after recrystallization,
2) samples once deformed (deformation degree a= 38%),
3) samples twice deformed (deformation state q=49%).
Denotations as in formula (1.1.)

Sample		Enthalpy ΔH, [kJ/mole of atoms]	Average value ΔH, [kJ/mole of atoms]
1)	1	36,07	34,89 ± 0,97
	2	33,95	
	3	33,94	
	4	35,66	
	5	34,83	
2)	1	34,85	35,03 ± 1,45
	2	36,82	
	3	32,81	
	4	35,49	
	5	35,19	
3)	1	35,71	35,16 ± 1,39
	2	32,91	
	3	36,68	
	4	35,44	
	5	35,04	

Having analyzed the results obtained with the solving method, one can state that the plastic deformation applied on samples before examination has no impact on energy state of aluminum, in the limit of error.

Lack of any major differences noticed in energy state of aluminum samples with various deformation degrees is a very positive result when aluminum is used as a calibrating material for a calorimeter. It means that sample history does not significantly influence the received results. Substantial stacking fault energy (SFE) which is typical for aluminum might be one of the possible explanations of such state. Every metal features its characteristic value of SFE and it is well known that the bigger this value is, the smaller the frequency of fault existing in the lattice. SFE greatly affects the metal behaviour during plastic strain, the accumulated deformation energy, poligonization and recrystallizing. This impact is connected mainly with the dependence between SFE and dislocation tendency to climb and to cross slips. When SFE value is high, as in aluminum, this deformation is easier and the accumulated deformation energy is lesser. In metals of this type it is easier for edge dislocation to climb and to cross slip [5, 6, 7].

To sum up the results of the first part of measurements, it can be said that no influence of deformation on energy state of the samples and physicochemical characteristics of aluminum indicate that this material used for calibrating of calorimeter is a very reasonable choice and the preparation of samples is not crucial in terms of the degree.

The second problem concern, the verification of the assumption whether the sample dropped into the bath from room temperature still holds the temperature close to room temperature the moment it reaches the bath. This problem seems essential as for as the solution calorimetric technique is concerned. The properties of thin samples which heat faster were taken into consideration, as heat conductivity occurs from the outside to the inside of a sample. Table 4 contains output data and calculated values of calibration coefficient for an experiment carried out in IMMS PAS.

TABLE 4

Data and values of calibrating coefficient calculated for the second part of measurement (IMMS PAS), where:
1) Samples after recrystallization of ϕ=2,94mm diameter,
2) Samples after recrystallization of ϕ=2,15mm diameter,
3) Samples after recrystallization of ϕ=1,46mm diameter. Denotations as in formula (1.1.)

Sample		A, [c.u.]	m, [g]	T, [K]	ΔH, [kJ/mole of atoms]	K, [kJ/c.u.]	Average value K, [kJ/c.u.]
1)	1	-3969	0,206	1124	34,89	$-6,72 \cdot 10^{-5}$	$-6,94 \cdot 10^{-5}$ $\pm 1,88 \cdot 10^{-6}$
	2	-3729	0,206	1123	34,86	$-7,13 \cdot 10^{-5}$	
	3	-3596	0,198	1122	34,83	$-7,12 \cdot 10^{-5}$	
	4	-4228	0,222	1122	34,83	$-6,78 \cdot 10^{-5}$	
	5	-3750	0,202	1124	34,89	$-6,95 \cdot 10^{-5}$	
2)	1	-2385	0,126	1124	34,89	$-6,83 \cdot 10^{-5}$	$-6,97 \cdot 10^{-5}$ $\pm 2,42 \cdot 10^{-6}$
	2	-2491	0,130	1122	34,83	$-6,72 \cdot 10^{-5}$	
	3	-2221	0,125	1122	34,83	$-7,27 \cdot 10^{-5}$	
	4	-2349	0,128	1122	34,83	$-7,05 \cdot 10^{-5}$	
3)	1	-1201	0,064	1124	34,89	$-6,85 \cdot 10^{-5}$	$-6,89 \cdot 10^{-5}$ $\pm 7,31 \cdot 10^{-7}$
	2	-1157	0,063	1122	34,83	$-6,98 \cdot 10^{-5}$	
	3	-1210	0,065	1122	34,83	$-6,89 \cdot 10^{-5}$	
	4	-1242	0,066	1123	34,86	$-6,81 \cdot 10^{-5}$	

Likewise in the first part of the research, the values of calibration coefficient obtained were similar. The same approach as in the first part was applied in order to verify the thesis that samples when dropped into bath at room temperature do not change their temperature. In order to calculate the value of enthalpy change for the tested samples the value of calibration coefficient was used for a sample of diameter ϕ=2,94mm, which for each case was used in 1.2. Samples of diameter ϕ=2,94mm are the largest possible to be used in a calorimeter, on account of their diameter in the dosing sample device. The obtained enthalpy values are presented in Table 5.

This part of the research was repeated in Department of Metallurgy of Silesian University of Technology (DM SUT). Data and calculated values of calibration coefficient for this experiment are presented in Table 6.

TABLE 5

Enthalpy values for samples of different diameters (IMMS PAS), where:
1) Samples after recrystallization of ϕ=2,94mm diameter,
2) Samples after recrystallization of ϕ=2,15mm diameter,
3) Samples after recrystallization of ϕ=1,46mm diameter.
Denotations as in formula (1.1.)

Sample		Enthalpy ΔH, [kJ/mole of atoms]	Average value ΔH, [kJ/mole of atoms]
1)	1	36,07	$34,89 \pm 0,97$
	2	33,95	
	3	33,94	
	4	35,66	
	5	34,83	
2)	1	35,47	$34,75 \pm 1,21$
	2	35,96	
	3	33,27	
	4	34,30	
3)	1	35,33	$35,13 \pm 0,39$
	2	34,61	
	3	35,07	
	4	35,51	

TABLE 6

Data and values of calibration coefficient calculated for the second part of measurements (DM SUT), where:
1) Samples after recrystallization of ϕ=2,94mm diameter,
2) Samples after recrystallization of ϕ=2,15mm diameter,
3) Samples after recrystallization of ϕ= 1,46mm diameter. Denotations as in formula (1.1.)

Sample		A, [c.u.]	m, [g]	T, [K]	ΔH, [kJ/mole of atoms]	K, [kJ/c.u.]	Average value K, [kJ/c.u.]
1)	1	-645887	0,1958	1132	35,14	$-3,95 \cdot 10^{-7}$	$-4,02 \cdot 10^{-7} \quad \pm 9,70 \cdot 10^{-9}$
	2	-594113	0,1907	1132	35,14	$-4,18 \cdot 10^{-7}$	
	3	-572234	0,1765	1132	35,14	$-4,02 \cdot 10^{-7}$	
	4	-698844	0,2115	1131	35,11	$-3,94 \cdot 10^{-7}$	
	5	-617230	0,1903	1131	35,11	$-4,01 \cdot 10^{-7}$	
2)	1	-379054	0,1080	1132	35,14	$-3,71 \cdot 10^{-7}$	$-4,05 \cdot 10^{-7} \pm 2,03 \cdot 10^{-8}$
	2	-333521	0,1078	1132	35,14	$-4,21 \cdot 10^{-7}$	
	3	-358241	0,1117	1132	35,14	$-4,06 \cdot 10^{-7}$	
	4	-315453	0,1018	1132	35,14	$-4,20 \cdot 10^{-7}$	
	5	-385541	0,1205	1131	35,11	$-4,07 \cdot 10^{-7}$	
3)	1	-171680	0,0522	1132	35,14	$-3,96 \cdot 10^{-7}$	$-4,09 \cdot 10^{-7} \pm 1,63 \cdot 10^{-8}$
	2	-185510	0,0576	1132	35,14	$-4,04 \cdot 10^{-7}$	
	3	-154602	0,0506	1131	35,11	$-4,26 \cdot 10^{-7}$	
	4	-180036	0,0589	1131	35,11	$-4,26 \cdot 10^{-7}$	
	5	-190563	0,0573	1131	35,11	$-3,91 \cdot 10^{-7}$	

TABLE 7

Enthalpy values for samples of different diameters (DM SUT), where:
1) Samples after recrystallization of ϕ=2,94mm diameter,
2) Samples after recrystallization of ϕ=2,15mm diameter,
3) Samples after recrystallization of ϕ=1,46mm diameter.
Denotations as in formula (1.1.)

Sample		Enthalpy ΔH, [kJ/mole of atoms]	Average value ΔH, [kJ/mole of atoms]
1)	1	35,77	$35,14 \pm 0,82$
	2	33,78	
	3	35,16	
	4	35,83	
	5	35,17	
2)	1	38,06	$34,94 \pm 1,84$
	2	33,55	
	3	34,78	
	4	33,60	
	5	34,69	
3)	1	35,66	$34,59 \pm 1,38$
	2	34,92	
	3	33,13	
	4	33,15	
	5	36,06	

Approximate values of calibration coefficient were obtained once more. Accordingly the same approach, as described in previous experiments was applied and the enthalpy was calculated using formula 1.2. The calibration coefficient obtained for samples of diameter ϕ2,94mm was applied and the results are presented in Table 7.

Having analyzed the obtained values of calibration coefficient (Table 4 and 6), for both calorimeters, one can state that the diameter of a sample does not have a meaningful impact on its value. Enthalpy values (Table 5 and 7) are within the limits of measuring error. This experiment was supposed to show, whether samples of a smaller diameter become heated more while being dropped into the bath. It would mean that the temperature of a sample falling into the bath at room temperature is supposed to be different in the very moment of its contact with the bath. From the obtained values of enthalpy, it can be concluded that sample temperature at its dropping does not change to such an extent as to affect the obtained results.

On the basis of the results obtained in the second part of measurements it can be assumed that temperature of a sample reaching the bath surface is the same for samples of different diameters. It means that samples reaching the bath surface have the temperature close

to room temperature. This information is advantageous as far as high-temperature solution calorimetry is concerned and justifies its use in determining the enthalpy of formation. The use of samples with maximal diameters equal 3mm is recommended because of the construction of a sample dosing system in calorimeter. The main advantage of samples of this thickness is that the greatest thermal effect can be achieved. It is important that the heat effect is close to thermal effect of tested samples which are usually heavier.

3. Conclusions

1. Plastic deformation applied to samples used for calorimetric calibration has no influence upon energy state of aluminum within the limits of a measuring error. It suggests that preparation method of aluminum for calibration is not important from plastic strain point of view.

2. Lack of any substantial differences in the obtained values of enthalpy at dropping samples of different diameters into calorimeter was recorded. It means that thin samples do not reach higher temperatures than samples of greater diameter when dropped into the bath. This could influence the values of calibration coefficient. As performed experiments showed, the assumption that the sample temperature at the point of its contact with a bath is close to room temperature is correct.

3. It is recommended that the samples of diameter of ϕ=3mm are used in experiment. This diameter is the biggest possible size because of the construction of a dosing system in the calorimeter. It gives the greatest effect registered during solving close to the thermal effect accompanying solving of samples during experiment.

4. The use of the same material as that of a bath (in this case – aluminum) is the most advantageous way of calibrating the device. It is the most precise solution from thermodynamic point of view because heat of solution is equal zero, enthalpy of heating and melting of Al are well defined and the bath doesn't change its composition. There is also faint possibility of destroying the stirrer. This problem occurs when metal which is insoluble in bath for instance molybdenum, is used for calibration.

5. The reliability of obtained results is confirmed by use of two independent devices.

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