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THE SURFACE TENSION DETERMINATION THROUGH THE ESTIMATION OF THE PARAMETERS OF THE SESSILE DROP EQUATION

WYZNACZANIE NAPIĘCIA POWIERZCHNIOWEGO POPRZEZ ESTYMACJĘ PARAMETRÓW RÓWNANIA KROPLI LEŻĄCEJ

Basing on the literature data concerning the sessile drop topic, a method of surface tension of liquid metals and alloys measurements using numerical methods has been developed. The computational procedure used in the experiment was the least square estimation of the parameters of the differential equation describing the shape of a sessile drop of liquid. After a series of tests which confirmed the correctness of the employed computational procedure, the method was used in the surface tension measurements of liquid copper.

W oparciu o publikacje dotyczące metody kropli leżącej opracowano metodykę pomiarów napięcia powierzchniowego ciekłych metali i stopów z wykorzystaniem metod numerycznych. Zastosowana procedura obliczeniowa polega na estymacji metodą najmniejszej sumy kwadratów parametrów równania różniczkowego opisującego kształt leżącej kropli cieczy. Po wykonaniu szeregu testów, które potwierdziły poprawność przyjętej procedury obliczeniowej, opracowana metodyka wykorzystana została w pomiarach napięcia powierzchniowego ciekłej miedzi.

1. Introduction

The surface tension of liquid metals and metal alloys is an important parameter describing the physicochemical properties of the interface in heterogeneous systems. In the measurements of the surface tension we meet with several problems concerning, among others, the proper choice of the materials to produce some parts of the experimental apparatus as well as providing relevant protective gases. It is also necessary to eliminate all the possible chemical reactions between the liquid, the apparatus parts and the atmosphere components which can affect the results of measurements.

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There are significant differences between the values of the surface tension of liquid metals presented in various literature data. For instance, for liquid copper, its value determined at the melting point by various researchers changes from 1.212 N m^{-1} [1] to 1.400 N m^{-1} [2]. The mentioned experimental difficulties occurring at high temperatures are probably responsible for such noticeable discrepancies.

The following measurement methods can be used in order to determine the surface tension:

– the maximum bubble pressure method,
– the sessile drop method,
– the pendent drop method,
– the capillary rise method,
– the drop weight method,
– the detachment of thin plate, ring or cylinder method,
– the levitating drop method.

In high-temperature measurements of surface tension one of the most popular techniques is the sessile drop method. In this method, a liquid metal drop placed on the appropriate solid surface is observed and its shape is measured. In the traditional variant of the method, first the parameters characterizing the drop shape are measured from camera photographs or *X*-ray photographs taken during the experiment. Next, the surface tension values of the liquid are determined on the basis of the appropriate tables. The most common are the Tables of Bashforth and Adams [3], the Tables of White [4] and the Tables of Koshevnik [5]. In view of the fact that the use of the traditional tables is complicated and time-consuming, computer techniques find more and more common application in the determination of the surface tension of liquids. They were introduced, among others, by Butler and Bloom [6], Maze and Burnet [7, 8] as well as Rotenberg, Boruvka and Neumann [9]. Computer calculating programs and modern methods of picture processing make it possible to enhance the efficiency and accuracy of calculations due to the analysis of a great number of sessile drop profiles. In addition, in some cases it is possible to eliminate problems related to photograph processing.

Basing on the literature sources concerning the sessile drop topic, a method of measuring surface tension of liquid metals and alloys using numerical methods has been developed. After a series of tests which confirmed the correctness of the employed computational procedure, the method was used in the surface tension measurements of liquid copper.

2. Measurement method and calculation procedure

The measurements of the surface tension of liquid copper by the sessile drop method were carried out at the temperatures: 1393, 1433, 1473, 1513 and 1553 K.

The experiments were conducted using the measuring apparatus PR-37/1600 produced by the Industrial Electronics Institute. It consisted of a high-temperature microscope (a horizontal high-temperature pipe furnace allowing the observation of an inserted sample) and a camera, both coupled with a computer equipped with a program ("Tempat") enabling the regulation and control of the device work parameters as well as the registration and analysis of the picture. A schematic view of the apparatus is presented in Fig.1.

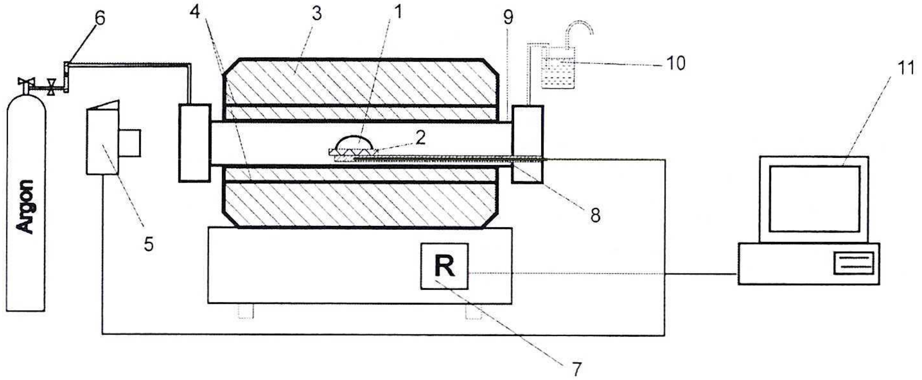

Fig. 1. Schematic view of the measuring apparatus: 1 – drop of liquid metal; 2 – substrate; 3 – high-temperature furnace; 4 – heating elements; 5 – CCD camera; 6 – gas delivery system; 7 – furnace work regulator; 8 – loading system with thermoelement; 9 – reactor; 10 – gas outlet system; 11 – PC computer.

MOOB copper samples, sized approximately 4.5 mm both in diameter and height, were placed in the heating chamber of the high-temperature microscope on the substrates made of Al_2O_3 and produced by the Institute of Refractory Materials. Argon of 99.9999% purity was used as the protective gas during the measurements.

During the experiment, a picture of the sample was observed on the monitor and saved into the hard disk, which enabled further measurements of the appropriate geometrical parameters of a liquid drop. Simultaneously, the time and temperature of the measurement were registered. The experiment was carried out at increasing temperature levels, and each consecutive required level was kept steady for about 10 minutes. At each temperature, six independent measurements were carried out under identical experimental conditions. In Fig. 2 an example of a shape of a liquid copper drop is presented.

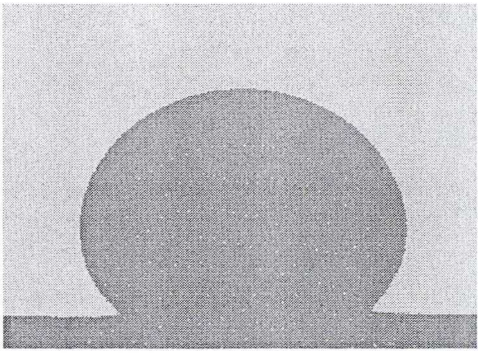

Fig. 2. A liquid copper drop at 1393 K

The starting point of the surface tension calculations from the shape of a liquid sessile drop is the relation between the surface tension and the difference in pressures on both sides of the curved liquid surface (capillary pressure) described by the well known Young and Laplace equation:

$$P_\gamma = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right), \tag{1}$$

where: $P\gamma$ – the capillary pressure,
γ – the surface tension,
R_1, R_2 – the principal radii of curvature at a point on the liquid surface.

For symmetric figures such as sessile liquid drops (Fig.3) Bashforth and Adams suggested the following version of the Young and Laplace equation:

$$\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \rho g z + \frac{2\gamma}{b}, \tag{2}$$

where: ρ – the density of liquid,
g – the acceleration of gravity,
z – the vertical coordinate of a point on the surface measured downwards fromthe drop apex (Fig.3),
b – the radius of curvature at the apex (z=0).

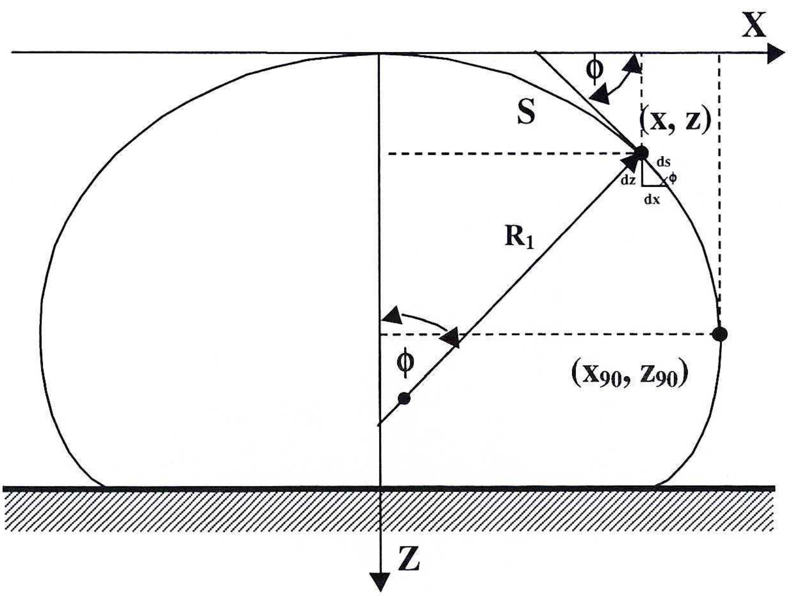

Fig. 3. The sessile drop profile

If φ is the angle made by the Z-axis and the line perpendicular to the drop surface at the point described by (x, z) coordinates, the radius of curvature in the plane perpendicular to the plane of the picture (Fig.3) is determined from the equation:

$$R_2 = \frac{x}{\sin\phi}, \tag{3}$$

where: x – the horizontal coordinate of the point (Fig.3).
Considering (2) and (3) we obtain:

$$\gamma\left(\frac{1}{R_1} + \frac{\sin\phi}{x}\right) = \frac{2\gamma}{b} + \rho g z. \tag{4}$$

After the transformation, (4) can be described as follows:

$$\frac{b}{R_1} + \frac{\sin\phi}{\frac{x}{b}} = 2 + \frac{\rho g b}{\gamma} z. \tag{5}$$

While substituting the equation for the radius of curvature [10]:

$$R_1 = \frac{ds}{d\phi} \tag{6}$$

we obtain the differential equation describing the shape of a sessile drop:

$$b\frac{d\phi}{ds} = 2 + Bbz - \frac{\sin\phi}{\frac{x}{b}}, \tag{7}$$

where:

$$B = \frac{\rho g}{\gamma} \tag{8}$$

While determining the surface tension of liquid copper, the computational procedure [6-9, 11] was employed. It is the least square estimation of the parameters (b, B) of the differential equation describing the shape of a sessile drop on the basis of the coordinates of points measured on the drop surface (Fig.3).

The measurement data obtained from the experimental sessile drop pictures were saved into the hard disk files as the matrix M_p (n x 2):

$$\mathbf{M}_p = \begin{bmatrix} x_{p1} & z_{p1} \\ x_{p2} & z_{p2} \\ \dots & \dots \\ x_{pn} & z_{pn} \end{bmatrix}, \tag{9}$$

where:

(x_{pi}, z_{pi}) – the coordinates of a point on the drop surface; i = 1, 2, ..., n,

n – the number of measured points.

The estimation of the parameters describing the size (b) and shape (B) of the drop leads to the solution of the following non-linear optimisation problem [12-14]:

$$\left.\begin{matrix} \min\limits_{b,B} f_{Mp}(b, B) \\ b, B > 0 \end{matrix}\right\}, \tag{10}$$

where:

$$f_{Mp}(b, B) = \sum_{i=1}^{n}(z_{pi} - z_i^*(x_{pi}, b, B))^2 \tag{11}$$

and:

$z_i^*(x_{pi}, b, B)$ – the theoretical coordinate corresponding to the value of x_{pi} and described, for the b, B parameters, through the system of differential equations:

$$\frac{d\phi}{ds} = \frac{2}{b} + B \cdot z^* - \frac{\sin\phi}{x} \tag{12}$$

$$\frac{dx}{ds} = \cos\phi \tag{13}$$

$$\frac{dz^*}{ds} = \sin\phi \tag{14}$$

In order to solve the optimisation problem (10), the non-gradient iterative method of Nelder-Mead (the so-called simplex method) was employed [12-14]. For calculating the value of the objective function $f_{Mp}(b, B)$, the Runge-Kutta method was used [14], by means of which, through solving the system of differential equations (12-14), the values of the coordinates $z_i^*(x_{pi}, b, B)$ were determined. The program for numerical calculations was written in the Matlab [15], which itself contains the 'fmins' (with the algorithm of the simplex method) and the 'ode 23' (used for solving the system of differential equations by the Runge-Kutta method) procedures. For a given measurement matrix M_p, the algorithm of the function $f_{Mp}(b, B)$ value calculating was diagrammatically presented in Fig.4, and it was an additional function (cooperating with the 'fmins') written in the Matlab.

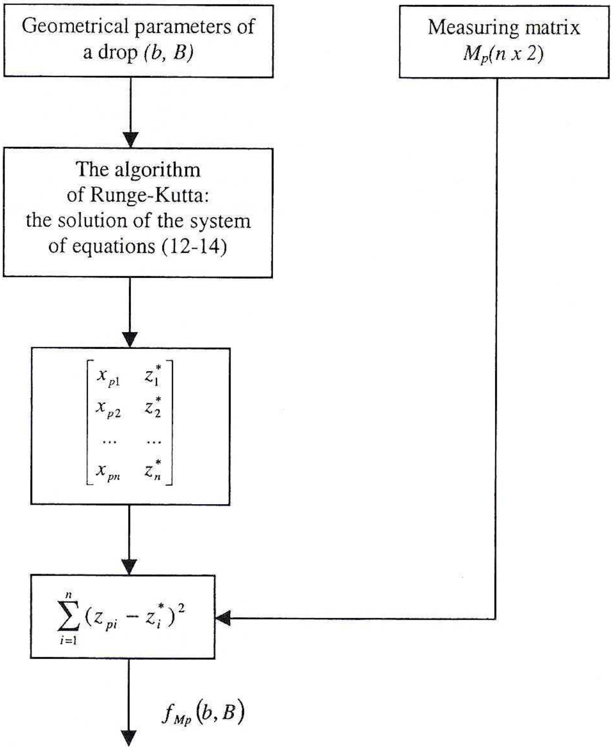

Fig. 4. The algorithm of the function $f_{Mp}(b, B)$ value calculating appearing in the optimisation problem (10)

The b^* and B^* parameters obtained through the optimisation (10) satisfy the criterion $\sum_{i=1}^{n}(z_{pi} - z_i^*(x_{pi}, b^*, B^*))^2 = \min$. Basing on the shape parameter (B^*), we can calculate the surface tension of the liquid from the equation:

$$\gamma = \frac{\rho g}{B^*}. \tag{15}$$

A set of tests was carried out in order to check the appropriateness of the estimation algorithm of the drop parameters. In the tests, the coordinates of a theoretical drop points (x_i, z_i) were generated by solving the system of equations (12-14) for b and B. Next, the generator of quasi-random numbers was used for simulating the errors ξ_i of the coordinates measurement. Taking into consideration the additive model of disturbances, the coordinates of the points were determined:

$$(x_{pi}, z_{pi}) = (x_i, z_i + \xi_i), \tag{16}$$

where:

ξ_i – a random variable with the normal distribution $N(0, \sigma)$; σ – standard deviation.

The obtained points (16) were used in the least square estimation algorithm described above. The b^* and B^* values, determined this way, were compared with the previously known b and B parameters of a theoretical drop. The results of the tests confirmed the appropriateness of the suggested estimation algorithm.

Fig. 5 presents an example of test points arrangement obtained by solving the system of equations (12-14) using the Runge-Kutta method for b=0.33·10^{-2} m and B=0.8·10^{5} m^{-2} and, consecutively, employing the additive disturbances model in the form of a random variable with the normal distribution N(0, 0.1·10^{-3}). The full line in Fig. 5 represents a drop profile obtained by means of the estimation based on the test points with b^*=0.32826·10^{-2} m and B^*=0.78357·10^{5} m^{-2}.

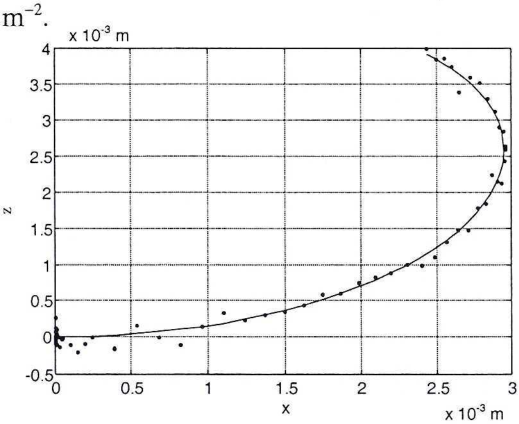

Fig. 5. A drop profile (b^*=0.32826·10^{-2} m, B^*=0.78357·10^{5} m^{-2}) obtained by the estimation of the parameters describing the drop shape and size on the basis of the test points

TABLE 1

The parameters of the test procedure of the estimation algorithm

Test No.	$b\cdot 10^{2}$ m	$B\cdot 10^{-5}$ m	$\sigma\cdot 10^{4}$ m	$b^*\cdot 10^{2}$ m	$B^*\cdot 10^{-5}$ m^{-2}	$\left\|\frac{b-b^*}{b}\right\|\cdot 100\%$	$\left\|\frac{B-B^*}{B}\right\|\cdot 100\%$
1	0.30	0.6	1.0	0.30060	0.63224	0.20	5.37
2	0.30	0.6	0.6	0.29941	0.59867	0.20	0.22
3	0.30	0.6	0.28	0.30022	0.60664	0.07	1.11
4	0.33	0.8	1.0	0.32826	0.78357	0.52	2.05
5	0.33	0.8	0.6	0.32839	0.78729	0.49	1.59
6	0.33	0.8	0.28	0.32946	0.80544	0.16	0.68
7	0.35	1.0	1.0	0.35152	1.03433	0.43	3.43
8	0.35	1.0	0.6	0.35019	0.97935	0.05	2.06
9	0.35	1.0	0.28	0.35000	1.00001	0	0

In Table 1 the values of parameters describing the size and shape of a liquid drop which were used for verifying the estimation algorithm are listed. Simulated errors as well as b^*, B^* parameters obtained through the presented test procedure are also taken into consideration.

Fig.6 presents example results of a geometrically measured copper drop. The full line shows the shape of the drop described by the system of differential equations (12-14) with b=0.30993·10^{-2} m, B=0.594142·10^5 m^{-2}. The values of b, B were obtained through the estimation based on the measurement points.

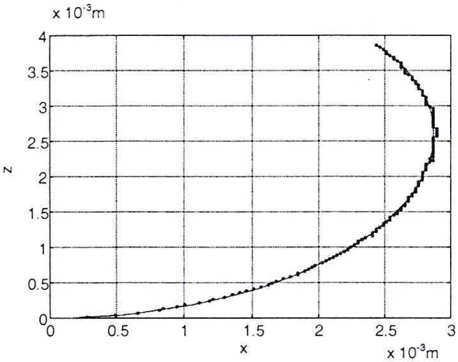

Fig. 6. A copper drop shape at 1433 K (the full line represents the solution of the system of differential equations (12-14) for b^*=0.30993·10^{-2} m and B^*=0.59414·10^5 m^{-2})

The relation (15) shows that in order to determine the surface tension by means of the sessile drop method, it is necessary to know the densities of liquid metals at the given temperature. The density of liquid copper in the temperature range 1393-1553 K was obtained from Nizienko and Floka [16]:

$$\rho_{Cu} = 8.039 - 9.6 \cdot 10^{-4} (T-T_m) \text{ g cm}^{-3}. \quad (17)$$

3. Results and discussion

In Table 2 the results of the surface tension measurements of liquid copper are presented:

Column 1 – the number of the measurement (for example: 1.1 denotes Sample 1 inthe given measurement series – the measurement at the first planned temperature; 2.3 denotes Sample 2 in the given measurement series- the measurement at the third planned temperature),

Column 2 – the temperature T in K at which the experiment was conducted,

Column 3 – the density ρ in kg m^{-3}, used for the surface tension calculations,

Column 4 – the values of the radius of curvature at the drop apex b^* (in m),

Column 5 – the values of the shape parameter B^* (in m^{-2}),

Column 6 – the values of the surface tension γ in N m^{-1}, obtained in a single measurement,

Column 7 – mean values of the surface tension $\bar{\gamma}$ in N m^{-1}, calculated from the series of measurements conducted under the same conditions,

Column 8 – the standard deviation $S(\gamma)$ in N m^{-1}.

TABLE 2

The results of the surface tension of liquid copper measurements

No.	T K	$\rho \cdot 10^{-3}$ kg m^{-3}	$b^* \cdot 10^2$ m	$B^* \cdot 10^{-5}$ m^{-2}	γ N m^{-1}	$\bar{\gamma}$ N m^{-1}	$S(\gamma) \cdot 10^2$ N m^{-1}
1.1			0.31316	0.58975	1.330		
2.1			0.31088	0.58584	1.339		
3.1	1393	8.00	0.30955	0.59057	1.328	1.331	0.60
4.1			0.30459	0.59353	1.322		
5.1			0.31424	0.58741	1.335		
6.1			0.31639	0.58812	1.334		
1.2			0.31324	0.59153	1.321		
2.2			0.31299	0.59375	1.316		
3.2	1433	7.97	0.30993	0.59414	1.315	1.318	0.58
4.2			0.30648	0.59721	1.309		
5.2			0.31623	0.59132	1.322		
6.2			0.31655	0.58972	1.325		
1.3			0.31144	0.59430	1.308		
2.3			0.32021	0.59298	1.311		
3.3	1473	7.93	0.31345	0.59643	1.304	1.304	0.66
4.3			0.30806	0.59900	1.298		
5.3			0.31703	0.59470	1.308		
6.3			0.32057	0.60078	1.294		
1.4			0.31642	0.59611	1.298		
2.4			0.32021	0.59298	1.305		
3.4	1513	7.89	0.31693	0.60544	1.278	1.289	1.05
4.4			0.30822	0.60238	1.284		
5.4			0.31661	0.60109	1.287		
6.4			0.31688	0.60366	1.281		
1.5			0.32051	0.60430	1.274		
2.5			0.32115	0.59481	1.294		
3.5	1553	7.85	0.31684	0.60694	1.268	1.275	0.99
4.5			0.31558	0.60419	1.274		
5.5			0.31691	0.60823	1.266		
6.5			0.31818	0.60440	1.274		

On the basis of the conducted experiment it has been found that, for liquid copper,the temperature rise is accompanied by the fall of the surface tension. At 1393 K the value of the surface tension is 1.331 N m^{-1}, then at 1473 K it decreases to 1.304 N m^{-1}, and finally at 1553 K to 1.275 N m^{-1}. The changes of the surface tension are linear and are described as the function of temperature by the following relation:

$$\gamma = 1.826 - 0.355 \cdot 10^{-3}\, T \text{ N m}^{-1}. \tag{18}$$

The values of the surface tension of liquid copper measured in the experiment, after extrapolating to the melting point can also be described by the Gibbs-Helmholtz equation:

$$\gamma = 1.345 - 0.355 \cdot 10^{-3}\, (T - 1356) \text{ N m}^{-1}. \tag{19}$$

The value of 1.345 N m^{-1}, which corresponds to the melting point, is in very good agreement with the value 1.351 N m^{-1} determined by means of the correlation suggested by Strauss [17]:

$$\gamma_m = 0.166\, \Delta H_{vap}\, V^{-\frac{2}{3}}, \tag{20}$$

where:

γ_m – the surface tension at the melting point,

ΔH_{vap} – the molar heat of vaporization extrapolated to 0 K,

V_m – the molar volume at the melting point.

The values of the copper molar volume (V_m=7.91 cm^3 mol^{-1}) necessary for calculations were taken from Turkdogan [18], and the values of the vaporization heat (ΔH_{vap}=323 kJ mol^{-1}) from Miedema and Boom [19].

The obtained results are also in agreement with most data presented by other authors, especially with the results obtained by Nogi, Ogino, McLean and Miller [20], Uchov, Vatolin and Ciencov [21] as well as Nogi, Oishi and Ogino [22]. These researchers used the sessile drop method, too. On the other hand, the presented results differ distinctly from the results obtained by other authors, for instance Darrell-Ownby and Lui [2] (γ_m=1.400 N m^{-1}) and Pawlek, Thielsch and Wuth [23] (γ_m=1.270 N m^{-1}), who used the sessile drop method, as well as from the results obtained by the maximum bubble pressure method by Laty, Joud and Desre [24] (γ_m=1.290 N m^{-1}). It can be assumed that the reason for the differences between the results presented by various authors were experimental difficulties mentioned in the introduction. Also, the purity of the metal used for preparing samples could affect the values of the obtained results. Fig.7 presents a comparison between the results of the conducted experiment and the literature data [2, 20-24].

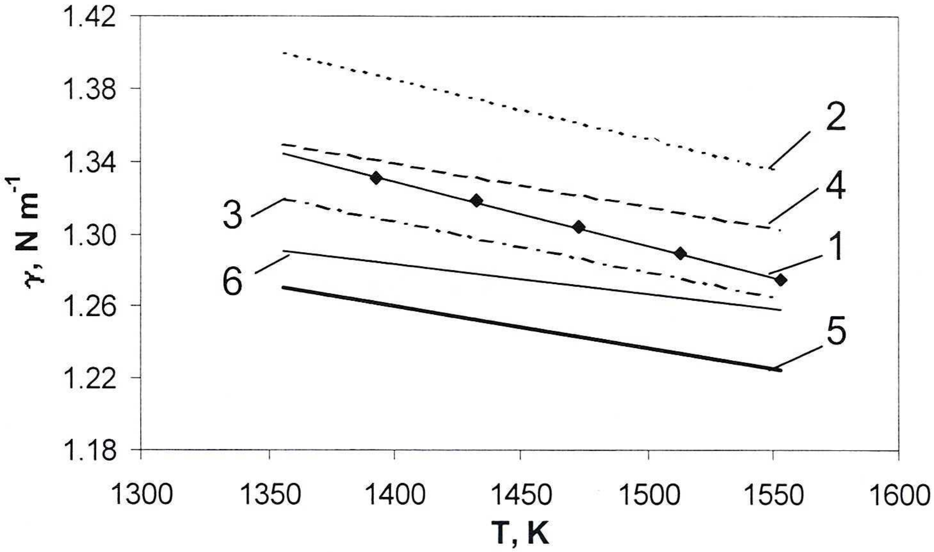

Fig. 7. A comparison between the liquid copper surface tension measurements and the literature data in the temperature range 1356-1553 K (1 – present work, 2 – [2], 3 – [20, 22], 4 – [21], 5 – [23], 6 – [24]).

4. Summary

The measurements of the surface tension in the temperature range 1393-1553 K were carried out using the sessile drop method. In order to determine the surface tension an original computer program was used. The appropriateness of the computational procedure used in the experiment was confirmed by tests conducted on theoretically generated drop shapes.

It has been found that the temperature rise is accompanied by the fall of the liquid copper surface tension. The changes of the surface tension as a temperature function are of a linear character

Computer techniques employed both in the analysis of the drop shape and determination of the surface tension considerably increase the rate of calculations in comparison with the traditional method including tables.

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