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Capillary characteristics of high temperature melts measured by sessile-drop method using computer-aided TV system

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An automated TV system with a computer for measuring the capillary constant, surface tension, density, and wetting angles of melts by the sessile-drop method is described. Hardware and software support issues have been treated. Surface tension and density of a number of high temperature melts, including copper, CaF_2, and alloys Pb + 0.34 at % S, 5Cu + 0.5Ge + 94.5Sn (at %) were measured. The surface tension–concentration isotherm (1100 °C) obtained for the Cu–alloy Ga–Ge (1 : 1) system was found to have a smooth run and show a sharp decrease of surface tension σ_{lg} on adding of Ga–Ge alloy to copper. The obtained results are in good agreement with the manual measurements data. The use of a standard TV camera (625 lines) as a data acquisition device with the subsequent statistical processing of data was found to provide the accuracy of surface tension determination within the range of 1% and an appreciable measurement time reduction.

1. Introduction

Experimental investigations into the capillary properties of metallic and non-metallic melts, which are of major importance in many production processes of metallurgy and materials science, include surface tension, σ_{lg}, wettability, liquid-to-solid adhesion (studied by the widely employed sessile-, and pendant-drop, as well as melt meniscus methods [1–3]), conventionally use the photo-optical methods of image recording which do not allow prompt acquisition of final experimental data and thus reduce the efficiency of experiments. This is due to the necessity to perform labour-consuming and lengthy procedures of photomaterial processing, manual measurements of photographs as well as the calculations of capillary characteristics, using, for example, Bashforth–Adams tables [4], and other techniques. The extensive application over recent years of computer facilities resulted in a drastic reduction of time required for the calculation of surface tension and other characteristics. In addition, a number of efficient computation algorithms were developed (for example, [5, 6]). As for the measurements of relevant geometrical parameters of the shape of meniscus or a drop of liquid, these are determined normally through manual measurements. Recently, attempts were undertaken to create systems with a computer-aided measurement of the above parameters. Thus, the paper [7] looks into the potential use of conventional TV camera as a sensor for acquisition of data on dimensions of a sessile drop and calculation of σ_{lg}, but no experimental data have actually been given. A TV system has been described [8] for automatic measurement of surface tension of low temperature liquids by the pendant-drop method. The authors have found that the use of this system provides the accuracy of measuring σ_{lg} within the range of 1% and allows the kinetics of adsorption to be investigated. The recently published paper [9] describes the use of the TV camera on a CCD-matrix with a size of 512 × 512 pixels as a data acquisition device whose major advantage in comparison with conventional TV cameras is the absence of non-linear distortions and high reliability of image signal shaper (at an insufficient resolution of the matrix). By means of this system, the authors have succeeded in measuring surface tension of molten gold from the photograph of a sessile drop and obtaining the value (one point) in good agreement with the literature data.

Therefore, even though research into automation of experiments in this area is underway, the available individual developments have found no extensive application so the problem of creating fast, simple and reliable methods for measuring capillary characteristics remains as crucial as ever. It is also necessary to take measurements of the set of characteristics, such as surface tension, wetting angle, density of liquids. These problems underlie the goals of this paper.

2. Experimental procedure

2.1. Apparatus

A method of automatic contact-free remote measurement of co-ordinates of a drop profile points by means of a TV sensor has been employed for determination of characteristics of high temperature melts, including surface tension, wetting angle, and drop volume by the sessile-drop technique. The computer-aided system

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has been developed and created [10] on the basis of standard hardware incorporating a conventional vacuum plant [2], industrial TV system with a decomposition frequency of 15 625 Hz to 625 lines at 25 frames s^{-1}, and a control computer microsystem with relevant peripherals. The system also accommodates an image processing, a buffer storage, an interface, and an experimental set-up control unit (Fig. 1). The basic functional unit, that of image processing is composed in turn of comparators, counters, sync pulse generator for 20 MHz and buffer units (Fig. 2) and performs the following functions: 1. separation of sync pulses (line and frame ones); 2. comparison of a video signal with the preset level; 3. computation of data address in the working memory; 4. counting of the fill-up pulses, and 5. shaping the pulse of data recording in the working memory. Without description of other functional units, one may note that the thermal and the temporal operating conditions of the experimental apparatus are software-controlled with the use of a thyristor circuit, digital-to-analog converter, a timer unit and thermocouples in the temperature sensor role.

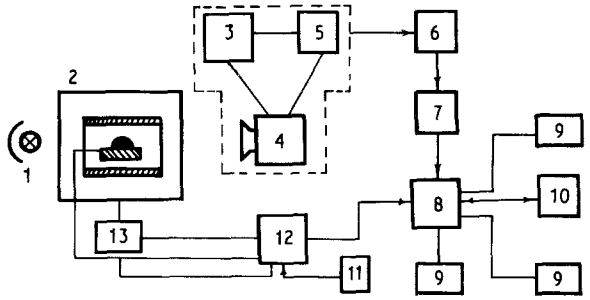

Figure 1 Block diagram of the computer-aided system for measurement of melt capillary characteristics: (1) lighting device; (2) vacuum plant; (3) monitor; (4) TV camera; (5) control console; (6) image processing unit; (7) buffer storage unit; (8) interface unit; (9) peripherals; (10) control computer microsystem; (11) thyristor unit; (12) plant controller and (13) effector.

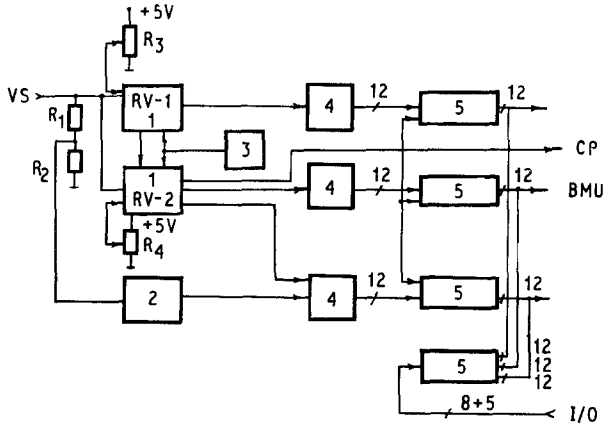

Figure 2 Block diagram of image processing unit: (1) comparators; (2) operation amplifier; (3) sync pulse generator; (4) pulse counters; (5) buffers; (VS) video signal; (RV) reference voltage; (CP) control pulse; (BMU) buffer memory unit; and (I/O) input/output.

2.2. The principle of measurement of profile curve point coordinates from the TV image

The measurement of image parameters required for calculation of capillary characteristics is based on the time–pulse method (discrete count technique) whose essence consists of the following: an image of the object under study, for example, of a melt drop on a substrate (as is the case with the experiment using the sessile-drop method) (Fig. 3), is projected *via* an optical system to the TV camera vidicon target and is controlled on the monitor screen. The relevant (standard) video signal (Fig. 4a) reaches one input of the comparator with the reference voltage being fed to the other input. If the video signal exceeds the reference voltage, a high voltage level (2.4–5.0 V) appears across the comparator output. High voltage of the comparator enables (*via* the element AND) the passage of sync pulses from pulse generator to the counter (Fig. 4b). The pulse counter counts the number of pulses generated through the time gate. The use of 20 MHz generator yields 1040 fill-up pulses per one television line. Counter outputs are connected to the buffer memory unit *via* the interfacing elements (amplifiers–inverters). The buffer memory stores binary data recorded from counters and supplies all information to the computer through the interface unit. During one data acquisition cycle (60 ms), the buffer storage unit records data

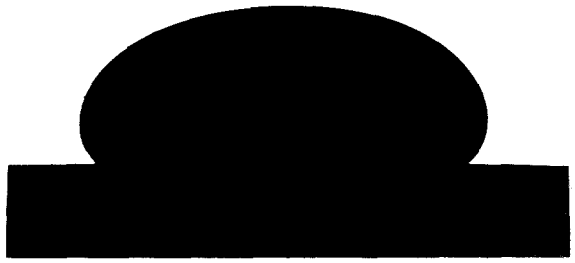

Figure 3 Melt drop on a substrate in a sessile-drop experiment.

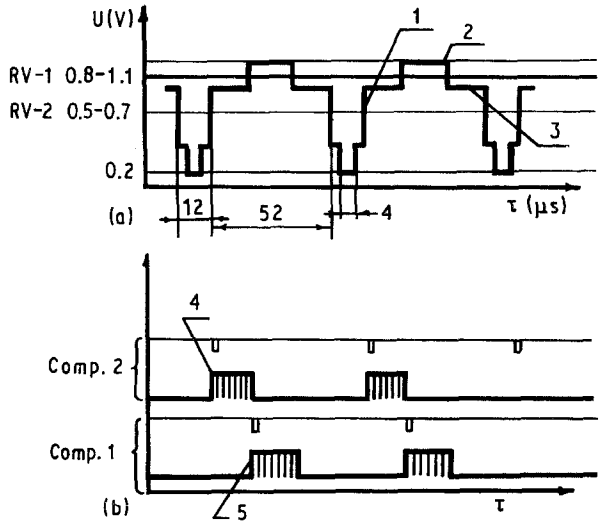

Figure 4 (a) Input signal of the image processing unit and (b) output signals of comparators' circuits: (1) line sync pulse; (2) white level; (3) black level; (4) train of pulses of the chord origin coordinate; (5) train of pulses characterizing the chord length; (RV) reference voltage.

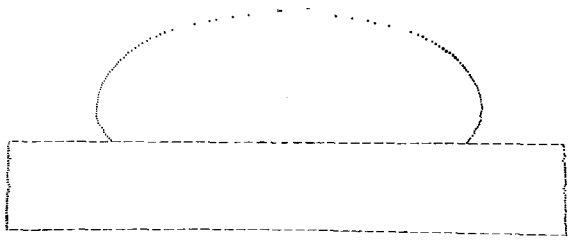

Figure 5 Digitized drop representation in the pulse number–line number coordinates (experimental data).

on three semi-frames of a TV image. By counting the number of pulses in each scan line contained in the dark (reference) and bright (chord) parts of an image and the number of lines, one obtains the digitized representation of a profile of the object under study – the array of geometrical parameters in the form of secant lengths and their number by height, or the image profile points coordinates. In other words, the horizontal size of an image is determined by the number of fill-up pulses, and the vertical one by the number of scan lines (Fig. 5). To start calculating the capillary characteristics, two sequential semi-frames (making up a television frame) are selected from the data array, the image is then filtered from random bursts followed by isolation of reference image and drop contour from data array. The isolation of reference image, such as, for example, a rectangle with accurately pre-determined linear dimensions (width and height) is performed by the principle of repeating identical (or similar) values of pulse numbers. The reference image is used for calibration of the system during which one determines the number of pulses and lines per 1 mm, and for recalculation of contour co-ordinates into real dimensions one has to make allowance for the image magnification factor. In addition, the drop is fixed to a coordinate system in which both axes run through the drop's pole. These operations completed, with all manipulations done by the computer, the system is ready for calculation of capillary characteristics.

2.3. Brief software description

The calculation of capillary characteristics from the array of coordinates of the profile curve points under the predeterminated temperature condition is performed using the algorithm developed for the sessile-drop on the Bashforth technique basis, whose block diagram is given in Fig. 6. The calculation program makes use of experimental data which are an array of Cartesian co-ordinates of drop profile points $\{x_{ex}, y_{ex}\}$. Because of the non-monotonous variation of the function $y = f(x)$, the transformation of Cartesian co-ordinates into polar ones envisaged is with the subsequent approximation of contour points by the polynomial by the least-squares technique where the Gaussian method is employed for calculation of polynomial coefficients. The resulting equation of drop contour in the form of the polynomial is used for deriving equator co-ordinates ($r_{eq}(90)$, $h_{eq}(90)$), by the gold section method (which involves the search for the maximum of a function of one variable when dividing

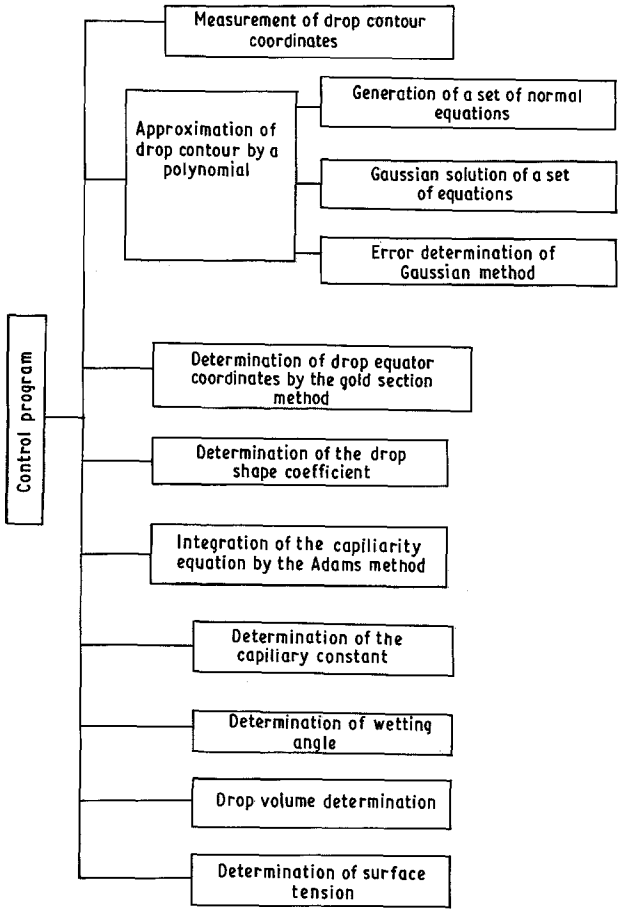

Figure 6 Structural diagram of software support for determination of melt capillary characteristics.

the search interval by the gold section rule). The obtained drop equator coordinates are employed to calculate the coefficient of drop shape β, from the previously determined coefficients of the polynomial

$$\beta = \sum_{i=0}^{n} a_i (r/h)^i$$

(the accuracy of β determination is better than $5 \cdot 10^{-3}$%). Next, one uses the Adams method [11] and the angle φ as an independent variable to integrate the known Laplace capillarity equation in the form

$$x' = R_1 \cos\varphi$$

$$z' = R_1 \sin\varphi$$

where

$$\frac{1}{R_1} = 2 + \beta z - \frac{\sin\varphi}{x}$$

here x, z are the drop contour points coordinates, R_1 is the curvature radius of the profile curve in this point, φ is the tangent slope in this point to the x-axis. The integration is discontinued when $\varphi = \varphi_{given}$ is reached, or when the wetting angle (equal to φ_{given}) is unknown, at the experimentally determined $z = z_{given}$. The co-ordinates $r_i = x/b$ and $h_i = z/b$ obtained through integration at $\varphi = 90°$ (b is the curvature radius at the drop apex) agree with the measured equator coordinates $r_{eq}(90)$ and $h_{eq}(90)$, hence $b = r_{eq}(90)/r_i$. Next, one finds the capillary constant $a^2 = b^2/\beta$ as well as the value of surface tension, $\sigma = a^2 \rho g$ where ρ is the melt

density and g the free fall acceleration. The wetting angle is found from z_{given}, and the drop volume, v, confined by the wetting angle is determined from the formula $v/b^3 = \frac{\pi x^2}{\beta}\left(\frac{1}{R_1} - \frac{\sin\varphi}{x}\right)$.

3. Results and discussion

The measured values of surface tension are known to depend on a number of variables, such as the purity of material under study, ambient atmosphere, substrate material, etc. Therefore, the reference literature gives specific approximate values of σ_{lg} as a function of experimental conditions, as is the case with [12]. This leads to some difficulties in testing and calibration of the computer-aided measurement system in the absence of absolute criterion of comparison. That is why, even though the system has been designed for data acquisition from real drops of molten metals, at the initial operation testing stage we have confined ourselves to measuring the capillary characteristics on simulated objects – the photographic images. This allowed elimination of the above factors related to experimental conditions and permitted us to directly compare the automatic measurement data and the data obtained through manual measurement of these photographs. Hence, to carry out tests, we have made use of high-quality contrast photographs (photoplates) of melt drops obtained in different laboratories by various (independent) investigators for different substances.

A photograph was fixed on a goniometric device. Then, the operations to adjust the optical television system were performed, including the focusing of the image, the setting of horizon, adjustment of diaphragm, selection of illumination intensity for producing the best image. Image and video signal were monitored by means of a monitor screen and the standard oscillograph. In a number of experiments the magnification of drop image was varied on the vidicon target (1.5–5 times). In the case of a drop on a substrate, used as a reference image was a substrate (whose vertical and horizontal dimensions were preliminarily measured under the microscope), and when taking each measurement, the automatic measurement of the reference image and the drop under study was taken simultaneously to control the stability of system hardware operation and the reproducibility of measurements of linear dimensions. The maximum resolution (theoretical one), proceeding from the geometrical configuration of the employed vidicon (12.7 $\times$ 9.5 mm^2) and the discretization level (1040 pulses $\times$ 576 lines), amounts to about 12 μm pulse^{-1} along the horizontal and 16 μm line^{-1} along the vertical. This is below the resolution level attained when measuring photographs manually by means of an optical microscope ($\sim$ 5 μm) but above the resolution for the CCD-camera in [9] which equals about 20 μm.

TABLE I Results of measurement of capillary characteristics under an automatic conditions (melt Cu–Ge–Sn)

r_{eq} (90) (cm)	h_{eq} (90) (cm)	a^2 (cm^2)	ϕ (deg)	v (cm^3)	σ (mJ m^{-2})
0.84714	0.39598	0.07553	126.5	0.86009	500.83
0.84775	0.39300	0.07408	128.0	0.86486	491.21
0.84977	0.40472	0.07970	127.5	0.88916	528.49
0.85357	0.39961	0.07698	124.5	0.87262	510.48
0.84964	0.40693	0.08083	129.5	0.90239	535.95
0.85176	0.40181	0.07815	127.5	0.88734	518.20
0.84983	0.40220	0.07844	127.5	0.88402	520.10
0.84953	0.40671	0.08072	124.5	0.87865	535.80
0.84289	0.39400	0.07478	127.5	0.85248	495.83
0.84624	0.40068	0.07787	133.5	0.89802	516.31
0.84936	0.39887	0.07682	129.5	0.88479	509.41
0.84564	0.39956	0.07734	129.5	0.87831	512.85
0.84865	0.40015	0.07749	118.5	0.83277	513.79
0.85018	0.40917	0.08195	128.0	0.90389	543.40
0.85079	0.40184	0.07822	127.5	0.88531	518.60
0.84903	0.40739	0.08110	129.0	0.90206	537.76
0.84778	0.39904	0.07698	124.5	0.85932	510.46
0.84756	0.39793	0.07645	130.5	0.88315	506.95
0.85134	0.40599	0.08026	124.5	0.88101	532.19
0.84793	0.40045	0.07767	128.5	0.88075	514.99
0.84777	0.40257	0.07873	127.0	0.88039	522.02
0.84971	0.41094	0.08290	127.5	0.90206	549.69
0.84592	0.39997	0.07753	123.5	0.85690	514.10
0.84932	0.39682	0.07583	130.0	0.88467	502.81
0.84998	0.40862	0.08168	123.5	0.87856	541.59
Mean values					
0.84876	0.40180	0.07832	127.22	0.87934	519.22
Coefficient of variation (standard deviation) (%)					
0.26	1.18	2.95	2.38	1.97	2.95
Standard deviation of the mean (%)					
0.05	0.24	0.59	0.48	0.39	0.59

When taking measurements, we adopted a statistically-oriented approach, that of multiple measurements with the subsequent averaging of results.

Given by way of an example in Table I is a data fragment for automatic determination of geometrical parameters (drop equator radius $r_{eq}(90)$ and equator-to-pole height $h_{eq}(90)$) and capillary characteristics – capillary constant, a^2, drop volume v, surface tension, σ_{lg}, as well as the drop contour slope, ϕ, in a cup relative to the horizontal line at its base (it corresponds to the φ angle in the Bashforth technique). The performed data analysis for the measured substances indicates that the average spread in values for individual measurements (coefficient of variation) of linear parameters of the reference image makes about 0.05% along the horizontal and 0.5% along the vertical line. For equator radius and the height calculated from the measured coordinates of the profile curve points, the coefficient amounts to 0.2 and 1%, respectively, and for the angle ϕ and σ_{lg} to about 2 and 4%, respectively. The variation of magnification on the vidicon target or on the photograph does not significantly affect the error value. The lower vertical resolution of the TV camera is estimated to make the basic contribution to the variance of the measurement data; in addition, one is to take into consideration the contribution of errors caused by non-linear distortions of the TV tube (for the minimization of the latter, the drop image was projected into the tube centre). The most probable values of the measured parameters obtained by averaging 25 profile curves and the thus reduced standard deviations of the mean are also listed in Table I. It should be noted that given the known mass drops, drop volume data can be used for determination of density of substances under study. The time it takes to obtain an ultimate result is limited by the calculation of capillary characteristics (integration of the capillarity equation) and depends on the computer speed taking from several minutes to tens of seconds per one value.

Thus, the computer-aided TV system allowed measurement of the capillary constant, surface tension and density of a series of melts including pure copper, CaF_2, alloys Pb + S (0.34 at %), 5Cu + 0.5 Ge + 94.5 Sn (at %). For the system Cu + alloy Ga–Ge (1:1) we have obtained the surface tension–concentration isotherm. This alloy is important as a basis in solder development. The drops were formed in crucibles in the shape of cups (large drop method [2]) made of graphite (alumina) and had the volume of about 1 cm^3. Experiments were performed in vacuum of 10^{-4}–10^{-5} Pa. Results are shown in Tables I, II and in Fig. 7. As can be seen, the isotherm for surface tension (1100 °C) of alloy Cu–(Ga–Ge) has a smooth run, and the adding of Ga–Ge alloy to copper produces a sharp decrease of σ_{lg} from 1300 mJm^{-2} for pure copper to 610 mJm^{-2} for the alloy with a composition of 20 wt % Cu–(Ga–Ge). The automatic TV measurements data feature a good agreement with manual measurements and calculations data (which are assumed to be reference ones in this case). It also concerns other measured melts. Coincidence by ϕ varies from the absolute one to about 3% in the worst case, and by σ from 0.1 to 2% (Table II), i.e. on the average it equals 1% which is close to values given in [8, 9].

It also may be noted that the preliminary testing of the system using the full-scale specimens – drops of metal in the installation's furnace – has yielded a positive result and demonstrated that by meeting the usual requirements for optical instrumentation one can obtain a high-quality image of an object on

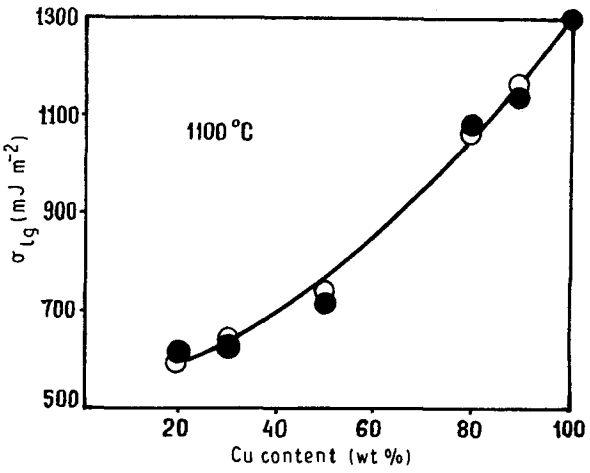

Figure 7 Isotherm of surface tension (1100 °C) for the system Cu + alloy Ga–Ge (1:1): (○) manual measurement data and (●) automatic measurement data.

TABLE II Comparison of automatic and manual measurement data

Substance, alloy	Temperature (°C)	Atmosphere	Density (g cm^{-3})	σ_{lg} (mJ m^{-2})		ϕ (deg)	
				manual	automatic	manual	automatic
20Cu + (Ga–Ge) (wt %)[a]	1100	vacuum	5.71	608	610 ± 5	126.5	128.0 ± 0.5
30Cu + (Ga–Ge)	1100	vacuum	6.08	639	632 ± 3	122.0	123.0 ± 1.0
50Cu + (Ga–Ge)	1100	vacuum	6.72	736	719 ± 4	125.0	125.0 ± 0.6
80Cu + (Ga–Ge)	1100	vacuum	7.89	1083	1084 ± 12	114.5	114.0 ± 0.5
90Cu + (Ga–Ge)	1100	vacuum	7.80	1168	1147 ± 12	120.0	120.0 ± 0.5
5Cu + 0.5Ge + 94.5 Sn[b]	600	vacuum	6.77	522	519 ± 4	–	127.0 ± 1.0
Cu	1120	helium	8.28	–	1300 ± 10	–	122.0 ± 0.3
CaF_2	1420	helium	2.55	302	299 ± 7	–	115.0 ± 1.0
Pb + 0.34 S (at %)	700	vacuum	9,99	382	387 ± 4	131.0	126.0 ± 1.0

[a] Ga:Ge = 1:1
[b] at %

vidicon target, a relevant video signal, as well as sufficient accuracy of measurements. At present, these experiments continue.

4. Conclusion

An automated television instrumentation system has been created on the basis of standard hardware with the purpose of determination of capillary characteristics of high temperature melts: capillary constant, surface tension, wetting angle, drop volume (melt density) by the sessile-drop method.

The system's operation was tested by taking measurements of surface tension and density of a series of high temperature melts, including copper, CaF_2, Pb + S (0.34 at %), 5 Cu + 0.5 Ge + 94.5 Sn (at %), Cu + alloy Ga–Ge (1:1), from drop photographs and through direct comparison of the obtained results with the conventional manual measurements data. It was found that application of the standard TV camera (625 lines) followed by the statistical processing of data allows surface tension to be determined with an accuracy of 1% and provides an essential reduction of measurement time.

The method in question features fast data acquisition, operative calculation of capillary characteristics, and the potential for processing large data arrays, averaging the obtained data and performing the statistical analysis. This permits significantly higher efficiency of an experiment and rids the investigator from cumbersome manual measurement of photographs and tabular calculations. Moreover, the method promises to eliminate photographic procedures in the fast analysis of capillary properties of melts in various materials studies and control tests.

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References

1. D. V. KHANTADZE, E. G. ONIKASHVILI and F. N. TAVADZE, in "Nekotoriye prilosheniya teorii kapillyarnosti pri fisikokhimicheskom issledovanii rasplavov" (Metsniyereba, Tbilissi, 1971) p. 13 (in Russian).
2. Y. V. NAIDICH, in "Kontaktniye yavleniya v metallicheskikh rasplavakh" (Naukova dumka, Kiev, 1972) p. 34 (in Russian).
3. YU. N. IVASHCHENKO, V. N. YEREMENKO, in "Osnovy pretsisionnikh izmereniy poverkhnostnoy energii rasplavov po metody leshashchei kapli" (Naukova dumka, Kiev, 1972) p. 35 (in Russian).
4. F. BASHFORTH and J. C. ADAMS, "An attempt to test the theories of capillary action" (Cambridge University Press, Cambridge, 1883).
5. C. MAZE and G. BURNET, *Surface Sci.* **24** (1971) 335.
6. V. ROTENBERG, Z. BORUVKA and A. W. NEUMANN, *J. Coll. and Interf. Sci.* **93** (1983) 169.
7. A. G. AMBROK, S. A. GRUSINTSEV, E. L. LUBE and V. V. PELLER, *Adgeziya rasplavov i paika materialov*, **N12** (1984) 12 (in Russian).
8. H. H. J. GIRAULT, D. J. SCHIFFRIN and B. D. V. SMITH, *J. Coll. and Interf. Sci.* **101** (1984) 257.
9. L. LIGGIERI and A. PASSERONE, *High Temp. Technol.* **7** (1989) 82.
10. Y. V. NAIDICH, N. F. GRIGORENKO, V. N. MOROZ, T. E. DRAGAN and T. S. IVANOVA, *Adgeziya rasplavov i paika materialov*, **N25** (1991) 35 (in Russian).
11. A. N. KRYLOV, in "Lektsii o priblishennikh vychisleniyakh" (Metallurgiya, Moscow, 1954) p. 75 (in Russian).
12. V. I. NISHENKO and L. I. FLOKA, "Poverkhnostnoye natyasheniye shidkich metallov i splavov" (Metallurgiya, Moscow, 1981) 9 (in Russian).

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