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Application of a Wollaston wire probe for quantitative thermal analysis

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Abstract

In this work, we have investigated the properties of the Wollaston wire thermal resistive probe which is frequently used for microthermal analysis. Special attention was drawn to the frequency dependence of the performance of the probe. We demonstrated that at frequencies above 5 kHz, the temperature of the Wollaston wire probe becomes increasingly insensitive to modulations of the driving current. We submerged such a probe in air and a number of liquids to measure the heat conductivities by simultaneous determination of the applied power and increase in temperature. The heat conductivities were established both by application of direct current (dc) and modulated current. The advantages and disadvantages of different techniques of thermal analysis with this type of resistive probe are discussed. A method of multifrequency analysis at a fixed location for the elimination of the effects of contact area and thermal resistance is proposed for analyses in the frequency range of 10–100 Hz. Crown Copyright © 2002 Published by Elsevier Science B.V. All rights reserved.

Keywords: Local microanalysis; Frequency dependence; Wollaston wire probe; Heat conductivity

1. Introduction

Investigation of the local thermal properties of the surfaces with sub-micrometer spacial resolution has become possible lately due to the introduction of scanning thermal microscopy (SThM) [1]. First attempts of getting thermal images of the surfaces were based on scanning tunneling microscopy (STM) [2]. The general disadvantage of this method was the requirement of electrically conductive surfaces. Another problem was that the tunneling current was used to control the sample-to-tip distance, whereas the temperature profile was obtained from thermo-voltages. The later-developed atomic force microscopy (AFM) has eliminated these constraints. The AFM-based systems are much more suited for SThM. They do not require electrically conductive surfaces, and the force feedback system does not interfere with the operation of the thermal sensors. The thermal measurements by this method were implemented by either of three means: thermocouple junctions [3–5], electrical resistances [6–8], or bimetallic strips [9,10].

Currently, the resistive thermal sensor made of a Wollaston wire is one of the most frequently used thermally sensitive probes for SThM. It is produced commercially and used in the recently introduced Microthermal Analyzer$^{\mathrm{TM}}$ of TA Instruments Inc., US. Usage of the resistive probe made of a Wollaston wire allows to obtain a spatial resolution up to 1 μm. The next generation of thermal probes based on

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measuring of resistance change with temperature is in the development stage, to be made by microfabrication. The technology of preparation of such probes by electron-beam lithography which allows a resolution up to 50 nm was reported recently [11,12]. Resistive probes can be used for thermal imaging of the surfaces with contrast of the images related to thermal conductivity and heat capacity. Typically, the resistive sensor acts simultaneously as a highly localized heat source and the temperature-sensitive element. Applying of modulated heating can bring additional analysis possibilities to this method. Thus, the depth of heat penetration into the sample can be controlled by the frequency of the temperature modulation [13,14]. Up to date, however, only a small number of publications deal with quantitative characterization of the thermal properties of the surfaces [15,16]. Our main interest is connected with quantitative local thermal analysis. We have chosen the resistive Wollaston wire probe for more detailed investigations, especially in the frequency domain, to determine its applicability to quantitative thermal analysis.

2. Experimental

In this work, we used commercial Wollaston wire probes for microthermal analysis (TA Instruments Inc., US). Such a type of the resistive sensor was originally developed by Dinwiddie et al. [6] as a thermal probe for SThM. Later, it was used by Hammiche et al. [8,13,17] who further developed this method and made possible to perform localized thermal analysis of the surfaces. This method is utilized now in the Microthermal Analyzer μTA™ 2990, commercially produced by TA Instruments Inc., US. The Wollaston wire resistive probe used in this work was intended for this microcalorimeter. We investigated the properties of the probe in the frequency domain and applied it to the direct measurement of heat conductivity of air and liquids.

The Wollaston wire consists of a 90% platinum/10% rhodium core with a diameter of about 5 μm, covered with a layer of silver with 75 μm diameter. The wire is formed in a V-shape, and the silver is etched at the bend-point of the V so that in the region of sensitivity, the Pt/Rh core is uncovered. The region of the core without silver cover, the tip, has a much higher electrical resistance than all the remaining wire, so that by measuring the resistance of the wire, the average temperature of its sensitive region can be determined. When an electrical current is applied to such a probe, most of the Joule heating will be generated in the tip. The heat losses in all the remaining electrical system can be either neglected, or calibrated and subtracted from the total power applied.

The probe was submerged in several substances with different heat conductivities placed in a precision thermostated bath filled with silicon oil (poly(dimethylsiloxane): PDMS). The bath was kept at constant temperature, and the electrical current through the probe was controlled as a function of time. It is quite important to ensure that all of the sensitive part of the probe is well below the surface of the liquid being investigated, otherwise poor reproducibility results from additional heat losses from the measuring wire to the uncontrolled atmosphere. A method for the elimination of these losses will be discussed at the end of the paper.

To measure the true temperature of the probe, a very simple experiment was used. Its electrical schematic is shown in Fig. 1. The electric current I_{drive} goes through a transistor connected to the bridge circuit with an emitter follower. This ensures that the probe will be power-limited. The resistance of the probe R_{pr} is obtained directly from the measurement of the voltage U_{pr} on the probe and voltage U_{r} on the constant resistance R_{r}. The latter either can be just a known, constant resistance when it is used for direct measurement of the temperature of the probe, or can be adjusted by bridge balancing and used for measurements with temperature modulation in the quasi-isothermal mode. For this electrical scheme, the resistance of the probe

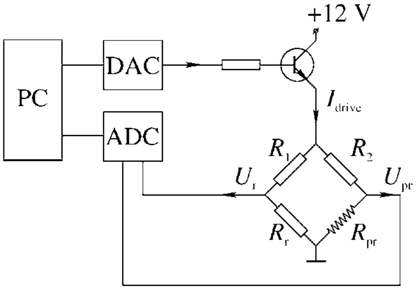

Fig. 1. Circuit diagram of the experimental arrangement used for the measurement of the probe temperature.

in the case of direct current (dc) can be calculated by the following formula:

$$R_{\mathrm{pr}} = \frac{R_2}{(U_{\mathrm{r}}/U_{\mathrm{pr}})((R_1/R_{\mathrm{r}}) + 1) - 1}. \tag{1}$$

When the driving current is modulated, which means a simultaneous application of a dc current and a small sinusoidally modulated alternating current (ac):

$$I_{\mathrm{drive}} = I_{\mathrm{drive}}^{\mathrm{dc}} + I_{\mathrm{drive}}^{\mathrm{ac}} \sin \omega t, \tag{2}$$

then the voltages are changing also sinusoidally at R_{r} and R_{pr}. The first voltage oscillates strictly in-phase with the driving current, while the second one demonstrates some phase shift φ, because in addition to a larger part which arises from modulation of I_{drive}, it contains also some contribution caused by the modulation of the temperature of the probe:

$$\begin{aligned} U_{\mathrm{r}} &= U_{\mathrm{r}}^{\mathrm{dc}} + U_{\mathrm{r}}^{\mathrm{ac}} \sin \omega t, \\ U_{\mathrm{pr}} &= U_{\mathrm{pr}}^{\mathrm{dc}} + |U_{\mathrm{pr}}^{\mathrm{ac}}| \sin(\omega t + \varphi). \end{aligned} \tag{3}$$

The voltage $U_{\mathrm{pr}}^{\mathrm{ac}}$ can also be represented as a complex number. By Fourier transformation, it is then separated into its real and imaginary parts $U_{\mathrm{pr}}^{\mathrm{ac}} = U_{\mathrm{pr}}^{\mathrm{ac}\prime} + iU_{\mathrm{pr}}^{\mathrm{ac}\prime\prime}$. The amplitude of the modulation of the probe resistance $R_{\mathrm{pr}}^{\mathrm{ac}}$ can also be separated into two components, namely the in-phase component $R_{\mathrm{pr}}^{\mathrm{ac}\prime}$ and the out-of-phase component $R_{\mathrm{pr}}^{\mathrm{ac}\prime\prime}$. Both can be calculated as follows:

$$R_{\mathrm{pr}}^{\mathrm{ac}\prime} = \frac{R_2}{(U_{\mathrm{r}}^{\mathrm{dc}} + U_{\mathrm{r}}^{\mathrm{ac}})/(U_{\mathrm{pr}}^{\mathrm{dc}} + U_{\mathrm{pr}}^{\mathrm{ac}\prime})((R_1/R_r) + 1) - 1} - R_{\mathrm{pr}}^{\mathrm{dc}}$$

and

$$R_{\mathrm{pr}}^{\mathrm{ac}\prime\prime} = \frac{R_2}{(U_{\mathrm{r}}^{\mathrm{dc}} + U_{\mathrm{r}}^{\mathrm{ac}})/(U_{\mathrm{pr}}^{\mathrm{dc}} + U_{\mathrm{pr}}^{\mathrm{ac}\prime\prime})((R_1/R_{\mathrm{r}}) + 1) - 1} - R_{\mathrm{pr}}^{\mathrm{dc}}. \tag{4}$$

If we connect a constant resistance in place of the thermal probe, then $R_{\mathrm{pr}}^{\mathrm{ac}}$ will be 0, because in this case $\varphi = 0$, $U_{\mathrm{r}}^{\mathrm{dc}}/U_{\mathrm{pr}}^{\mathrm{dc}} = U_{\mathrm{r}}^{\mathrm{ac}}/U_{\mathrm{pr}}^{\mathrm{ac}} = (U_{\mathrm{r}}^{\mathrm{dc}} + U_{\mathrm{r}}^{\mathrm{ac}})/(U_{\mathrm{pr}}^{\mathrm{dc}} + U_{\mathrm{pr}}^{\mathrm{ac}})$, and the left parts of Eq. (4) will be equal to $R_{\mathrm{pr}}^{\mathrm{dc}}$. If only dc current is applied (i.e. $U_{\mathrm{pr}}^{\mathrm{ac}} = 0$ and $U_{\mathrm{r}}^{\mathrm{ac}} = 0$), then $R_{\mathrm{pr}}^{\mathrm{ac}}$ will also be equal to 0.

The voltages were measured by an experimental setup based on a PC. For this purpose, two different measuring boards were applied. One of them was a standard commercial 16-bit analog–digital converter (ADC) with a sampling rate of 100 kHz. It was used for all dc measurements and also for high-precision recording of the modulated voltages at lower frequencies (up to 4 kHz). These voltages were recorded as a function of time. The amplitude and phase of the ac signals were obtained by further data treatment using Fourier transformations.

The second measuring board used in this work was built for this work. It was a digital lock-in amplifier (Kamasa, Research Institute of Solid State Physics, HAS, Budapest), having a 10-bit, 20 MHz ADC and able to detect ac signals up to 400 kHz. Amplitude and phase are recorded in real time. This board was used for high-frequency measurements. It includes also a two-channel 16-bit digital–analog converter (DAC) which was used as a source of the driving current. One of the DACs generates dc, the other ac. Both DACs are connected consecutively. This allows easy control of both dc and ac components of the driving current, having a mean value of the current equal to the dc component. A modulated current is generated based on a table of the sine loaded into memory. Any shape of the modulation can be programmed in the memory, including multifrequency saw-tooth modulations.

The samples for investigation in this study were chosen to represent a somewhat wider range of heat conductivities than is typical for most polymers. The measured liquids were toluene, ethanol, glycerol, and water. The organic liquids were obtained from Fisher and Malinkrodt. Furthermore, PDMS was used as a liquid polymer (fluid 200, Dow Corning). Finally, the heat conductivity of air was measured under the same conditions. The latter case was of special interest, because it represents the experimental conditions which are closest to those ones observed when performing localized thermal microanalysis of the surfaces by SThM.

3. Results

3.1. Determination of heat conductivity by dc measurement

The purpose of the dc measurements was to make a temperature calibration of the probe and to prove the applicability of this method for the determination of heat conductivities of liquids and gases. We have performed a direct temperature calibration of the probe, rather than the common indirect calibration by fixing of melting temperatures during scanning, typical of SThM. The resistance of the probe submerged in different substances was recorded as a function of the power on the probe, as shown in Fig. 2(a). All curves measured cross at zero power. To measure the temperature of the probe (which is obtained from its resistance), it is necessary to apply a certain power. This in itself results in a heating of the probe, therefore the true temperature of the medium in which the probe is submerged must be determined by extrapolation of the probe temperature to zero power. Because of some nonlinearity of the dependence of the power on resistance, such an extrapolation was done for the region of low power.

The temperature calibration involved five measurements at different temperatures of the bath. The data for heating of the probe submerged in PDMS are shown in Fig. 2(b). The resistance was linear with temperature within the accuracy of the precision bath (±0.5 K). The probe temperature at zero power is equal to the temperature of the medium. Thus, the resistance extrapolated to zero power can be converted to temperature. The temperature dependence of the resistance for Pt/Rh can be considered to be almost linear for the range of temperatures investigated, so that one writes

$$R = R_0[1 + \alpha(T - T_0)]. \tag{5}$$

The temperature coefficient of resistance was determined from Fig. 2(b) to be $\alpha = 0.00152\ \mathrm{K}^{-1}$. The literature value of α for the Pt (90%)/Rh (10%) alloy was given as $0.00165\ \mathrm{K}^{-1}$.[1]

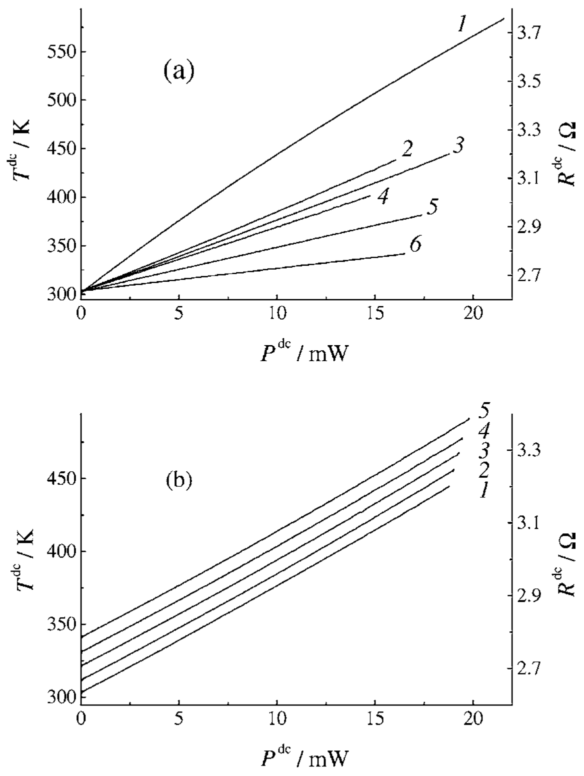

Fig. 2. (a) Resistance R^{dc} and temperature T^{dc} of the probe vs. power P^{dc}: (1) air; (2) toluene; (3) PDMS; (4) ethanol; (5) glycerol; (6) water. The temperature of the bath $T_0 = 305$ K. (b) Plots of R^{dc} and T^{dc} of the probe vs. P^{dc} for PDMS with different temperatures of bath T_0: (1) 305 K; (2) 314.5 K; (3) 324 K; (4) 333.5 K; (5) 343 K.

This dependence of power on temperature means that when some power is applied to the probe which is in contact with the medium, the equilibrium between the probe and the medium is established at some temperature which is determined by the heat conductivity of the substance. The power P^{dc} necessary to maintain the temperature of the probe T^{dc} is given by the following relationship:

$$\frac{P^{dc}}{T^{dc} - T_0} = A\lambda + C, \tag{6}$$

where λ is heat conductivity of the sample investigated, and T_0, the temperature of the bath. The coefficient A has a linear size-dimension and depends on the shape and area of contact between the probe and the medium, and C is a constant value which includes all losses of power over the experimental installation (heat dissipation in electronic components and wires, heat transfer from the sensitive region of the probe to highly conductive silver-covered wires, etc.). Both constants are properties of the particular probe and experimental setup and can be calibrated. For the same probe fully submerged in different liquids, they should be the same. Therefore, the slope of the $P^{dc}(T^{dc})$ dependence being proportional to the value of λ, it should be possible to determine A and C from one calibration substance and then apply them to the measurement of the heat conductivity of any other liquid. The measured $P^{dc}/(T^{dc} - T_0)$ are plotted in Fig. 3 against the literature value [18] of the heat

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[1] http://www.topometrix.com/products/probepdf/sthm.pdf.

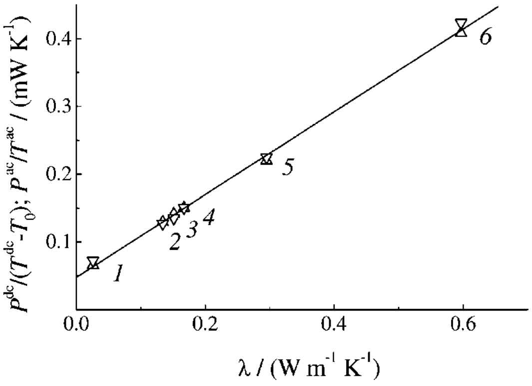

Fig. 3. Plots of $P^{dc}/(T^{dc} - T_0)$ calculated from dc data (Δ), and P^{ac}/T^{ac} calculated from ac data at 0.07 Hz frequency (∇) vs. literature values of λ for different liquids and air: (1) air; (2) toluene; (3) PDMS; (4) ethanol; (5) glycerol; (6) water. The temperature of the bath is 305 K.

conductivity of several liquids investigated in this fashion (Δ).

From Fig. 2(a), it can be observed that the power–temperature dependence for liquids like toluene and ethanol can be recorded up to a temperature about 50 K above the boiling point of the liquid. To understand these results, it must be taken into account that the temperature measured in these experiments is not the temperature of the medium, but the temperature of the probe. Only a very thin layer of the medium investigated which is in direct contact with the probe has the same temperature as is recorded. With an increase in the distance from the probe, the temperature of the medium quickly drops, and at infinite distance, it reaches the temperature of the bath. Therefore, even if the layer of the liquid adjacent to the probe has a temperature above the boiling point, it is still unable to boil until its thickness reaches a certain value. The high values of superheating necessary to start a phase transition in the liquid mean that the thickness of this high-temperature liquid layer is quite small.

3.2. Frequency range of thermal sensitivity of the Wollaston wire probe

When modulating any parameter (including temperature) to measure some property, it is important to know the behavior of the measuring system itself as the frequency changes. Therefore, we have investigated the frequency response of the Wollaston wire probe. The probe was used in a "programmed current mode". This means that the driving current is either constant, or it follows some program and the temperature feedback is not activated. An alternative way would be a "programmed temperature mode" which means usage of the temperature feedback to keep the temperature of the probe following some program.

To make sure that the observed effect is not an instrumental artifact, two tests were carried out: one of them with the resistive thermal probe, the other using a constant resistance in place of the probe. This constant resistance is equal to the resistance of the probe without modulation heated to the temperature of the experiment. A sinusoidally modulated current with some underlying dc value was applied in both cases. Fig. 4 shows the amplitude of the modulated temperature (resistance) on the probe in air and on the constant resistance over a wide frequency range.

When the modulated current is applied to the constant resistance, the measured amplitude of voltage across it is some constant value, independent of the driving frequency. This constant voltage amplitude comes only from the modulation of the current, therefore in Eq. (4) $R^{ac}_{pr} = 0$. When the Wollaston wire probe is used however, the amplitude of the voltage across it at low frequencies is higher than at high frequencies. As long as the temperature of the probe (and therefore its resistance) follows the modulation of the driving current, it brings an additional increment to the amplitude of the probe voltage. The amplitude of temperature modulation of the probe in the air stays constant up to about 100 Hz. In the frequency range

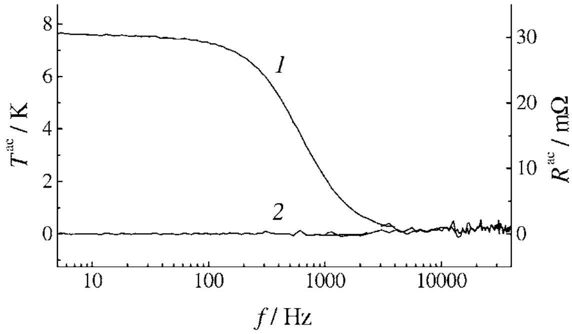

Fig. 4. Typical frequency dependence of the amplitude of the modulated temperature and resistance of the Wollaston wire probe (1) and a constant resistance (2) in air.

100–5000 Hz, it decreases, and above 5 kHz, it is again constant, and now equal to the amplitude of the voltage across the constant resistance. This means that at frequencies above 5 kHz, the thermal probe becomes insensitive to the current modulation and behaves like a constant resistance.

These data show that such Wollaston wire resistance in air can be used only for direct quantitative thermal measurements at frequencies below 100 Hz in the programmed current mode. At frequencies up to 5 kHz, it can be used conditionally, but it would be necessary to make some correction that takes into account the strong frequency dependence. Fortunately, it was found that each individual probe is usually very reproducible and can be calibrated.

In the "programmed temperature mode", the range of the linear temperature–frequency relation can be slightly extended. The decrease in the temperature modulation amplitude is compensated by a higher amplitude of the driving current. In this case, the maximum possible frequency is achieved when the ac-amplitude becomes equal to the underlying dc level. Higher ac-amplitudes do result in an asymmetric profile of the modulation, being cut at the low side. Another limitation is still the same 5 kHz frequency where the temperature of the probe is not dependent any more on the modulation.

When a perturbation of any parameter (e.g. the driving current) is applied to the measuring system, the time–temperature response of the system can be described by the following differential equation:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{\tau}(T_0 - T), \tag{7}$$

where T_0 is the final temperature, and τ a time constant characteristic of the relaxation time of the system. The solution of Eq. (7) is an exponential function $\mathrm{e}^{-t/\tau}$. The temperature response to a step in the driving current can be found as $T = T_0\,\mathrm{e}^{-t/\tau}$ or $T = T_0(1 - \mathrm{e}^{-t/\tau})$ depending on the initial step in the driving current being of positive or negative value.

From the above discussion, it can be seen that the frequency-dependent temperature response is a complex function consisting of

$$T'(\omega) = T^{\mathrm{dc}} + \frac{|T^{\mathrm{ac}}|}{1+\omega^2\tau^2} \quad \text{and} \quad T''(\omega) = \frac{|T^{\mathrm{ac}}|\omega\tau}{1+\omega^2\tau^2}, \tag{8}$$

where $|T^{\mathrm{ac}}|$ is the module of the temperature amplitude, and ω, the angular frequency. The real part $T'(\omega)$ decreases with frequency, while the imaginary part $T''(\omega)$ has a maximum at $\omega_\tau = 1/\tau$. At this point, $T^{\mathrm{ac}\prime}(\omega_\tau) = T^{\mathrm{ac}\prime\prime}(\omega_\tau) = (1/2)|T^{\mathrm{ac}}|$. This point corresponds to $1/e$ of the temperature response in the time domain.

We have measured a time constant of the probe by applying of a single square pulse to the driving current, as shown in Fig. 5. The time constant of the probe in air is $\tau_1 = 200$ μs for heating and $\tau_2 = 270$ μs for cooling. If we change from the time to the frequency domain:

$$f_\tau = \frac{1}{2\pi\tau}, \tag{9}$$

we obtain the corresponding frequencies $f_{\tau_1} = 800$ Hz and $f_{\tau_2} = 590$ Hz. In Fig. 6, the frequency dependence is plotted for the measured real part $R^{\mathrm{ac}\prime}$ and imaginary part $R^{\mathrm{ac}\prime\prime}$ of the probe resistance, together with those values reconstructed from the time constants by a Fourier transformation. The measured frequency characteristic of the probe resistance is in good agreement with the larger time constant τ_2 of cooling, because the behavior of the probe is limited by the slowest process.

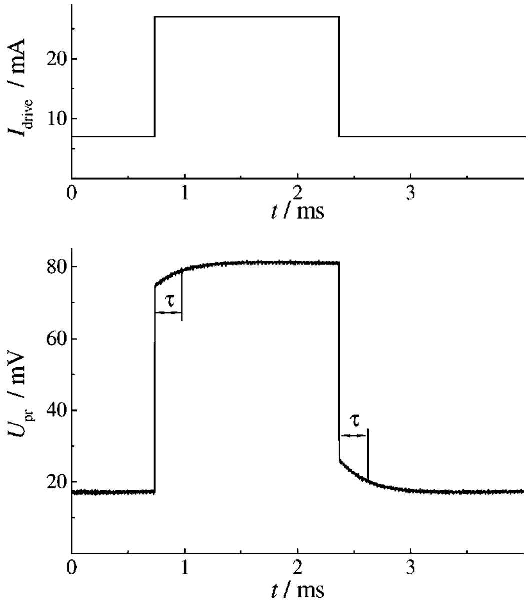

Fig. 5. A single square pulse of driving current I_{drive} and the resulting jump in probe voltage U_{pr} used for calculation of the time constant of the probe τ.

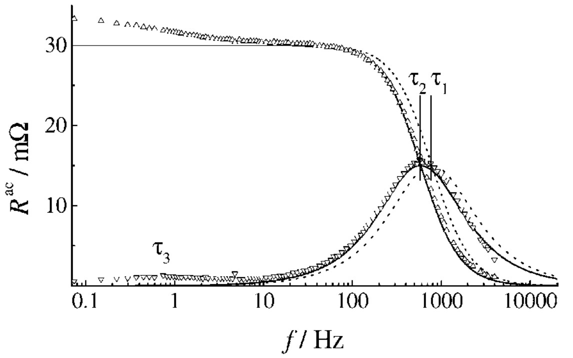

Fig. 6. Frequency dependence of the measured real (Δ) and imaginary (∇) amplitudes of the modulated resistance on the probe in air, and the frequency behavior of the probe reconstructed from the time constants τ_1 (- - -) and τ_2 (—) of the probe in air.

An additional time constant, $\tau_3 \approx 0.3$ s, which corresponds to a frequency of about 0.5 Hz, is observed for the probe in air. It is accompanied by a much smaller amplitude of the temperature-relaxation process, and is probably connected with the heat transfer from the tip where the modulated heat is generated to the much bulkier silver-covered part of the Wollaston wire. The temperature of the Wollaston wire (or more precisely, the temperature of the region adjoining the uncovered tip) can also be slightly modulated, but only up to some low frequencies. Thus, the best range of frequencies for quantitative local thermal analysis is 10–100 Hz. In this range, the amplitude of temperature modulation of the sensitive part of the probe is still constant, and the temperature of the bulk of the Wollaston wire is not modulated anymore.

3.3. Application of the temperature modulation for heat conductivity determination

Applying the modulated current to the probe submerged in different liquids gives similar results as those for air. Fig. 7 shows a plot of the frequency dependence of the amplitudes of the real and imaginary parts of the probe resistance ($R^{ac\prime}$ and $R^{ac\prime\prime}$) and the probe temperature ($T^{ac\prime}$ and $T^{ac\prime\prime}$). In this case, the region of constant $T^{ac\prime}$ is shifted to lower frequencies (below 5 Hz) in comparison to air. The frequency above which the temperature of the probe is not modulated, however, starts from 5 kHz that is nearly the same as in air. The imaginary part $T^{ac\prime\prime}$ has a maximum between 200 and 600 Hz, and moves to lower frequencies with increasing heat conductivity of the sample.

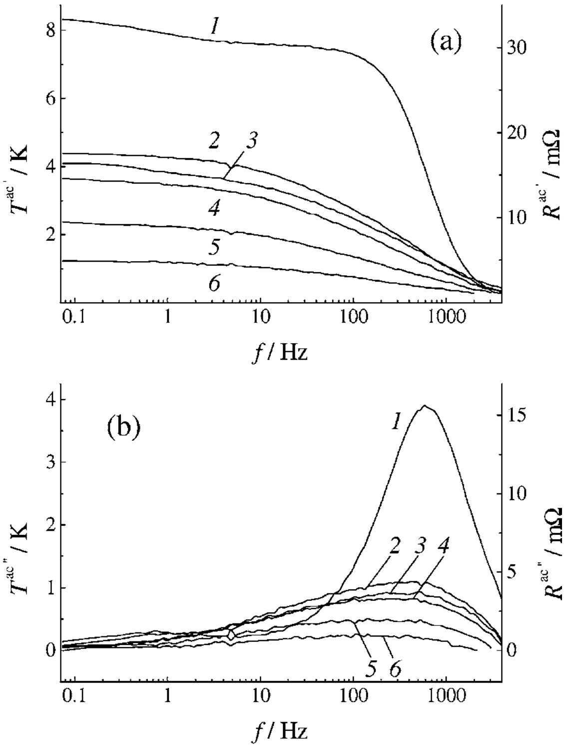

Fig. 7. Frequency dependence of the real (a) and imaginary (b) parts of the amplitude of modulated temperature (resistance): (1) air; (2) toluene; (3) PDMS; (4) ethanol; (5) glycerol; (6) water. Temperature of the bath is 305 K.

The heat conductivity of the medium can be determined also from the experiment with modulated current applied to the probe. Taking into account that

$$T^{ac} = \frac{R^{ac}}{\alpha R^{dc}}, \tag{10}$$

the ratio of the ac power (P^{ac}) on the probe to the amplitude of the probe temperature can be calculated as follows:

$$\frac{P^{ac}}{T^{ac}} = \alpha R^{dc}\left(\frac{R^{dc}}{R^{ac}}(2I^{dc}I^{ac} + (I^{ac})^2) + (I^{dc} + I^{ac})^2\right). \tag{11}$$

The ratio of R^{dc}/R^{ac} is usually big enough to simplify this equation to

$$\frac{P^{ac}}{T^{ac}} \approx \alpha\frac{(R^{dc})^2}{R^{ac}}(2I^{dc}I^{ac} + (I^{ac})^2). \tag{12}$$

For the region of lower modulation frequencies, where T^{ac} is independent of frequency, the ratio of power amplitude to temperature amplitude is proportional to heat conductivity of the medium. In Fig. 3, P^{ac}/T^{ac} plotted against λ is shown for the 0.07 Hz frequency (∇). It can be written as

$$\frac{P^{ac}}{T^{ac}} = A\lambda + C, \tag{13}$$

where A and C are the same calibration constants as were determined from the dc measurement (Eq. (6)).

4. Discussion

The problem of application of microcalorimetry for quantitative thermal analysis of the surfaces remains still unsolved. The advantage of the method tested in this work, however, is that it allows a direct determination of the probe temperature.

This method differs from the one developed by Hammiche et al. [13] which is utilized in the commercial μTA 2990. In the commercial apparatus, some programmed current is applied to the system consisting of two equal Wollaston wire thermal probes which are connected differentially. One of them acts as a sample probe, the other as a reference resistance. A programmed current is applied to both resistances, and the feedback is used to ensure that the sample probe has the same temperature as the reference probe. Thus, the only value really measured during the experiment is the power applied to the probe. The temperature of the probe is not measured, but obtained from the program for the current, using a relative calibration by heating of samples with known phase transition temperatures [14]. As a result, this method allows only to determine the onset temperatures of some phase and relaxation transitions in the sample, especially those connected with changes in area of contact between tip and sample surface. Any quantitative measurement of the heat is thus quite complicated. The method suggested in this work, in contrast, is based on simultaneous and direct measurement of both power and temperature of the probe which is in thermal contact with the investigated substance. This allows to set up well-defined quantitative conditions of heat transfer between the probe and the sample.

Typically, the area of contact between the top of the Wollaston wire probe and the surface being investigated for compliant polymeric materials is about 1.0 μm^2, and is much smaller for hard surfaces like metals (about 1000 nm^2) [15]. A typical geometry of part of the Wollaston wire probe which is uncovered from silver has a diameter of 5 μm and a length of 200 μm. This results in an area of 3000 μm^2. Thus, the area of the sensitive part of the probe from which the heat is dissipated is by three orders of magnitude higher than the area of contact with the polymeric sample. The temperature obtained from the resistance is an average temperature over the total area of the sensor uncovered by the silver layer. Therefore, such method of local thermal analysis has very high requirements of precision of heat and temperature measurements. This limitation might be partly overcome using a differential technique with a second probe used as a reference [13]. Due to the inequality of the hand-made probes, however, it is still quite problematic to get quantitative results.

Application of the modulated heating has two distinct advantages [13]. It generates thermal waves whose diffusion length is frequency dependent, i.e. it allows to use relatively well-established principles of temperature-modulated differential scanning calorimetry (TMDSC) for acquisition of local thermal analysis data. It was shown that the thermal penetration depth d can be estimated for the modulated heat supplied to the semi-infinite medium as [14]

$$d = \sqrt{\frac{2D}{\omega}}, \tag{14}$$

where D is the thermal diffusivity of the medium. If the modulation frequency is changed, the depth profile of thermal conductivity and thermal diffusivity can be obtained. Thus, modulation of the temperature of the probe is a necessary condition for extraction of quantitative thermal information. Our data show, however, that at frequencies above approximately 5 kHz, the temperature of the standard Wollaston wire probe is not modulated by the driving current. This means that the range of frequencies available in the commercial μTA 2990 (2–100 kHz) is not well suited for quantitative measurements of the local thermal properties of surfaces. This device is mainly intended for thermal imaging, where high modulation frequencies are necessary, the use of lower frequencies will result in too slow imaging. Extending the commercial software to the lower frequency region would, however, expand the usefulness of the microcalorimeter considerably for local analyses.

Dinwiddie et al. [6] reported that using differential temperature control, it was possible to achieve 33–100 kHz frequency response of a similar probe. The probe with core wire made of pure platinum was connected consecutively with a trim inductance. By adjustment of the latter, it was possible to minimize the period of feedback instability when applying a square temperature wave of 10–30 μs. This corresponds to a vertical part of the response U_{pr} which is shown in Fig. 5. In our case, this period was equal to 5 μs. This value should depend mainly on the electronic scheme used. The temperature of the probe, however, during this period of time is not changed and this time represents the reaction time of the electronics itself. As it was mentioned above, for quantitative analysis, the thermal response of the probe is of crucial importance.

Another disadvantage of the μTA 2990 design, which also prevents it from obtaining of calorimetric information is its inability to support a constant force of interaction between the probe and the sample surface during local thermal analysis experiments. This force usually changes during the experiment because of reasons like thermal expansion of the probe and sample, phase and relaxation transitions in the sample, and changes in mechanical compliance of the sample surface. In the absence of the force feedback, it results in different deflections of the cantilever (the value which is proportional to force in AFM). In the μTA 2990, the deflection of cantilever is recorded during the local thermal analysis as ‘‘thermomechanical signal’’. This signal, of course, carries some information about changes occurring in the sample during localized heating, however, the thermal signal loses its ability to generate any quantitative information, because the thermal contact between the probe and the sample changes during the experiment and it is now temperature-dependent. A better approach would be to use the force feedback also during such experiments. Any changes in the sample surface position will then be compensated by a corresponding adjustments of the Z-piezo. The force of interaction will stay constant during local thermal analysis experiment, and nearly the same thermomechanical signal can be recorded from Z-piezo position needed to keep the force constant. These two methods can be described in terms typical for AFM imaging as constant height and constant force modes. The first one is usually used in AFM for imaging of atomically flat surfaces, where the deviations in cantilever deflection are expected to be extremely small. In the case of local thermal analysis, the change in the cantilever deflection due to heating of the sample and probe is typically larger, resulting in considerable uncertainty of thermal contact, therefore, obtaining of quantitative thermal analysis information is possible only in the constant force mode.

When the thermal probe is brought in contact with the sample surface, the thermal contact between probe and surface is never perfect. It results in some parasite thermal resistance, which arises always when the measurement technique requires flow through the interface. On the other hand, this resistance cannot be exactly reproduced from one approach of the probe to the surface to another. The surface investigated is never perfectly flat, the end of the probe also has some curvature, and the surface of the sample might undergo some deformation due to the force applied through the probe. For this reason, the contact resistance should always be taken into account when performing quantitative localized thermal analysis. The problem of undefined thermal contact between the probe and the surface can be eliminated using temperature-modulation techniques. Within one series of experiments, the probe is continually kept in contact with the surface at the same point. Thermal resistance in the point of contact is a constant value independent of frequency, assuming that the force of the probe–sample interaction is maintained. Thermal penetration depth, and therefore the amount of the sample which is involved in the modulation however, as it can be seen from Eq. (14), is proportional to $\omega^{-1/2}$. Therefore, several measurements performed at different modulation frequencies allow to make an extrapolation to zero frequency, where this thermal resistance will be negligible. An even better approach would be the usage of multifrequency modulation, which allows to apply to the sample several modulation frequencies in a single experiment and has led in TMDSC to the elimination of the effect of thermal resistance within the sample, and from the sample to the temperature sensor [19].

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