SIMPLE MODEL FOR SCANNING CALORIMETER WITH PYROELECTRIC HEAT SENSOR

I. A. Kleinman, A. Z. Rabinovich,
M. B. Roitberg, and M. S. Chupakhin

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The heat-conduction equation is solved for a simplified model of a scanning heat-conducting calorimeter with a working cell in the form of a spherical pyroelectric thermometer. The optimum material and dimensions for the pyroelectric sensors are determined by numerical analysis of the solution.

Detailed study of the kinetics of phase transformations in liquid-crystal compounds, ferroelectrics, and many other materials has become mandatory as a result of their broad application in various branches of science and technology.

One of the most promising approaches to this problem, in our opinion, is a calorimeter with programmed variation of working cell temperature – the scanning calorimeter.

The nonlinearity of the electrical output of pyroelectric materials with respect to temperature (or heat flow) [1] makes them suitable for a calorimeter of this kind.

A hollow pyrothermometer [1], which can form the container for the sample studied, is most promising for this application. The heat flow through the pyroelectric material is conducted through the calorimeter shell, consisting of a massive metallic block whose temperature is independent of the processes occurring in the calorimetric cell.

To determine the optimum cell parameters, a mathematical model of the calorimeter is examined, in approximate form, in order to obtain an expression for variation of average cell temperature with time. This enables one to optimize the sensor material and dimensions.

Oleinik [2] has developed a calorimeter model which is considered as a uniform core, enclosed in a shell of known thickness in an unbounded medium. This structure seems entirely suitable for a pyroelectric calorimeter. However, one of his basic assumptions is the absence of a temperature gradient in the shell. This is not applicable to a heat-conducting calorimeter.

We assume for simplicity that the shell is spherical, ideal thermal contact exists between the outer surface of the sphere and the medium (massive metallic block), and the heat transfer to the inner surface follows Newton's law. The thermal constants of the sphere are independent of temperature.

Since the sphere's wall thickness is much less than its radius, the heat-conduction equation can be considered one-dimensional and can be written in Cartesian coordinates, with the center as the origin [3, 4]:

$$\frac{\partial T}{\partial \tau} = a \frac{\partial^2 T}{\partial r^2}. \tag{1}$$

The initial condition can be written in general form as

$$T(r, 0) = T_0(r). \tag{2}$$

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To assign boundary conditions, we assume that the temperatures at the inner and outer surfaces of the sphere are given by arbitrary functions $f_1(\tau)$ and $f_2(\tau)$, respectively. Then

$$\left.\begin{array}{l}\lambda \dfrac{\partial T(R_1, \tau)}{\partial r} + \alpha [f_1(\tau) - T(R_1, \tau)] = 0 \\ T(R_2, \tau) = f_2(\tau)\end{array}\right\}. \tag{3}$$

In linear scanning, the outer surface temperature varies according to

$$T(R_2, \tau) = T_0 + b\tau. \tag{4}$$

As shown in [5], the inner surface temperature variation is also linear, but with a lag $b\tau_0$. Thus, at any instant during scanning

$$\left.\begin{array}{l} f_1(\tau) = b\tau - b\tau_0 \\ f_2(\tau) = b\tau \end{array}\right\} \tag{5}$$

and $T_0(r) \neq 0$. Here we assume that $T_0(r)$ is linear,

$$T_0(r) = b\tau_0 (R_2 - r)/\delta. \tag{6}$$

Let the cell temperature during scanning attain the value corresponding to the start of the process studied, which follows the exponential law

$$f(\tau) = T_M [1 - \exp(-kT)]. \tag{7}$$

The temperature variation of the inner surface is then given by

$$f_1(\tau) = b\tau - b\tau_0 + f(\tau), \tag{8}$$

and the outer surface temperature remains $f_2(\tau)$ [see Eq. (5)].

Because of the nonlinearity of the pyrothermometer, the solution of Eq. (1) is written in terms of $d\tilde{T}/d\tau$, where $\tilde{T}$ is the average sensor temperature, as indicated in [6]:

$$\frac{d\tilde{T}}{d\tau} = \frac{d}{d\tau}\left\{\frac{1}{V}\int_V T dV\right\}. \tag{9}$$

The solution of Eq. (1) in the form (9) can be substituted directly into the expression [1]

$$u \sim A\gamma d\tilde{T}/d\tau, \tag{10}$$

which describes the electrical output of the pyrothermometer.

Solving Eq. (1) by the method described in [7, 8], using the superposition principle [6], we find $d\tilde{T}/d\tau$ for linear scanning:

$$\begin{aligned}\frac{d\tilde{T}}{d\tau} = {} & \frac{3aR_2}{R_2^3 - R_1^3} \cdot \frac{T_M \mathrm{Bi}}{N} \exp(-k\tau)[R_2 + (a/k)^{1/2} \sin\delta (k/a)^{1/2} \\ & + R_1 \cos(k/a)^{1/2}\delta] + \frac{3a\,\mathrm{Bi}}{R_2^3 - R_1^3} \sum_{i=1}^{\infty} \left(\frac{b}{p_i^2} + \frac{T_M - b\tau_0}{p_i} - \frac{T_M}{k + p_i}\right) \\ & \times \frac{\exp(p_i\tau)}{M}\left(R_1 \cos\mu_i + \frac{\delta}{\mu_i}\sin\mu_i - R_2\right) - \frac{b\,\mathrm{Bi}}{\varphi_0} + \frac{b(\mathrm{Bi}+1)}{\varphi_0} \\ & \times \frac{R_2}{R_1} - \frac{3\delta^2 R_2}{R_2^3 - R_1^3} \cdot \frac{b}{a} \sum_{i=1}^{\infty} \frac{\exp(p_i\tau)}{\mu_i^3 M}\left[\frac{\delta}{\mu_i}\cos\mu_i - \delta/\mu_i\right. \\ & \left. + R_2 \sin\mu_i + \frac{\mathrm{Bi}+1}{R_1} \cdot \frac{\delta}{\mu_i}\left(\frac{\delta}{\mu_i}\sin\mu_i + R_1 - R_2\cos\mu_i\right)\right],\end{aligned} \tag{11}$$

where $\mathrm{Bi} = \alpha R_1/\lambda$ is the Biot criterion,

$$N = \sum_{n=0}^{\infty} (-1)^n \varphi_n k^n = \frac{\mathrm{Bi}+1}{R_1}(a/k)^{1/2} \sin(k/a)^{1/2}\delta + \cos(k/a)^{1/2}\delta;$$

TABLE 1. Roots of Eq. (14) for $\delta / R_1 = 0.05$

Bi	μ_1	μ_2	μ_3	μ_4	μ_5	μ_6
0,00	1,6014	4,7229	7,8564	11,000	14,1407	17,2816
0,10	1,6053	4,7242	7,8655	11,0008	14,1410	17,2818
0,20	1,6090	4,7254	7,8657	11,0012	14,1413	17,2821
0,40	1,6148	4,7274	7,8660	11,0022	14,1420	17,2827
0,60	1,6191	4,7291	7,8662	11,0029	14,1428	17,2832
0,80	1,6248	4,7312	7,8664	11,0038	14,1435	17,2838
1,00	1,6320	4,7335	7,8667	11,0047	14,1443	17,2845
2,00	1,6603	4,7439	7,8730	11,0092	14,1473	17,2874
4,00	1,7152	4,7647	7,8857	11,0188	14,1548	17,2932
6,00	1,7660	4,7653	7,8983	11,0273	14,1619	17,2990
8,00	1,8137	4,8057	7,9109	11,0363	14,1690	17,3047
10,00	1,8582	4,8259	7,9233	11,0454	14,1760	17,3105
15,00	1,9586	4,8751	7,9452	11,0677	14,1935	17,3249
20,00	2,1017	4,9585	8,0086	11,1076	14,2250	17,3552
49,00	2,3723	5,1599	8,1504	11,2143	14,3099	17,4211
99,00	2,6537	5,4544	8,3914	11,4086	14,4699	17,5562
199,00	2,8628	5,7606	8,7083	11,7027	14,7335	17,7908
999,00	3,0801	6,1606	9,2420	12,3247	15,4090	17,4953
∞	3,1416	6,2832	9,4248	12,5665	15,7080	18,8496

$$M = \frac{\delta}{R_1} \cdot \frac{\mathrm{Bi}+1}{\mu_i} \cos\mu_i - \left(1 + \frac{\delta}{R_1} \cdot \frac{\mathrm{Bi}+1}{\mu_i^2}\right) \sin\mu_i;$$

$$\varphi_n = \frac{\delta^{2n}}{a^n (2n)!}\left(1 + \frac{\delta}{R_1} \cdot \frac{\mathrm{Bi}+1}{2n+1}\right); \quad p_i = -\mu_i a/\delta^2,$$

the μ_i being the roots of the characteristic equation

$$\sum_{n}^{\infty} (-1)^n (a/\delta^2)^n \varphi_n \mu_i^{2n} = 0. \tag{12}$$

Equation (11) is considerably simplified for a constant outer shell temperature (b = 0), and only those sums which do not contain b remain in the first part.

In practice, the calorimeter must be stable against temperature fluctuations in the external medium. This is achieved by including in the calorimeter's outer shell a second sensor which is identical to the first and connected to it by a differential circuit. Solving the same problem for the second cell, a finite expression for $d\tilde{T}/d\tau$ is obtained. This expression contains on the right-hand side only those terms resulting from temperature changes in the measuring sensor, for both scanning and constant outer shell temperature:

$$\frac{d\tilde{T}}{d\tau} = \frac{3aR_2}{R_2^3 - R_1^3} \cdot \frac{T_{\text{M}}\mathrm{Bi}}{N} \exp(-k\tau)[R_2 + (a/k)^{1/2} \sin\delta (k/a)^{1/2}$$

$$+ R_1 \cos\delta (k/a)^{1/2}] - \frac{3a\,\mathrm{Bi}}{R_2^3 - R_1^3} \sum_{i=1}^{\infty} \frac{T_{\text{M}}}{k + p_i} \cdot \frac{\exp(p_i \tau)}{M} \left(R_1 \cos\mu_i + \frac{\delta}{\mu_i} \sin\mu_i - R_2\right). \tag{13}$$

The determination of numerical values of $d\tilde{T}/d\tau$ in Eqs. (11) and (13) requires solving the characteristic equation (12), which after transformation into the form

$$\operatorname{ctg}\mu = -\frac{\delta}{R_1} \cdot \frac{\mathrm{Bi}+1}{\mu} \tag{14}$$

is easily performed on a computer for any finite number of roots.

Using the Nairi-2 computer, we have tabulated the first six roots of Eq. (14) for various R. The table lists values of the first six roots for B_i at $\delta/R_1 = 0.05$.

The following results were obtained from the computer numerical analysis of Eqs. (11) and (13) taking account of the physical characteristics of the material (resistivity, dielectric constant, pyroelectric constant, and thermal constants).

1. $d\tilde{T}/d\tau$ increases somewhat with increased thermal-diffusion rate. A material with as large a value of a as possible should be used (other parameters being optimized).

2. $d\tilde{T}/d\tau$ increases significantly with decreased δ. However, the pyroelectric effect of the sphere material decreases, because of the increase in electrical conductivity and decrease in dielectric constant. The optimum value of δ is therefore 0.5 mm. For this value, a change in the physical characteristics of the sensor material does not affect its pyroelectric activity.

3. The calculated increase in $d\tilde{T}/d\tau$ with increasing R_1 does not give a true picture of the behavior of $d\tilde{T}/d\tau$, because at constant volume a change in spherical radius results in a change in the Biot criterion, and a simultaneous increase in R_1 and the sample volume can cause a significant temperature gradient in the sample. The optimum spherical radius is 10 mm for a sample volume not less than 4 cm^3.

We have therefore designed a sphere with $R_1 = 10$ mm and $\delta = 0.5$ mm. The material is lead titanate –zirconate with various additives.

NOTATION

R_1, R_2 are the inner and outer spherical radii, respectively, mm;
r is the coordinate;
τ is the time, sec;
T_0 is the temperature at zero time, °C;
a is the sphere thermal-diffusion coefficient, m^2/sec;
λ is the sphere thermal conductivity, $W/m \cdot deg$;
α is the heat-transfer coefficient of inner sphere surface, $W/m^2 \cdot deg$;
τ_0 is the calorimeter time constant, sec;
b is the scanning rate, deg/sec;
V is the spherical shell volume, m^3;
T_M is the maximum temperature increase at $\tau \to \infty$;
k is the thermal process rate constant;
γ is the pyroelectric constant, $C/m^2 \cdot deg$;
A is the pyrosensor electrode area, m^2;
u is the pyrovoltage, V;
$\delta = R_2 - R_1$.

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