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MEASUREMENTS OF THERMOPHYSICAL PROPERTIES OF LIQUID ELECTROLYTE BY MODIFIED HEAT PULSE TECHNIQUE

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Abstract—A new heat pulse technique is presented for measuring thermal diffusivity and conductivity of a liquid electrolyte. The method as originally proposed by Parker *et al.* was suitable for flat specimens only, and it is adapted here to a cylindrical geometry.

Theoretical and mathematical formulation, with appropriate boundary and initial conditions imposed, leads to an analytical solution on which the proposed method is based.

The technique was tested for some liquid metals having well-established property values and an accuracy of 5% was achieved for thermal diffusivities. Scatter of about 15% were noted for an electrolyte of $3\,NaF.AlF_3 + 10\%$ wt Al_2O_3 at 1273 K.

NOMENCLATURE

a,	thermal diffusivity;
c_p,	specific heat at constant pressure;
Fo,	Fourier's number;
J_0, J_1,	Bessel's functions of the first kind of zero and first order;
Q_0,	heat losses to surroundings;
Q,	heat pulse;
r,	radial coordinate;
R,	radius of specimen;
T,	temperature;
z,	axial coordinate of cylinder.

Greek symbols

α_n,	positive roots of equation $J_1(\alpha) = 0$;
τ,	time;
$\tau_{0.5}$,	time required for the outside sample surface to reach half of the maximum temperature rise;
ρ,	density;
λ,	thermal conductivity.

1. INTRODUCTION

A KNOWLEDGE of temperature dependence of thermal diffusivity and conductivity is important for temperature field modelling in the liquid electrolyte during the aluminium electrolysis process. Available experimental data differ greatly from each other and are of little use when the values are needed for direct calculations.

The inconsistencies of the data are caused by the strong influence of some factors, such as variations of chemical composition of the electrolyte, or difficulties in achieving sufficiently high accuracy of measurements. The high temperature (above 1200 K) and rapid corrosion of the apparatus caused by the electrolyte decomposition also impede reproducible results. Therefore any method used should be rather fast. This is the advantage of the Parker *et al.* impulse method [1], which was originally designed for solids. This paper describes an alternative technique using a cylindrical geometry (in the Parker method flat specimens are used) and is perhaps more suitable for liquids.

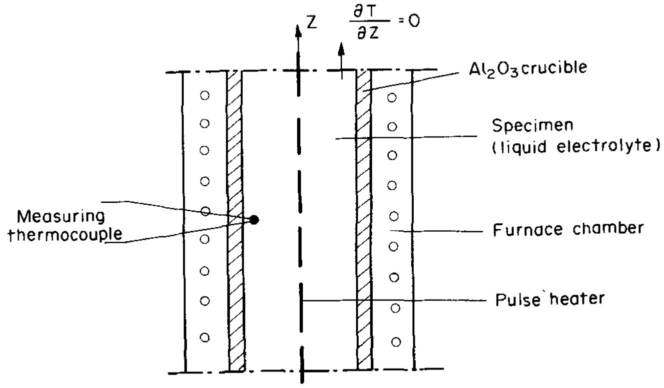

FIG. 1. General scheme of the assumed geometry of the model.

2. MATHEMATICAL FORMULATION OF THE PROPOSED METHOD

Let us consider an initial-boundary value problem for an infinite cylinder (Fig. 1).

A linear pulse heat source, viz. a thin electrically heated wire, was located along a specimen axis. A short heat pulse caused a sudden rise of temperature in the vicinity of the heat source. The temperature of the specimen at a distance $r = R$ was continuously recorded. The diffusivity can be determined directly from the analytical solution obtained. The thermal conductivity can also be calculated if the quantity of heat supplied during the pulse is known.

Let us assume that the specimen temperature-rise is small (of a few degrees only). Therefore a linear model of the heat transfer process can be applied and the influence of the convection neglected.

The heat conduction in a specimen can be described by the differential equation

$$a\left[\frac{\partial^2 T(r,\tau)}{\partial r^2} + \frac{1}{r}\frac{\partial T(r,\tau)}{\partial r}\right] = \frac{\partial T(r,\tau)}{\partial \tau}. \tag{1}$$

The solution of equation (1) for the boundary conditions

$$\left.\frac{\partial T(r,\tau)}{\partial r}\right|_{r\to R} = 0 \tag{2}$$

$$\left.\frac{\partial T(r,\tau)}{\partial r}\right|_{r\to 0} = 0 \tag{3}$$

and for the initial condition

$$T(r,0) = f(r) \tag{4}$$

is of the following form [2]

$$T(r,\tau) = \frac{2}{R^2}\int_0^{R_0} r' f(r')\,\mathrm{d}r' + \frac{2}{R^2}\sum_{n=1}^{\infty}\exp(-a\alpha_n^2\tau/R^2)\,\frac{J_0(r\alpha_n/R)}{J_0^2(\alpha_n)}\int_0^{R_0} r' f(r') J_0(r'\alpha_n/R)\,\mathrm{d}r' \tag{5}$$

where α_n are zeros of the characteristic equation

$$J_1(\alpha) = 0. \tag{6}$$

It can also be assumed that the instantaneous increase of the temperature in the vicinity of the heat source, say in a layer R_0 thick (Fig. 2) is

$$T(r,0) = \frac{Q}{\pi R_0^2 \rho c_p} \tag{7}$$

and

$$T(r,0) = 0 \quad \text{for} \quad r \in (R_0, R). \tag{8}$$

After substituting equations (7) and (8) into (5) we obtain

$$T(r,\tau) = \frac{Q}{\pi R^2 \rho c_p}\left\{1 + \sum_{n=1}^{\infty}\exp(-a\alpha_n^2\tau/R^2)\,\frac{J_1[(R_0/R)\alpha_n]}{(R_0/R)\alpha_n}\,\frac{J_0(r\alpha_n/R)}{J_0^2(\alpha_n)}\right\}. \tag{9}$$

Applying the Taylor expansion for the function

$$\frac{J_1[(R_0/R)\alpha_n]}{(R_0/R)\alpha_n} = \frac{1}{2} - \frac{[(R_0/R)\alpha_n]^2}{2^2 4} + \frac{[(R_0/R)\alpha_n]^4}{2^2 4^2 6}\cdots$$

we can confine ourselves to the first term only

$$\frac{J_1[(R_0/R)\alpha_n]}{(R_0/R)\alpha_n} \approx \frac{1}{2}$$

because

$$R_0\alpha_i/R \ll 1 \quad \text{for } i = 1,2\ldots.$$

Equation (9) then simplifies to the form

$$T(r,\tau) = \frac{Q}{\pi R^2 \rho c_p} \times \left\{1 + \sum_{n=1}^{\infty}\exp\left[-a\alpha_n^2\tau/R^2\,\frac{J_0(r\alpha_n/R)}{J_0^2(\alpha_n)}\right]\right\}. \tag{10}$$

For $r \to R$ we have

$$T(R,\tau) = \frac{Q}{\pi R^2 \rho c_p} \times \left\{1 + \sum_{n=1}^{\infty}\exp\left[-a\alpha_n^2\tau/R^2\,\frac{1}{J_0(\alpha_n)}\right]\right\}. \tag{11}$$

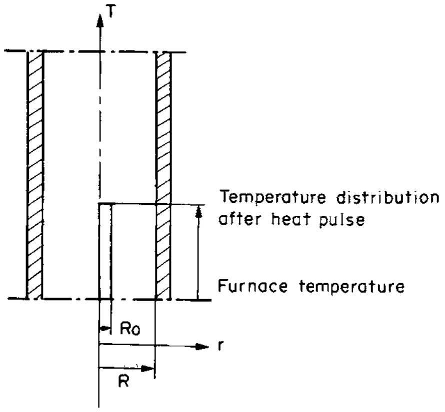

FIG. 2. Initial temperature distribution.

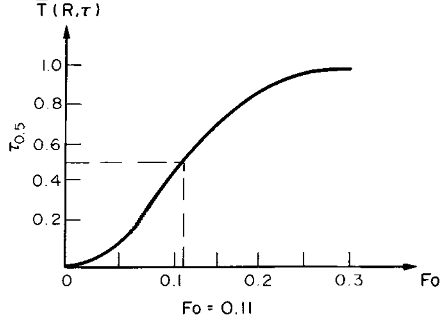

FIG. 3. Relationship of $\overline{T}(R,\tau)$ versus Fo.

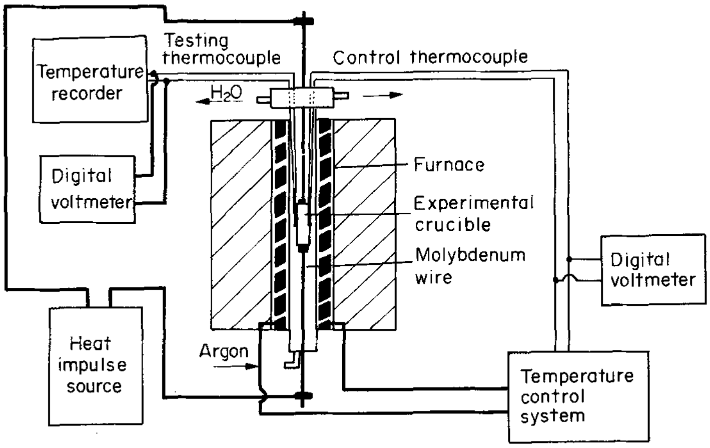

FIG. 4. Block diagram of the measurement system.

For $\tau \to \infty$ we obtain

$$T(R, \infty) = \frac{Q}{\pi R^2 \rho c_p}. \tag{12}$$

Introducing the normalized temperature

$$\bar{T}(R,\tau) = \frac{T(R,\tau)}{T(R,\infty)} \tag{13}$$

and

$$Fo = a\tau/R^2 \tag{14}$$

we finally get

$$\bar{T}(R,\tau) = 1 + \sum_{n=1}^{\infty} \exp\left[-\alpha_n^2 Fo \frac{1}{J_0(\alpha_n)}\right]. \tag{15}$$

This solution is presented in Fig. 3.

For $\bar{T}(R,\tau) = 0.5$ we find that $Fo = 0.11$. Hence

$$a = \frac{R^2 Fo}{\tau_{0.5}} = 0.11 R^2/\tau_{0.5}. \tag{16}$$

The value $\tau_{0.5}$ can be obtained from the experimental curve $\bar{T}$ vs τ (Fig. 3), and then the thermal diffusivity is directly given by equation (16).

It is evident, that the quantity of the heat transferred need only be known if the thermal conductivity has to be found. From the energy balance equation (12) we get

$$\pi R^2 \rho c_p T(R,\tau) = Q \tag{17}$$

and hence

$$\rho c_p = \frac{Q}{\pi R^2 T(R,\tau)}. \tag{18}$$

Applying the definition of the heat diffusivity $a = \lambda/\rho c_p$ we finally obtain

$$\lambda = a\rho c_p. \tag{19}$$

3. THE MEASURING SYSTEM

The measuring system is shown in Fig. 4.

4. THE EXPERIMENTAL TECHNIQUE

The proposed technique was carefully tested for the

Table 1. Experimental data for liquid metals from [3]

	Cu (l)	Zn (l)	Pb (l)	Bi (l)	Sn (l)
T, K	1357.6	692.6	600.0	544.6	505
	1400.0	700.0	700.0	600.0	600
	1500.0	800.0	800.0	700.0	700
	1600.0	900.0	900.0	800.0	800
	1700.0	1000.0	1000.0	900.0	900
	1800.0			1000.0	1000
a, $cm^2 s^{-1}$	0.421	0.157	0.0989	0.0809	0.173
	0.427	0.158	0.1140	0.0859	0.189
	0.440	0.179	0.1270	0.0940	0.206
	0.452	0.200	0.1390	0.1020	0.222
	0.463	0.222	0.1500	0.1090	0.237
	0.474			0.1120	0.253

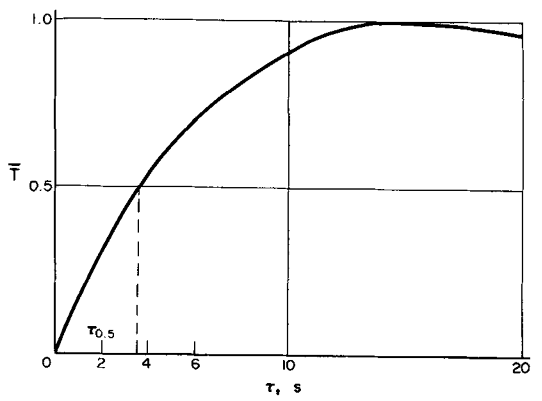

Fig. 5. Relation $\bar{T} = \bar{T}(\tau)$.

following liquid metals: Cu, Zn, Pb, Bi and Sn. The measured values of the thermal diffusivity were compared with the well-established data given [3], see Table 1. The temperatures were 1400 K for Cu and 873 K for Zn, Pb, Bi and Sn. Our results differ by no more than 5% from data given in Table 1, which shows a good degree of accuracy.

After validating the method it was applied to the electrolyte $3\,NaF.AlF_3 + 10\%$ wt Al_2O_3 at 1273 K. The value of the thermal diffusivity obtained was $0.00228\,cm^2\,s^{-1}$ with scatter ±15%. The derived dependence $\bar{T}(R,\tau) = f(Fo)$ is shown in Fig. 5. The half-time period $\tau_{0.5}$ was equal to 3.5 s.

5. CONCLUSIONS

This method can be used for measuring thermophysical properties of a liquid electrolyte with the scatter not exceeding ±15%. The method is particularly suitable for liquids.

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MESURE DES PROPRIETES THERMOPHYSIQUES D'UN ELECTROLYTE LIQUIDE PAR LA TECHNIQUE MODIFIEE DU CHOC THERMIQUE

Résumé — On présente une nouvelle technique de choc thermique pour mesurer la diffusivité thermique et la conductivité d'un électrolyte liquide. La méthode précédemment proposée par Parker *et al.* [1] pour les éprouvettes plates est adaptée ici à une géométrie cylindrique.

La formulation mathématique, avec des conditions aux limites et initiale appropriées, conduit à une solution analytique sur laquelle est basée la méthode. La technique est appliquée à quelques métaux liquides bien connus et on obtient une précision de 5 pour cent pour les diffusivités thermiques. On note un écart de 15 pour cent environ pour l'électrolyte $3NaF\,.\,AlF_3 + Al_2O_3$ (10% en masse) à 1273 K.

DIE MESSUNG THERMOPHYSIKALISCHER EIGENSCHAFTEN VON FLÜSSIGEN ELEKTROLYTEN DURCH EIN MODIFIZIERTES WÄRMEIMPULSVERFAHREN

Zusammenfassung — Es wird ein neues Wärmeimpulsverfahren zur Messung der Temperaturleitzahl und der Wärmeleitfähigkeit eines flüssigen Elektrolyten beschrieben. Das Verfahren, wie es ursprünglich von Parker u.a. [1] vorgeschlagen wurde, war nur auf ebene Proben anwendbar und wird hier einer zylindrischen Geometrie angepaßt. Ein theoretischer und mathematischer Ansatz mit entsprechenden Rand- und Anfangsbedingungen führt zu einer analytischen Lösung, auf der die vorgeschlagene Methode basiert. Das Verfahren wurde an einigen flüssigen Metallen mit gesicherten Stoffwerten erprobt, wobei für die Temperaturleitzahl eine Genauigkeit von 5% erreicht wurde. Bei einem Elektrolyten aus

$$3NaF\,.\,AlF_3 + 10Gew\%\ Al_2O_3$$

wurde bei 1273 K eine Streuung von 15% festgestellt.

ИЗМЕРЕНИЯ ТЕПЛОФИЗИЧЕСКИХ СВОЙСТВ ЖИДКОГО ЭЛЕКТРОЛИТА С ПОМОЩЬЮ УСОВЕРШЕНСТВОВАННОЙ МЕТОДИКИ ТЕПЛОВОГО ИМПУЛЬСА

Аннотация — В работе представлена методика теплового импульса для измерения температуропроводности и теплопроводности жидкого электролита. Первоначально предложенная Паркером и др. [13], она использовалась в измерениях для образцов с плоской геометрией, а в данном случае приспособлена для цилиндрических форм.

Теоретическая и математическая формулировка при соответственно заданных граничных и начальных условиях приводит к аналитическому решению, на котором базируется предлагаемый метод. Методика опробировалась на ряде жидких металлов с хорошо известными значениями свойств и при определении коэффициентов температуропроводности показала точность порядка 5%. Для электролита $3NaF\,.\,AlF_3 + 10\%$ по весу Al_2O_3 при 1273 K наблюдается разброс около 15%.