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RECONSTRUCTION OF THE ORIGINAL HEATFLUX CURVE FOR A CALORIMETRIC MEASURING DEVICE

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SUMMARY

The paper presents an improved method of de-smearing of calorimetric measuring curves. The advantages of this method, which is derived from an electrical analogy, will be discussed in comparison with the corresponding simplified de-smearing method of first approximation. The method to be discussed is of special interest for calorimetric investigations of relatively light specimens. In this case two different relaxation times exist. The signal reconstruction is based on a second order differential equation.

INTRODUCTION

Calorimetric measurements using a differential heatflux calorimeter lead to a measuring signal, which is in general distorted ("smeared") by the thermal measuring system.
One method of reconstructing the real heatflux curve can be derived from the electrical analogy to the caloric measuring setup. In contrast to the mathematically exact but complex procedure of deconvoluting the measuring curves /1/ this method only needs a little computing effort and works in spite of possible measuring inaccuracies.

DE-SMEARING METHODS

The Electrical Analogy to a Calorimetric Measuring System

The typical heatconducting problems of a differential heatflux calorimeter become clearly discernable by studying the equivalent electrical circuit. Then the thermal quantities can directly be substituted by the electrical ones.

C_p	heat capacity	------------------->	C	electric capacity
I_{th}	heat current	------------------->	I	electric current
R_{th}	heat resistance	------------------->	R	ohmic resistance
T	temperature	------------------->	U	electric potential

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Equations:

$$I_{th} = \frac{T}{R_{th}} = C_p \frac{dT}{dt} \text{ -----> } J = \frac{U}{R} = C \frac{dU}{dt} \quad .$$

The Simple De-Smearing Method

In a first approximation the calorimetric measuring setup will be described by a simple relaxing system, an electric RC-element. In order to calculate the correct signal ΔU_{corr} from the smeared one ΔU_{sig} the inhomogenous differential equation belonging to it has to be used /2/:

$$\Delta U_{corr} = \Delta U_{sig} + \tau_1 \frac{d}{dt} \Delta U_{sig} \qquad (1)$$

$$\tau_1 = R_{th}(C_s + C_c)$$

The time lag constant τ_1 is a characteristic value depending on the heat capacity C_s of the sample and the heat capacity C_c of the sample cell in the measuring device.

The Improved De-Smearing Method

In calorimetric experiments with samples of small masses and heat capacities, respectively, the use of the transformation equation (1) leads to a faulty reconstruction of the real heatflux curve. In that case the calculated time lag constant τ_1 is too small and does not completely describe the relaxation process.

A second time lagging process (τ_2), resulting from the measuring unit dealing with signal registration, should no longer be neglected. Therefore the influence of this unit on the smearing phenomenon is now considered with the help of an extended electric circuit. This substitutional diagram (Fig. 1) can be devided into three parts: the sample, the reference unit -both connected with the heating device- and the registration unit consisting of the thermocouples and the output on the recorder.

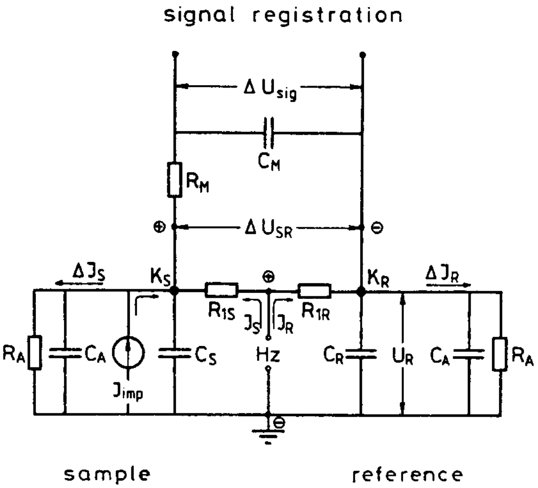

Fig.1: The thermal setup of a heatflux calorimeter represented in an electrical circuit diagram.

By applying the laws of Kirchhoff to the situation of the substitutional diagram, mathematical relations between electrical current and potential can be drawn up. Further computation leads to an inhomogenous diffenential equation of second order. This equation can be used as a new transformation formula to calculate corrected measuring values:

$$\Delta U_{corr} = \Delta U_{sig} + (\tau_1+\tau_2)\frac{d}{dt}\Delta U_{sig} + \tau_1\ \tau_2\ \frac{d^2}{dt^2}\Delta U_{sig}\ . \qquad (2)$$

APPLICATION

Calibrating Measurements to Determine the Relaxation Times

As in the case of the simplified de-smearing we also have to determine the values of the time lag constants for our thermal system. For this purpose we perform calibration measurements on a special specimen in the sample cell of the calorimeter. Its shape and material have to be the same as those of the object to be measured later on, with the difference that it contains an ohmic resistor (Pt100) (Fig. 2). During the calibration experiment no sample reaction is allowed.

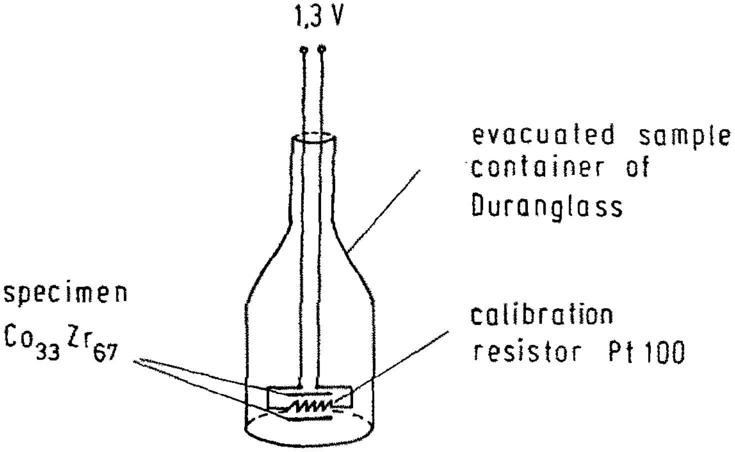

Fig.2: Calibration sample of the typical shape used in calorimetric investigations of $Co_{33}Zr_{67}$ specimens.

At different temperatures the response function of a pulse-like input signal $\delta(t)$, applied to the installed electric resistor, is registered. It is known that the analytical functions of these responses are the solutions of the homogenous differential equation belonging to (2) for different temperatures. By an act of curve fitting the relaxation times, which are identical to the parameters of the analytical functions, are computed /3/. Fig. 3 shows the results of curve fitting of the responsefunction on first and second approximation according to the simplified and improved method of de-smearing.

The following equations were used to calculate the curve shapes.

first approximation : $U = U_0 \, e^{-t/\tau_1}$,
second approximation : $U = U_0 \, (e^{-t/\tau_1} - e^{-t/\tau_2})$.

The temperature dependence of the two relaxation times τ_1 and τ_2 is presented in Fig. 4.

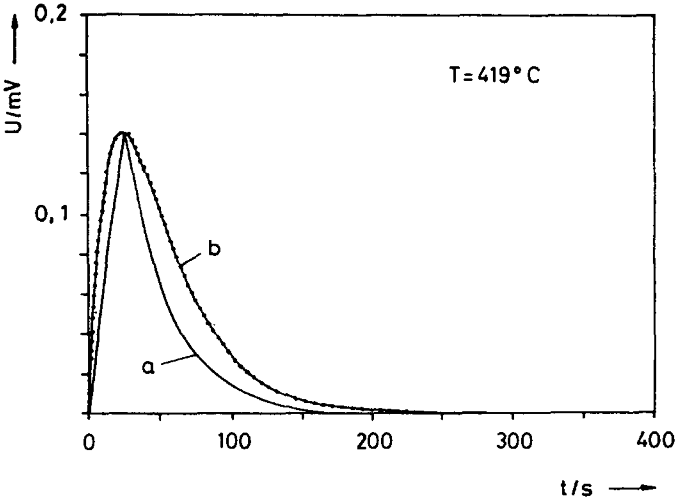

Fig.3: Actual responsefunction (•) of a pulse-like input signal δ(t).
a) calculated responsefunction of first approximation
b) calculated responsefunction of second approximation (deviation lower than 1%).

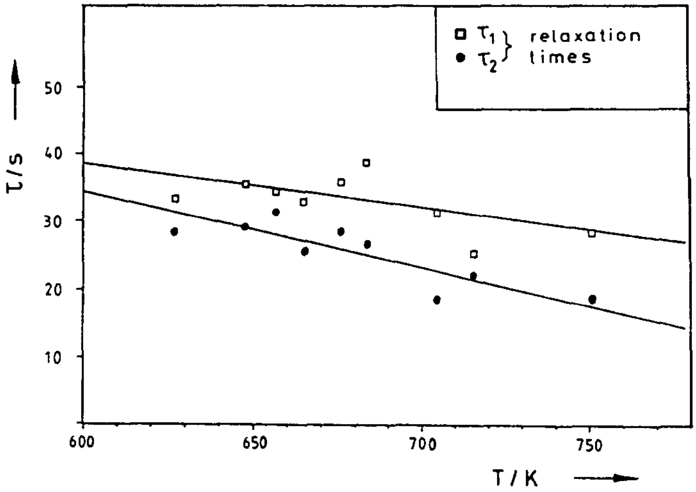

Fig.4: Temperature dependence of the relaxation times τ_1 and τ_2.

Crystallization Reaction of $Co_{33}Zr_{67}$ Investigated by a Differential Heatflux Calorimeter

A calorimetric measurement can be used to follow the course of the crystallization reaction of the metallic glass $Co_{33}Zr_{67}$. Such an experiment is representative of a calorimetric measurement of a sample of a small mass. Fig.5 shows the distorted normalized heatflux curve without correction and the reconstructed curves after using the de-smearing methods of first and second approximation.

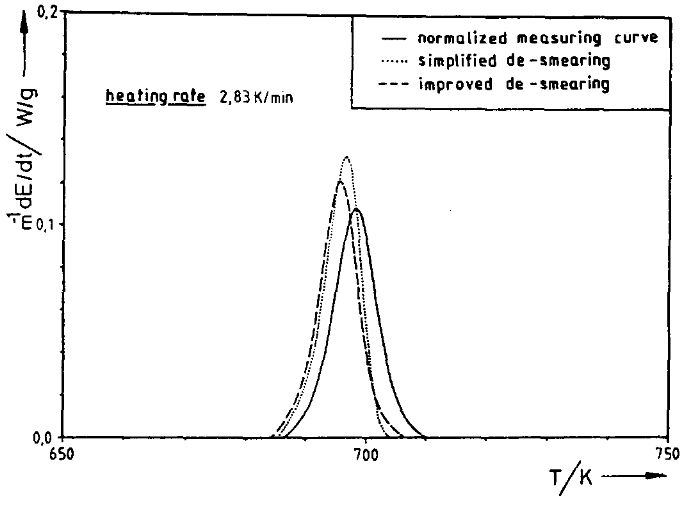

Fig.5: Crystallization reaction of the glassy metal $Co_{33}Zr_{67}$. Normalized heatfluxcurve without correction (–), reconstructed heatflux curve using the simplified de-smearing method (···) and using the improved one (---).

The use of the method of simplified de-smearing of the measurin curve produces too weak a correction of the peakmaximum position and a corrected curve, which ascends too steeply. Therefore the result of the integration used to calculate the total reaction hea is faulty.

Having performed the described calibration measurements, the application of the method of improved de-smearing makes it possibl to reconstruct relatively exactly (1%) the pulse-like input signa $\delta(t)$ from the response function. Regarding the measuring curve of the crystallization reaction of the glassy metal $Co_{33}Zr_{67}$ as the response of the still unknown original input signal, this yields the opportunity to compute the same still unknown input signal. Fo this, the inhomogenous differential equation (2) is needed together with the parameters τ_1 and τ_2, which have been determined in calibration measurements. With τ_1 and τ_2 -as functions of temperature- in equation (2) one has a direct transformation equation. It transforms the smeared signal into the de-smeared one, which is the looked for input signal.

ACKNOWLEDGEMENT

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