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METHOD OF QUICK THERMAL ANALYSIS

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ABSTRACT

Quick thermal analysis employs spontaneous heating of the sample suspended on the weld of thermocouple quickly transferred to the heating zone of preheated furnace. The time change of thermocouple voltage is read by digital voltmeter controlled by a programmable calculator. The calculator transforms the curve into a record analogous to DTA curve and carries out thermodynamical calculations. The high reproducibility of the method can be utilized for identification and calorimetry measurements and together with determination velocity it is fitting for operation control in production.

INTRODUCTION

The method of quick termal analysis (QTA) employs spontaneous heating realized by inserting a sample - suspended upon thermocouple weld - into the heating zone of the furnace preheeted to selected temperature. Supposing the sample heating is not accompanied by phase transitions or chemical reactions and supposing not heat transfer between the sample and the thermocouple takes place when heeting, the heat quantity received by the sample in dt interval is proportionate to temperature difference (T_2-T) between furnace space and sample and equal to the quantity of heat needed for sample heating:

$$C_T(T_2-T)\,dt = -mc_p dT \qquad (1)$$

where

m = mass of sample material

c_p = specific heat of the material with T temperature

C_T = heat transfer coefficient dependent on temperature.

The temperature dependance of the sample on the time of its heating is obtained by integration for starting conditions $t = 0$ and $T = T_1$

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$$T = T_2-(T_2-T_1)\ \exp\ (-\frac{C_T t}{mc_p}) \qquad (2)$$

The temperature dependance $C_T = f(T)$ in real measurement is determined by measurement carried out with standerd material of known dependance course $c_p = f(T)$. The C_T value in temperature interval $(T,T+\Delta T)$ corresponding with temperature change in Δt time is computed following relation (3) and the approximation of temperature dependance $C_T = f(T)$ is carried out by the method of Tschebysheff polynominals.

$$C_T = \frac{mc_p}{\Delta t}\quad \ln \frac{T_2-T}{T_2-(T+\Delta T)} \qquad (3)$$

The determination of real dependance course $C_T = f(T)$ makes it possible to determine the dependance $c_p = f(T)$ in examined sample whose heating is carried out under equal conditions. In case physical and chemical changes take place in the course of sample heating these changes reveal in the change of $(C_T m^{-1} c_p^{-1})$ value and the temperature dependance of this value can be - similarly to DTA curve - employed for the indication of these changes. Employing measurements carried out under identical conditions when heating examined and referential sample the DTA curve is obtained under the conditions of unequal heating velocity. One or several measurements carried out with examined samples can be related to the measurement carried out with standard material. The measurement carried out with standard material can be replaced by dependance $T = f(t)$ obtained by computing carried out following the determination of temperature dependance $C_T = f(T)$ and known temperature dependance $c_p = f(T)$ in selected standard material. The total change of enthalpy in the course of sample heating is - following relation (1) - proportionate to area above the curve $T = f(t)$ up to T_2 level.

REALIZATION OF THE METHOD

For the instrumental realization of QTA there was experimentally employed a furnace with manipulator (1) which by the way of handle makes it possible to transfer the sample suspen-

ded upon thermocouple weld into the centre of heeting zone in vertical, tubular, resistant furnace for the time of 0.5 s. The sample carrier has been adapted in order that the sample may be suspended upon thermocouple weld below the furnace and may be introduced into the furnace by turning the handle mechanism for 180°.As the thermocouple wires brought about an undesirable sample heating a tubular blind of Pt foil - whose upper border met the lower sample border - was coaxially placed in the furnace. The cylindrical sample of 3 mm in diameter and 5 mm in height was prepared by pressing the weighed material quantity in a precise steel form for defined volume mass. After stabilizing the furnace temperature the sample was suspended below the furnace upon thermocouple weld and employing the handle mechanism it was transferred into tha middle of furnace heating zone. The thermocouple voltage (Pt-Pt Rh 10) was measured by digital voltmeter (HP 3455A) controlled by programmable calculator (HP 85 F). The measured values were read by 10 s^{-1} frequency for 60 s and the terminal temperature (T_2) was read after 120 s. The values obtained by measurements were stored in magnetic tape and for processing the results of measurements a computing program was assembled which included the determination of temperature dependance ($C_T m^{-1} c_p^{-1}$) as well as of area computation (P_c) above the curve T = f(t) up to T_2 level.

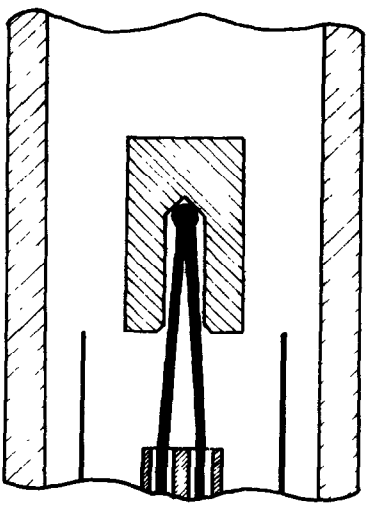

Fig.1 Section of burning zone in the furnace with sample.

RESULTS AND DISCUSSION

After checking the properties of the method as well as of the aplied instrumental equipment there were carried out mea-

surements in mixtures with graded proportion of highly sintered CaO (burning temperature 1800°C, 4 h) and $CaCO_3$ with assumed P_c linear dependance on the relation of mutually nonreacting components. The mixtures were prepared having granularity of $\leq$ 0.09 mm and CaO contents of 0,20,40,60,80 and 100 weight %. They were weighed in the quantities of 0.063 g. At first the accuracy of P_c determination was proved employing mixture containing 40 weight % of CaO. The directing deviation computed on the basis of ten measurements results was 0.68 %. The difference in the lowest and highest measured value was 2.2 % of average value. The measurement results carried out in the mixtures of CaO with $CaCO_3$ showed the linear dependance P_c/P_{CaO} on the content of CaO in mixture. The correlation coefficient of this dependance was 0.996.

All measurements were carried out with a provisionally adapted equipment and therefore they include not only the errors when preparing experimental mixtures but also the errors of temperature stabilization in the furnace and its influence when inserting the sample. However the obtained results signify fitness to apply this method for quick identification and calorimetry measurements.

CONCLUSION

The simplest applications of quick thermal analysis method were proved which do not require any calibration measurements necessary for obtaining absolute values. The attained results signify possibility how to employ this method which from the point of quickness and measurement results reproducibility is fitting for many applications with full automation employing relatively simple measuring and computing technique.

REFERENCE

1 S.Chromý, M.Zavadil, Silikáty 25 (1981) 383