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COMPUTER CONTROLLED THERMOGRAVIMETRIC STEPWISE ISOTHERMAL ANALYSIS

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ABSTRACT

A microprocessor system developed for Thermogravimetric Stepwise Isothermal Analysis is described. This system is especially useful in kinetic studies and, as an example, the results obtained in a study of the decomposition of Ce-carbonate are discussed. From this study it is concluded that the controlling mechanism for the first part of this reaction is three dimensional nuclei growth, whereas the last part is phase boundary controlled.

INTRODUCTION

Stepwise Isothermal Analysis (SIA) is a relatively new technique which has been used previously by the author in various thermogravimetric and dilatometric studies. As demonstrated in previous publications (refs 1-3) this technique is especially useful in kinetic studies as the reactions take place under isothermal conditions at one or several temperature levels depending on the mechanism controlling the reaction.

In the previous studies, the heating was controlled by switches operating on the derived signal (dw/dt or dl/dt) and the kinetic data were evaluated by manual calculations, which was very time consuming. In this paper is described a microprocessor system based on a personal computer especially designed for SIA. As an example of the advantages obtained by this system the results obtained in a preliminary kinetic study of the decomposition of Cerium carbonate is described.

PRINCIPLE

The principle of SIA has been described in previous publications. Here it suffice to mention that the overall heating program of the sample by this technique is controlled by the reaction rate in the following way: The samples is heated at constant rate until the derivative of the weight (or length)

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curve exceeds a preset limit at which point the heating is stopped. The reaction now proceeds isothermally until the derivative becomes smaller than the preset limit and the heating is again resumed. By this technique the reaction(s) thus characteristically takes place in isothermal steps.

KINETIC ANALYSIS AND MICROPROCESSOR SYSTEM

Taking the logarithm on both sides of the general expression describing the kinetics of a solid state reaction gives

$$\ln(d\alpha/dt) = \ln k + \ln f(\alpha) \tag{1}$$

Here α is the fraction reacted, t the time, $k(= A\exp^{-Q/RT})$ is the Arrhenius constant and $f(\alpha)$ is a function depending on the controlling mechanism. In the computer programme developed for these measurements calculations are performed on eight different functions. This gives the possibility to evaluate many different mechanisms such as nucleation, phase boundary and diffusion controlled reactions.

The microprocessor system is based on a Hewlett Packard HP-85B personal computer with a capacity of 64 kbytes and with a build in tape recorder. The data-acquisition and control is done with a datalogger operated by the computer whereas tabulation and plotting is performed on an external printer and plotter. Four computer programmes have been written for the SIA measurement, which is performed on a Netzsch STA 429 thermobalance.

SIA MEASUREMENTS ON CE-CARBONATE

Fig. 1 shows the sample weight corrected for buoyancy as a function of temperature as plotted during the measurement. From this plot it is clear that Ce-carbonate ($Ce_2O(CO_3)_2H_2O$) apparently decomposes in several steps; a fast one at about 235°C involving most of the total weight change followed by many smaller steps, which indicates that the last part of the decomposition takes place in a slow and temperature dependent reaction (this part was not completed in this measurement). With the software control used here, the program controller (Netzsch 400) is operated such that the furnace is cooled or heated at a constant rate depending on whether the sample temperature is above or below the temperature measured at the initiation of the decom-

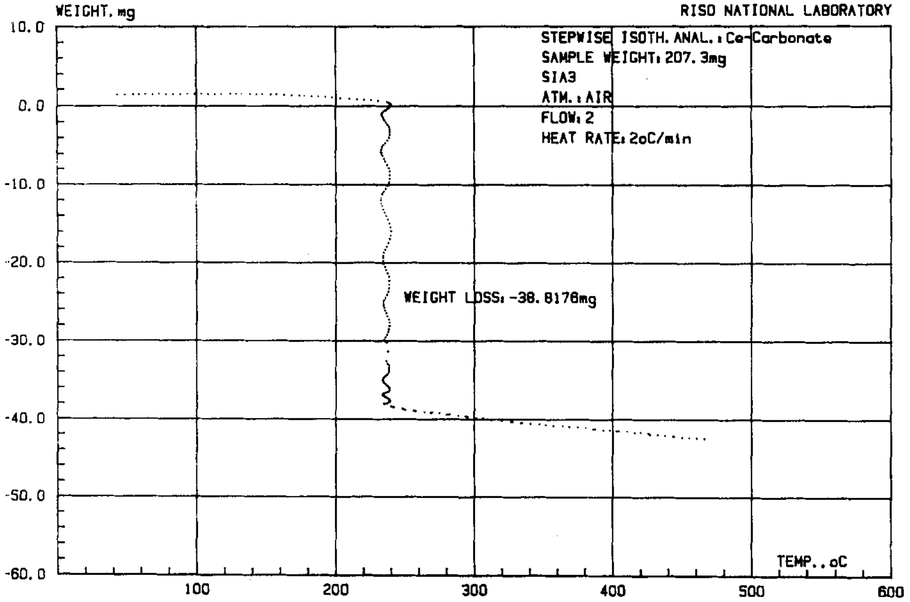

Fig. 1 Computer plot of corrected weight versus temperature recorded during a SIA measurement.

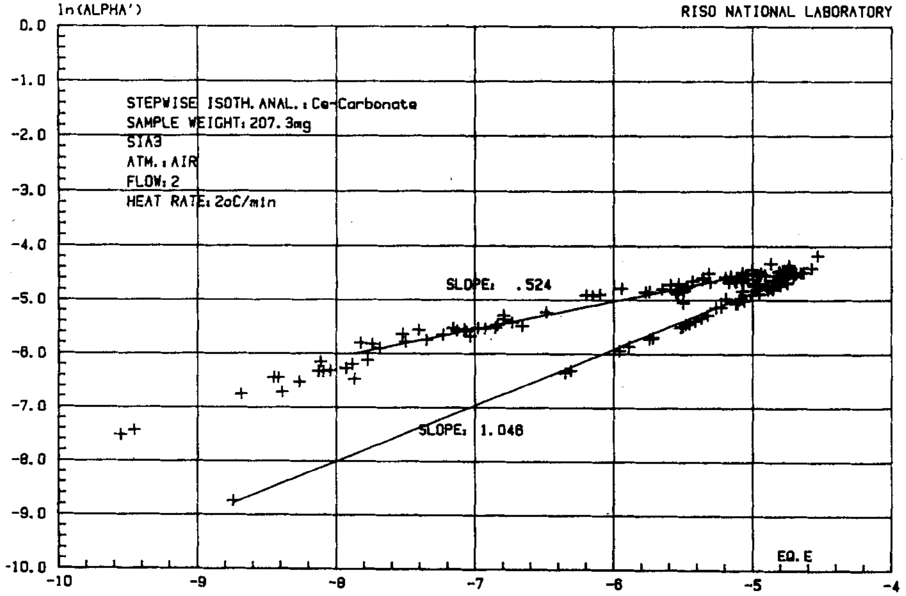

Fig. 2 $\ln\alpha'$ versus $\ln f(\alpha)$ for Avrami equation ($f(\alpha) = (1-\alpha)(-\ln(1-\alpha))^{2/3}$ - Eq. E in computer programme) for a process controlled by three-dimensional nuclei growth.

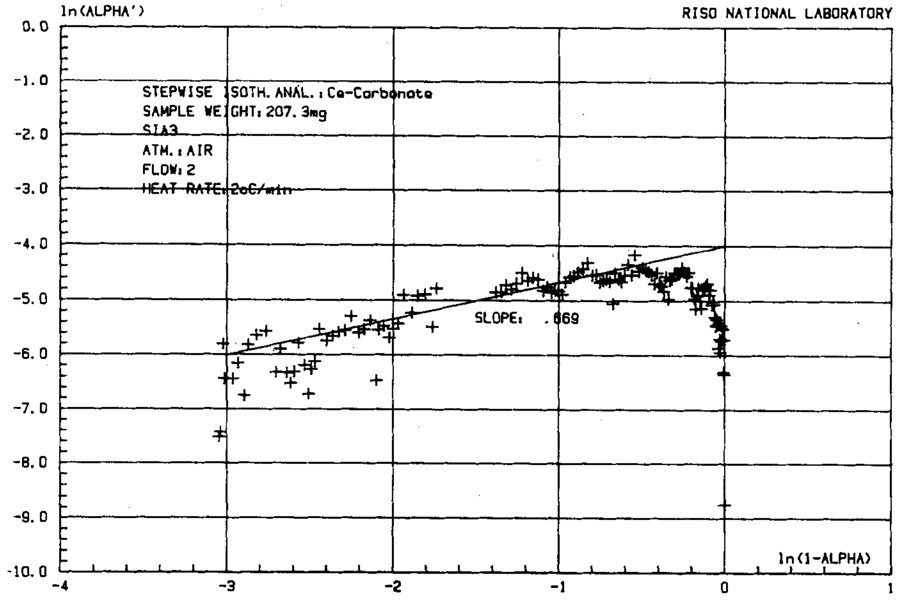

Fig. 3 $\ln\alpha'$ versus $\ln f(\alpha)$ for phase boundary controlled process ($f(\alpha) = (1-\alpha)^{2/3}$).

position. As shown in Fig. 1, this gave some temperature fluctuation, which, however, is restricted to ± 2°C in this system which is quite satisfactory.

The data collected during the measurement were treated in a separate analysis where α, α', $\ln\alpha'$ and $\ln f(\alpha)$ were calculated, tabulated and plotted. Typical plots obtained for the first step are shown in Figs 2 and 3. Apparently the mechanism controlling the first part of the decomposition is three-dimensional nuclei growth (Avrami equation; $f(\alpha) = (1 - \alpha)\,(-\ln(1-\alpha))^{2/3}$ (Eq. E)) which in this plot should give a slope of one, whereas phase boundary movement ($f(\alpha) = (1 - \alpha)^{2/3}$) is controling the last part of the decomposition. An erratic and non-linear plot was, however, obtained in the case of three-dimensional diffusion process (Jander equation; $f(\alpha) = (1 - \alpha)^{1/3}\,(-\ln(1 - \alpha))^{-1}$ indicating that decomposition of Ce-carbonate is not diffusion controlled. This might be the case for the slow and temperature dependent step observed after the main decomposition step, which, however, must await a more detailed analysis in a future study.

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