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COMPUTER CONTROLLED FORCED STEPWISE ISOTHERMAL ANALYSIS

P. L. HUSUM and O. T. SØRENSEN
Risø National Laboratory, Metallurgy Department,
DK-4000 Roskilde, Denmark

ABSTRACT

A new version of the Stepwise Isothermal Analysis technique is described in which the temperature is forced to increase in predetermined steps during the reaction. Data obtained by this technique can be used to determine not only the controlling mechanism but also the activation energy and the pre-exponential factor in the Arrhenius equation. As a demonstration of the advantages of this technique the results obtained in a kinetic study of the thermal decomposition of cerium carbonate in different atmospheres is described.

INTRODUCTION

Stepwise Isothermal Analysis (SIA) is a useful technique for kinetic studies by thermogravimetric and dilatometric measurements. As described in a previous publication (1), the overall heating of the sample is, in this technique controlled by the reaction rate in such a way that the heating is stopped when this rate exceeds a preset limit. The reaction(s) will thus characteristically take place in isothermal steps and data suitable for kinetic analysis can be obtained for each step.

The main draw back of the technique hitherto used is that it cannot be used to determine the activation energy if the reaction takes place in one isothermal step. In this paper a new version of SIA is described, in which the temperature is forced to increase in predetermined steps during the reaction. In this way data can be obtained at several temperature levels for each reaction and it is possible to construct an Arrhenius plot from which both the pre-exponential factor and activation energy of the Arrhenius equation can be calculated. As a demonstration of the advantages of this technique the results obtained in a kinetic study of the thermal decomposition of cerium carbonate are described.

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KINETIC ANALYSIS

For a heterogeneous reaction like the thermal decomposition considered in the present work, the kinetic equation for isothermal conditions can be expressed in the integral form as

$$k \cdot t = F(\alpha) \qquad (1)$$

Here t is the reaction time, k the rate constant (= A · exp(-E/RT)) and F(α) is a function of the reacted fraction, α. In the literature F(α) is also termed g(α).

The form of F(α) depends on the type of the rate-limiting process, i.e. the slowest process, that controls the overall reaction. Some examples of kinetic equations derived for various controlling mechanisms are given in Table I. For a more detailed information the comprehensive table published in Ref. 2 should be consulted.

TABLE I
Kinetic equations for various controlling mechanisms

Controlling mechanism	kt =
1. Nucleation	Power law: $p\alpha^n$ $(p,n) = (1/2,2),(2,1/2),(3/2,1/3),(4/3,1/4),(1,1)$ Exponential law: $\ln(\alpha)$
2. Nucleation followed by nuclei growth (phase boundary movement controlled)	$n(-\ln(1-\alpha))^{1/n}$ $(n = 2,3,4)$
3. Nuclei growth	
A. Phase boundary movement controlled	$n(1-(1-\alpha)^{1/n})$ $(n = 2,3)$
B. Diffusion controlled	$3/2(1-(1-\alpha)^{1/3})^2$ $3/2(1-2/3\alpha-(1-\alpha)^{2/3})$

A general and recognized method in kinetic studies is to evaluate the type of controlling mechanism(s) from an F(α) versus t plot, which according to Eq. 1, should be linear for the correct mechanism(s). With the computer programme developed in this work F(α) can be calculated from the measured weight changes for seventeen different kinetic equations as given in Table No. 6 in Ref.

2. This allows a very detailed kinetic analysis involving many important mechanisms such as nucleation, and phase boundary movement or diffusion controlled nuclei growth.

From Eq. 1 it is clear that the slope of the linear F(α) vs. t plot for the correct mechanism(s) is equal to 1/k, i.e. it will depend on the temperature. For the case of FSIA where the reaction is forced to take place at several temperature levels, this plot will split up into rectilinear parts with slopes characteristic of each temperature level. Thus from these slopes it is straightforward to determine both the activation energy, E, and the pre-exponential factor, A, as the temperature for each level is known.

In the present computer programme these parameters are determined from an ln k vs. 1/T plot (Arrhenius plot), which should be linear for a given reaction mechanism.

EXPERIMENTAL

Equipment

The measurements were performed with a Netzsch STA 429 thermobalance modified for control and data-acquisition from an external microprocessor system based on a Hewlett Packard HP-85 B personal computer (64 kbytes). The principle and main components of the experimental set-up are shown schematically in Fig. 1.

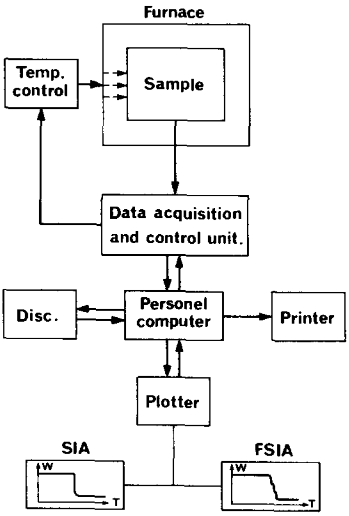

Fig. 1. Principle of computer controlled system for Stepwise Isothermal Analysis (SIA) and Forced Stepwise Isothermal Analysis (FSIA).

Materials and procedures

Measurements were performed on Ce-carbonate ($Ce_2O(CO_3)_2 \cdot H_2O$),(3), prepared by a homogeneous precipitation technique by hydrolysis of urea. In order to evaluate the nature of the processes involved in the thermal decomposition of this material the measurements were performed in air, He, CO and CO_2.

RESULTS AND DISCUSSION

Chemistry

Fig. 2 shows the sample weight corrected for buoyancy as a function of temperature recorded during the measurements in air, He, CO_2 and CO.

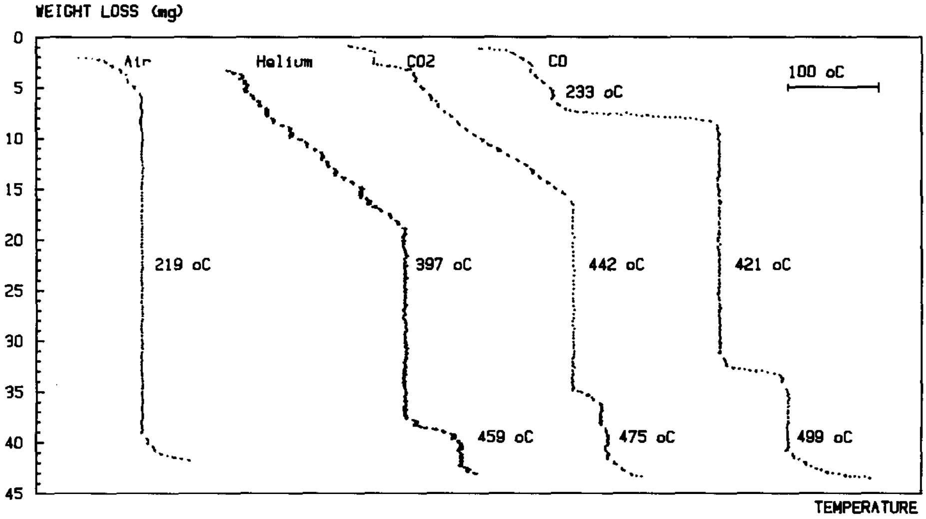

Fig. 2. SIA data obtained for Ce-carbonate in different atmospheres.

From the figure it will be noted that the decomposition temperature and the number of steps involved strongly depend on the atmosphere. In air, for instance, the main decomposition takes place in only one isothermal step at a rather low temperature (219°C), whereas in the other atmospheres studied several steps at higher temperatures are involved

To explain this behaviour we propose the following reaction scheme for the thermal decompositions of cerium carbonate:

(i) In air, where the decomposition takes place in one isothermal step, we believe that an oxidation is involved according to the reaction:

$$Ce_2O(CO_3)_2{\cdot}H_2O + 1/2\ O_2 \longrightarrow 2CeO_2 + 2CO_2 + H_2O \qquad (a)$$

(ii) In He the pattern of decomposition steps is similar to that observed in CO_2 - i.e. many small steps (reaction a) followed by two distinct decomposition steps (reactions (b) and (c)). In CO_2 atmosphere oxygen is supplied by the equilibrium

$$CO_2 \longrightarrow CO + 1/2\ O_2$$

In the case of He atmosphere, the CO_2 originates from the decomposition itself. CeO_2 is thus formed directly during reaction (a).

For reactions (b) and (c) we propose the reactions

$$Ce_2O(CO_3)_2{\cdot}H_2O \longrightarrow Ce_2O_2(CO_3) + CO_2 + H_2O \qquad (b)$$

$$Ce_2O_2(CO_3) \longrightarrow 2CeO_2 + CO \qquad (c)$$

This reaction scheme is consistent with the observation that reaction (b) takes place at higher temperature in CO_2 than in He and it is in good agreement with the scheme proposed by Meriani (4).

(iii) Finally in CO the same three reactions are apparently involved. In this atmosphere, however, reaction (a) is greatly reduced compared to the experiments performed in He and CO_2, whereas reactions (b) and (c) are even more pronounced than in these atmospheres. The reason for the smaller extent of reaction (a) is probably the presence of CO which reduces the oxygen pressure. Oxidation in this atmosphere is thus greatly reduced.

Kinetics - controlling mechanisms

The controlling mechanism was determined from F(α) vs. t plots as described previously. Typical examples of the plots obtained using the data obtained in air and CO are shown in Figs. 3 and 4, respectively.

For air a nearly perfect linear plot is clearly obtained using $F11(\alpha) = 1/2(-\ln(1-\alpha))^2$ (nucleation followed by two-dimensional

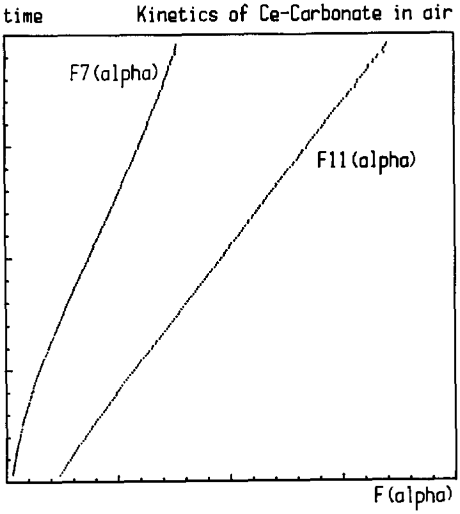

Fig. 3. F(α) vs. time plots for the isothermal decomposition of Ce-carbonate in air. The best linear correlation is obtained with F11(α).

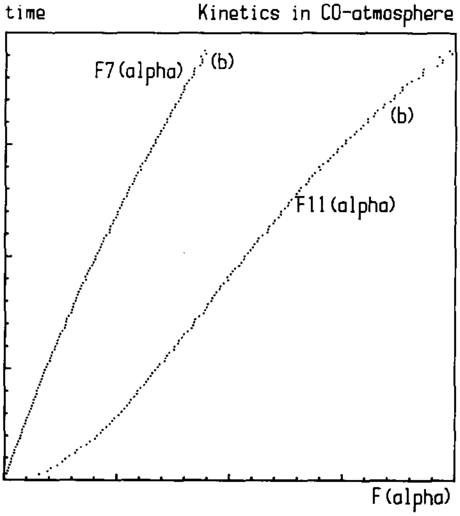

Fig. 4. F(α) vs. time plots for reaction (b) in CO-atmosphere. The best linear correlation is obtained with F7(α).

phase boundary movement controlled growth) whereas the plot obtained using $F7(\alpha) = 2(1-(1-\alpha)^{1/2})$ (phase boundary movement controlled growth) is s-shaped. Thus in this atmosphere this analysis indicates that the controlling mechanism for the decomposition, which takes place in one isothermal step, is nucleation of CeO_2 nuclei followed by a phase boundary movement controlled nuclei growth. It is interesting to note that this growth apparently takes place in two dimensions only.

As shown in Fig. 4 this situation is reversed in CO, where a better linear plot is obtained with F7(α) than with F11(α). In this atmosphere, where the decompositions take place at higher temperatures, nucleation is apparently so fast that it is the nuclei growth (phase boundary movement controlled) which becomes the controlling mechanism. In this case the growth also takes place in two dimensions.

Kinetics - activation energies, pre-exponential factors

Fig. 5 shows the experimental data obtained with the FSIA-

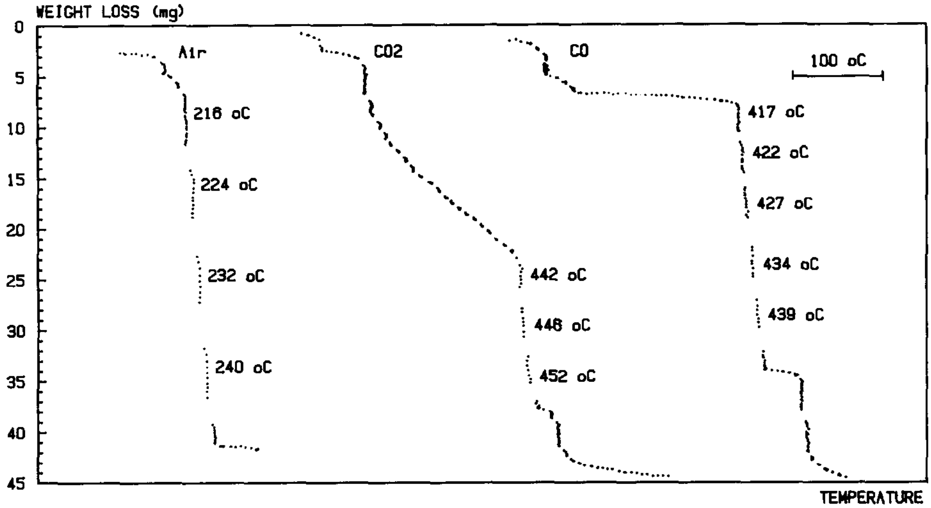

Fig. 5. FSIA data obtained for Ce-carbonate in various atmospheres.

technique using the atmospheres air, CO_2 and CO. As expected, the same types of decomposition steps were obtained with this technique as with the conventional SIA-technique. Using $F11(\alpha)$ and $F7(\alpha)$ for air and CO, respectively, the $F(\alpha)$ vs. t plot shown in Fig. 6 was obtained. Straight lines were again obtained but in this case in segments with characteristic slopes depending on the temperature. The Arrhenius plots constructed from these slopes are shown in Fig. 7, from which it will be noted that a linear relationship between ln(k) and 1/T was obtained.

The following activation energies and pre-exponential factors were calculated from these plots and the corresponding plot for measurements in CO_2:

TABLE 2.

Values of activation energies and pre-exponential factors.

	E (kJ/mole)	A (min^{-1})
Air (reaction (a))	104.9	$5.91 \cdot 10^{9}$
CO (reaction (b))	297.8	$5.03 \cdot 10^{20}$
CO (reaction (c))	407.5	$2.63 \cdot 10^{26}$
CO_2 (reaction (b))	374.8	$1.26 \cdot 10^{26}$

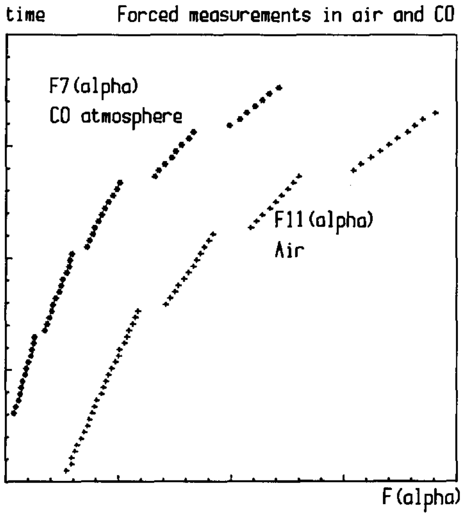

Fig. 6. F(α) vs. time plot for FSIA data obtained in air and CO.

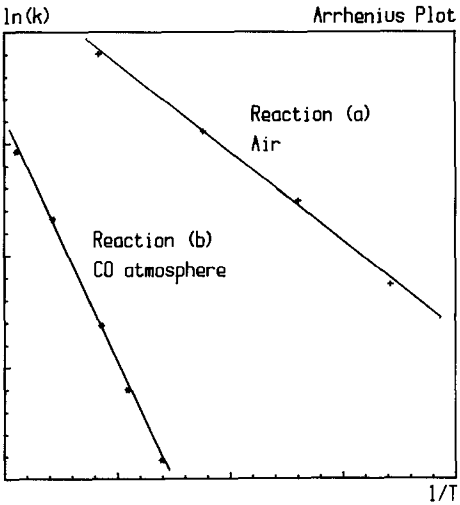

Fig. 7. Arrhenius plot obtained from FSIA data shown in Fig. 6.

The activation energy for the thermal decomposition of Ce-carbonate thus strongly depends on whether oxygen is present or not. This also supports the conclusion that the chemical reaction involved in air is quite different from those involved in reactions (b) and (c) in CO_2, CO and He.

Finally, it should be noted that the activation energies found by this technique are quite consistent with those observed for the thermal decomposition of other carbonates - see for instance Ref. 2.

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