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KINETIC ANALYSIS OF THERMAL DECOMPOSITION REACTIONS. PART IV: KINETICS OF FORMATION OF BARIUM TITANATE IN CRYSTALLINE MIXTURES OF BARIUM CARBONATE AND TITANIUM DIOXIDE

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ABSTRACT

The kinetics of formation of barium titanate from barium carbonate and titanium dioxide have been studied using isothermal and dynamic thermogravimetry techniques. Kinetic analysis of the isothermal data, considered from the point of view of various solid state reaction models, showed that the reaction is best described by the random nucleation Avrami equation. Analysis of dynamic TG data, according to the integral methods of Coats and Redfern and of Ozawa, gave results which are not in agreement with each other or with the results obtained under isothermal conditions.

INTRODUCTION

Titanates have become very important in the ceramic industry [1]. Attention has been given to barium metatitanate which is widely known as a ferroelectric material [2]. Numerous types of electro-mechanical and ultrasonic converters are made from titano-barium ceramics for different technologies. The process of forming titanates in crystalline mixtures is, therefore, of great practical interest. The formation of barium metatitanate in a mixture of barium carbonate and titanium dioxide has been noted at 550 °C, but at 850–900 °C, this process is completed in one hour [1,3].

One of the interesting applications of thermal analysis is the investigation of the behaviour and kinetics of solid state reactions. In the kinetic analysis of thermogravimetric data, agreement between isothermal and dynamic results has been reported for several cases [4,5]. However, the accuracy and

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interpretation of non-isothermal TG data has been questioned [6]. Non-isothermal data are dependent on the heating rate and are subject to possible inaccuracies due to the influence of sample size and shape on heat flow. For these reasons, isothermal kinetic measurements are, in general, more reliable [7].

In the present study, the kinetics of formation of barium titanate in a 1 : 1 mole ratio mixture of barium carbonate and titanium dioxide (anatase) were investigated using isothermal and dynamic TG techniques. Kinetic analysis of dynamic TG data were discussed in view of two integral methods, one of Coats and Redfern [8] and the other of Ozawa [9], and the results were compared with those of the isothermal technique. The thermoanalytical behaviour of the $CaSO_4$–TiO_2 and $CaCO_3$–TiO_2 systems, and the introduction of other metal oxides were discussed by Ishii et al. [10].

EXPERIMENTAL

AnalaR barium carbonate and titanium dioxide (anatase) were supplied by BDH Chemical Co. Samples were prepared for kinetic study by the impregnation technique by thoroughly mixing the powders of $BaCO_3$ and TiO_2 in a molar ratio of 1 : 1, then the mixture was dried in a thermostatted oven at 115 °C for 5.0 h.

The kinetics of formation of $BaTiO_3$ in the crystalline mixture of barium carbonate and titanium dioxide were studied in an air atmosphere using a Shimadzu Model 30 thermal analyser. In the isothermal studies, the reaction temperatures were varied between 830 and 900 °C, whereas the dynamic experiments were carried out at heating rates of 5, 10, 20 and 50 °C min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows the DTA and TG curves obtained for pure $BaCO_3$ and the $BaCO_3$–TiO_2(anatase) system. At room temperature, barium carbonate belongs to the orthorhombic system and high temperature X-ray analysis has shown that at 805 °C it undergoes transformation to the hexagonal form and, at 976 °C, it transforms to the cubic form [11]. The DTA curve (a) in Fig. 1 shows, in addition to the two endothermic peaks corresponding to the phase transitions, a third highly endothermic broad peak at 1280 °C due to the decomposition of $BaCO_3$. DTA curve (b) in Fig. 1 shows that for the $BaCO_3$–TiO_2 system, the two endothermic peaks due to the phase transitions of $BaCO_3$ occur at approximately the same positions as in curve (a), but these are followed by a small endothermic peak at 1140 °C due to the simultaneous decomposition of $BaCO_3$ and formation of $BaTiO_3$.

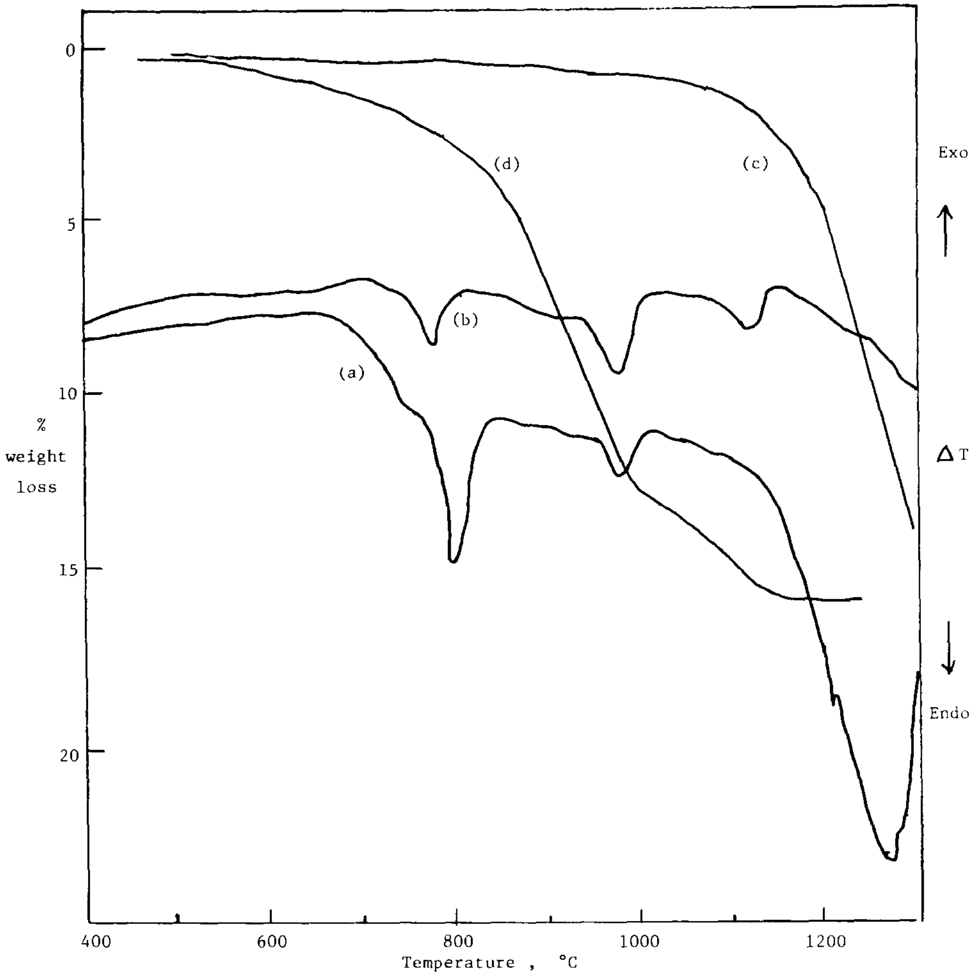

Fig. 1. DTA and TG curves of the $BaCO_3$-TiO_2 system in air. (a), DTA of $BaCO_3$; (b), DTA of $BaCO_3$-TiO_2; (c), TG of $BaCO_3$; (d), TG of $BaCO_3$-TiO_2.

The thermogravimetry curve (c) in Fig. 1 for pure $BaCO_3$ shows that the decomposition of $BaCO_3$ occurs in one step, whereas curve (d) of the $BaCO_3$–TiO_2 system shows that the reaction proceeds in two steps, a rapid chemical reaction occurs in the initial step, followed by a second step at higher temperatures, which is possibly a diffusion-controlled step through the compact $BaTiO_3$ layer. The formation of $CaTiO_3$ in the $CaSO_4$–TiO_2 system was also shown to proceed in two steps [12]. In the present study, the kinetics of the initial reaction step, which plays an important role in the reactivity of the solids, is discussed. The titanate formation reaction starts at a temperature which is about 300 °C below that required to start the decomposition of pure $BaCO_3$. This shows that when the temperature of the mixture approaches the temperature required for the decomposition of pure

TABLE 1

Kinetic equations examined in this work

Reaction model	$g(\alpha)$	Function symbol
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2
Jander equation, three-dimensional diffusion	$[1-(1-\alpha)^{1/3}]^2$	D_3
Ginstling–Brounshtein equation, three-dimensional diffusion	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	D_4
Two-dimensional phase boundary reaction	$[1-(1-\alpha)^{1/2}]$	R_2
Three-dimensional phase boundary reaction	$[1-(1-\alpha)^{1/3}]$	R_3
First-order kinetics	$[-\ln(1-\alpha)]$	F_1
Random nucleation: Avrami equation	$[-\ln(1-\alpha)]^{1/2}$	A_2
Random nucleation: Erofeev equation	$[-\ln(1-\alpha)]^{1/3}$	A_3

$BaCO_3$, essentially most of the barium carbonate has reacted with TiO_2 to form $BaTiO_3$. This has been demonstrated by X-ray diffraction analysis of samples at various temperatures in the DTA experiment.

Under isothermal conditions, the reaction rate constant k is independent of reaction time and so $kt = g(\alpha)$. Table 1 lists some of the more important kinetic equations [13–15] which were examined in the present study in order to find the most appropriate kinetic expression and reaction model to describe the reaction. The function $g(\alpha)$ depends on the mechanism controlling the reaction and on the size and shape of the reacting particles. In diffusion-controlled reactions, D_1 for a one-dimensional diffusion process is governed by a parabolic law, with a constant diffusion coefficient; D_2 is a two-dimensional diffusion-controlled process in a cylinder; D_3 is Jander's equation for a diffusion-controlled reaction in a sphere; and D_4 is the Ginstling–Brounshtein equation for a diffusion-controlled reaction starting on the exterior of a spherical particle. If the reaction is controlled by movement of an interface at constant velocity and nucleation occurs virtually instantaneously, then for such phase-boundary-controlled reactions, equations relating α and t are the R_2 function for a circular disc reacting from the edge inward and the R_3 function for a sphere reacting from the surface inward. If the solid state reaction follows first-order kinetics (F_1 function), then the rate-determining step is the nucleation process and there is equal probability of nucleation at each active site. In phase boundary reactions, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particle is covered with a layer of product. Nucleation of the reactant, however, may be a random process, not followed by rapid surface growth. As nuclei grow larger they may eventually impinge on one another, so that growth ceases where they touch. This process has been considered by Avrami and by Erofeev, who have derived the functions A_2 and A_3, respectively.

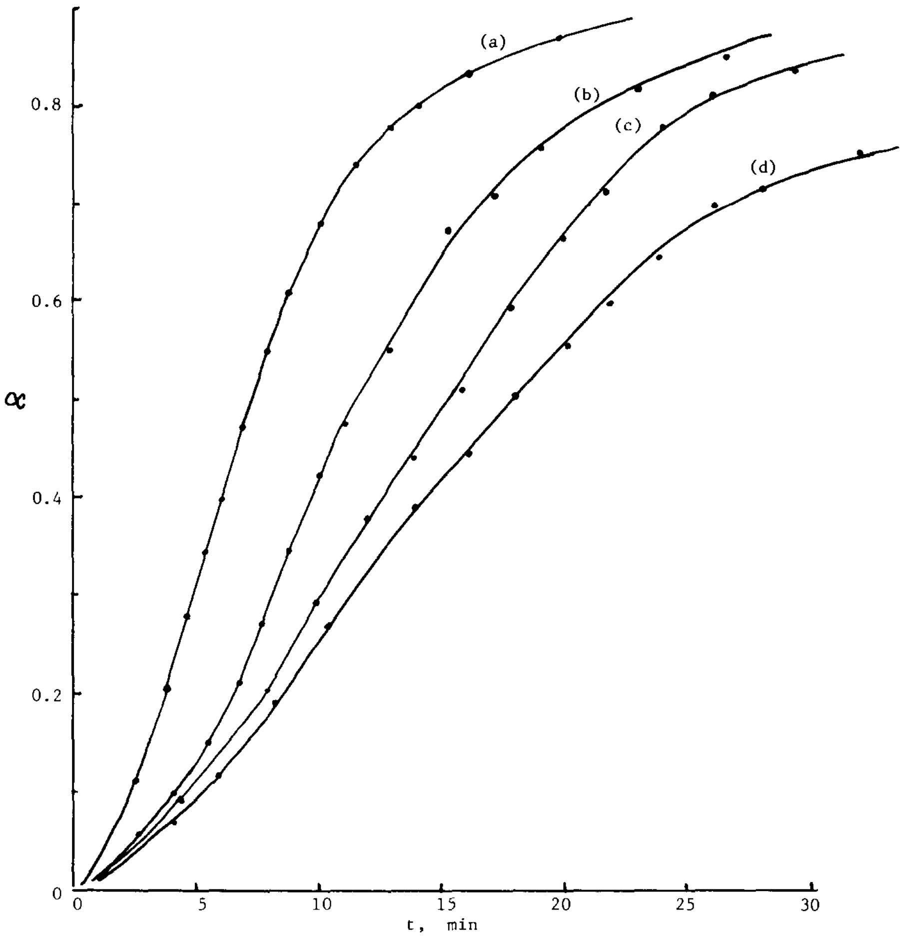

Fig. 2. Isothermal α/t curves for the formation of barium titanate in a crystalline mixture of barium carbonate and titanium dioxide.

Figure 2 shows the α/t curves for the isothermal formation of barium titanate in a crystalline mixture of $BaCO_3$ and TiO_2(anatase), in a 1 : 1 molar ratio. The isothermal data were analysed according to the kinetic equations listed in Table 1 by LR analysis and the comparison of fit showed that the random nucleation (A_2 and A_3) functions and the phase boundary (R_2 and R_3) functions give the best fit of data with comparable correlation coefficients. The reactivities of the $CaSO_4$–TiO_2 and $BaSO_4$–TiO_2 systems [12] examined by isothermal TG studies were found to fit Jander's diffusion equation. The kinetics of the reaction between alumina and barium carbonate [16] were described in view of the nuclei-growth equation and the Ginstling–Brounshtein diffusion equation. However, analysis of the initial reaction step in barium titanate formation in the $BaCO_3$–TiO_2 system has

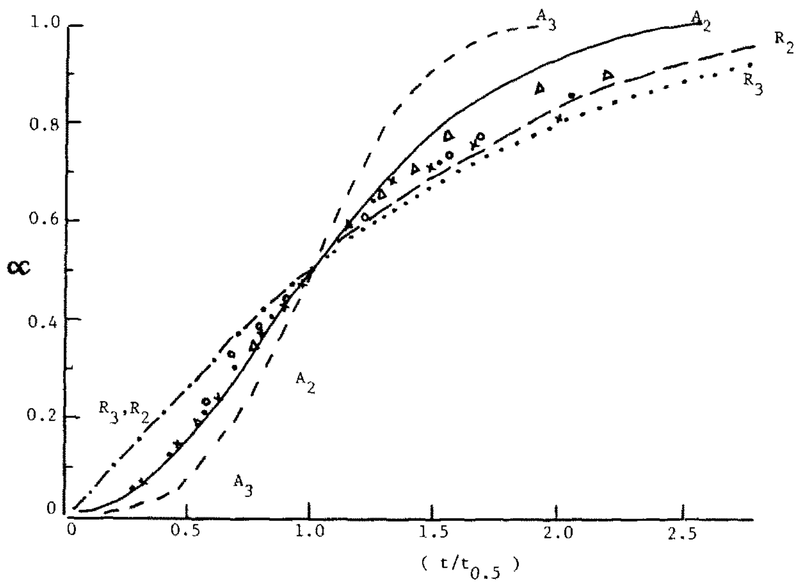

Fig. 3. Reduced plots for the isothermal formation of $BaTiO_3$ in the $BaCO_3$–TiO_2 system. Lines, theoretical for absolute correlation. Experimental points: ●, 892° C; ×, 873° C; △, 853° C; ○, 833° C.

shown here that the diffusion functions give a less satisfactory fit to the experimental data.

In order to distinguish between the different models, use was made of the reduced-time theoretical method suggested by Sharp et al. [13]. In this method, the time scale in the kinetic equation $g(\alpha) = kt$ is altered so that $g(\alpha) = A(t/t_{0.5})$ where $t_{0.5}$ is the time for 50% reaction and A is a calculable constant depending on the form of $g(\alpha)$. The time $t_{0.5}$ corresponding to $\alpha = 0.5$ was determined from the experimental data and was used to convert the data to curves of α against $t/t_{0.5}$ as shown in Fig. 3. The theoretical or master curves showing the variation of α with $t/t_{0.5}$ calculated for the A_2, A_3, R_2 and R_3 functions are shown in the same figure. It can be seen that the data give the best fit with the master curve of the A_2 model, although in the decay stage the experimental data tends more towards the R_2 model.

On the basis of the A_2 model, the activation parameters of the isothermal formation of $BaTiO_3$ in the $BaCO_3$–TiO_2 system were calculated and the results are shown in Table 2. The estimated activation energy is 160 ± 2 kJ mol^{-1}. Ishii et al. [10] reported a value of 295 kJ mol^{-1} for the formation of $CaTiO_3$ in the $CaSO_4$–TiO_2 system in isothermal kinetic experiments using DTA and applying Mampel's equation for the kinetic analysis of data. Such a large difference must be due to changes in the system, experimental technique and the model used for the kinetic analysis.

Figure 4 shows representative weight changes as a function of temperature for $BaTiO_3$ formation obtained under dynamic conditions. In view of

TABLE 2

Kinetic parameters for A_2 model calculated according to isothermal and dynamic methods

Method of analysis		E (kJ mol^{-1})	log A (min^{-1})	Correlation coefficient
Isothermal		162 ± 2	6.2 ± 0.8	0.997
Dynamic				
(a) Coats–Redfern method				
Heating rate (°C min^{-1}) =	5	57.0	1.04	0.987
	10	55.3	1.12	0.986
	20	50.2	1.16	0.991
	50	42.3	1.12	0.995
Average		51.2 ± 6.5	1.11 ± 0.05	
(b) Ozawa method				
$(1-\alpha)$ =	0.10	249.6	9.9	0.999
	0.20	257.3	11.3	0.999
	0.30	259.2	11.4	0.999
	0.40	271.6	11.6	0.999
	0.50	280.8	11.8	0.999
	0.60	291.9	11.9	0.998
	0.70	305.7	12.6	0.998
	0.80	300.7	12.5	0.992
	0.90	206.8	9.6	0.995
Average		270 ± 30	11.4 ± 1	

the conclusions from the isothermal studies and the reduced-time plots, the A_2 model should be used to analyse the results. In the analysis of dynamic TG curves, we have thus assumed the A_2 function and made a comparison between the two integral methods of Coats and Redfern [8] and of Ozawa [9]. In the first method, to allow for the calculation of the activation energy, the correct form of $g(\alpha)$ is used in the equation

$$-\ln(g(\alpha)/T^2) = -\ln(AR/\beta E)(1 - 2RT/E) + E/RT$$

The quantity $\ln(AR/\beta E)(1 - 2RT/E)$ appears to be reasonably constant for most values of E and in the temperature range over which most reactions occur. The advantage of the Ozawa method is that a master curve may be derived from the thermogravimetric data obtained at different heating rates, so that

$$(AE/R\beta_i)P(E/RT_i) = B$$

where B is considered constant for a given weight change during the TG dynamic measurements and $P(E/RT_i)$ was approximated by the equation

$$\log P(E/RT_i) = -2.315 - 0.4567(E/RT_i)$$

Hence, in this method, the activation energy is independent of the reaction mechanism and was determined from the TG curves obtained at different

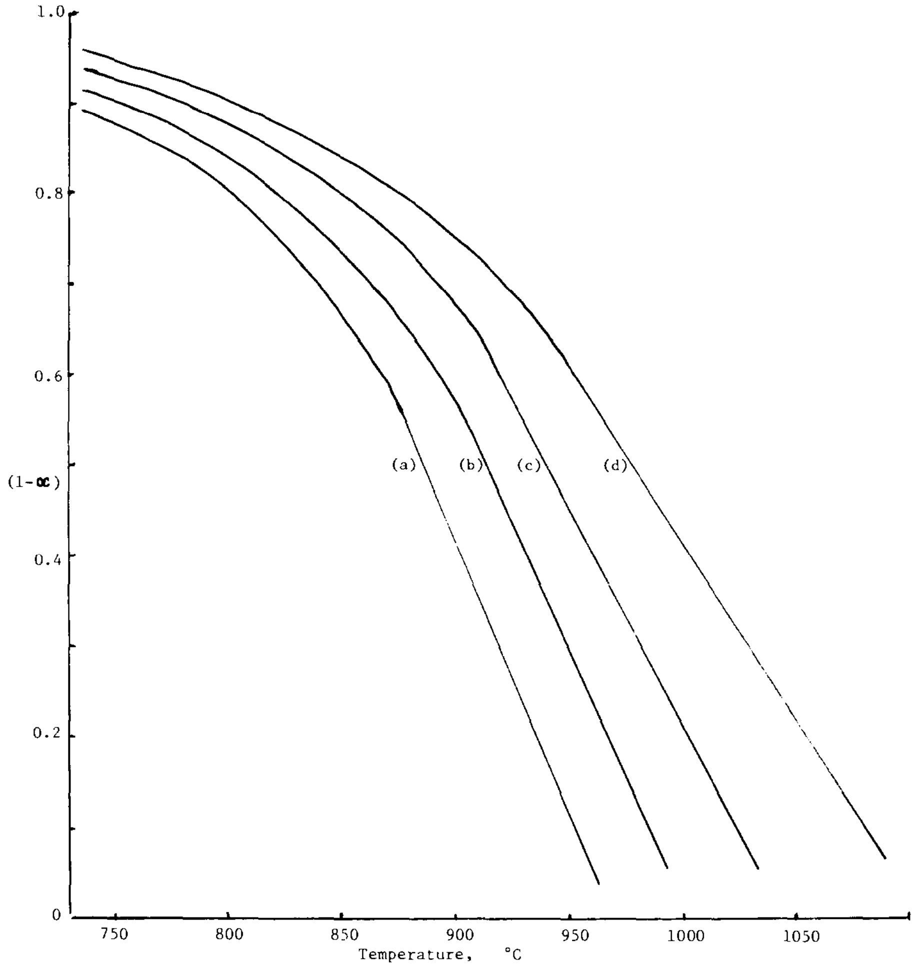

Fig. 4. Dynamic measurements of formation of barium titanate from barium carbonate and titanium dioxide. Temperature rate: (a), 5 °C min^{-1}; (b), 10 °C min^{-1}; (c), 20 °C min^{-1}; (d), 50 °C min^{-1}.

heating rates. The frequency factor was determined by the subtraction of $\log(E/\beta R)P(E/RT)$ from $\int d(1-\alpha)/f(1-\alpha)$ of the determined form of the $f(1-\alpha)$ function which depends upon the reaction mechanism. Table 2 shows the results of the calculations of the kinetic parameters for these two integral methods assuming that the reaction obeys the A_2 model.

The values of the activation parameters calculated from dynamic TG curves according to the Coats–Redfern and Ozawa methods show large differences between each other and both gave values which differ widely from the results obtained under isothermal conditions. The Coats–Redfern method gave a range of values which showed a decrease with increasing heating rates. In studying the thermal dehydration of calcium sulphate dihydrate, Dharwadkar and Phadnis [17] found a systematic decrease in the activation energies calculated according to the Coats–Redfern method with increasing sample size and heating rate. In the Ozawa method, although a single activation energy and frequency factor is obtained at the different heating rates, the values calculated at different weight changes during the dynamic measurements differ widely between each other and both the *E* and log *A* values go through a maximum at about 30% reaction. These results show that non-isothermal results are quite often not in agreement with the isothermal results. In many of the solid state reactions studied, a single model is not satisfactory to explain the reaction over the whole range. In the rising temperature technique, there is no model which can easily allow for the occurrence of several kinetic expressions whilst the reaction is proceeding [18].

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