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Modelling thermal decomposition of solids as reflected by gas-evolution curves

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Abstract

Results of modelling gas evolution during thermal decomposition of solids (EGA) are presented. The model assumes two components in the reaction system with a random nucleation mechanism being used in the simulation of EGA and ETA curves. It was demonstrated how the shapes of the EGA and ETA curves reflect the mechanism of the thermal decomposition reaction. Three model cases of morphology changes of solid samples accompanying thermal decomposition are presented to demonstrate the possible supplementary information gained from ETA. © 1998 Elsevier Science B.V.

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1. Introduction

In the investigation of the thermal decomposition of solids, most frequently thermogravimetry (TG) and evolved gas analysis (EGA) are used. Emanation thermal analysis (ETA) has been used by numerous authors [1–4] with the aim of characterising the morphology changes of solid samples taking place during thermal decomposition reactions. It is well known that the measurement of the release of the inert gases, previously introduced into the samples investigated, makes it possible to indicate continuously changes of the microstructure under the ‘in-situ’ conditions of thermal treatment [5]. ETA brings a new insight into the development of the microstructure of samples during their heat treatment.

We shall demonstrate how the shapes of EGA and ETA curves are able to reflect the mechanisms of

thermal decomposition reactions that are accompanied by the release of reaction products. Statistical modelling of radon nucleation of the new phase will be used. This paper should stimulate the parallel use of the results of TG and gas-evolution methods (EGA and ETA) in the determination of reaction mechanisms.

2. Statistical methods used in modelling

2.1. Monte-Carlo simulation

Thermal decomposition in homogeneous systems is fully described by kinetics. On the other hand, in heterogeneous solids, reaction depends on kinetics, diffusion and the morphology of the interspersed reacting material. The introduction of internal geometry into the description of diffusion and reaction phenomena makes solving the problem more com-

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plex, requiring the use of computer modelling methods [6].

The software package [7,8] used in the mathematical modelling to simulate thermal decomposition under isothermal conditions was THERMOKIN which in combination with the DIGS (diffusion of inert gases in solids) package [9] gave us the possibility of simulating the inert gas diffusion in disordered solids under various experimental conditions. The THERMOKIN-DIGS package makes it possible to treat experimental data obtained by means of different techniques of thermal analysis. A mechanism of random nucleation of the new phase throughout the whole volume of sample was assumed in the modelling.

In this work, the Monte-Carlo simulation is used to study the diffusion of gaseous products and inert gas during the solid-state reaction. The Monte-Carlo method assumes that gas molecules diffuse via a random walk, with each step being independent of the previous step. The simplest approach is to construct a regular lattice and to assume that, at each step, a particle moves from one lattice point to an adjacent lattice point. For example, in a simple three-dimensional solid, the particle can move in six directions.

The simulation uses a homogeneous set of lattice points of initial phase with randomly distributed clusters of the new phase. Adsorbed gas molecules in sites can have any desired degree of reversibility. The reversibility is defined as the chance that an adsorbed particle leaves a site. A two-dimensional 100×100 lattice is used. Constant boundary conditions are used for two of the dimensions to represent the infinite length, surface and width of the sample. The symmetry of the problem is accounted for by assuming the last row to be a perfect reflector. The last row of the lattice represents the midplane of the sample.

The following characteristics of the thermal decomposition reaction were analysed in order to observe how the TG and EGA (ETA) curves are able to reflect the thermal decomposition processes:

- the diffusion coefficients of the gaseous reaction products in the initial (D_1) and newly formed (D_2) solid phases;
- the diffusion coefficients of the inert gas in the initial ($D_{1,Rn}$) and newly formed ($D_{2,Rn}$) solid phases;

- the rate constants of the thermal decomposition reactions; and
- the numbers of lattice units of the new phase formed as a result of the transformation of one elementary lattice unit of the initial phase.

2.2. Percolation theory

The transport of gaseous products taking place during thermal decomposition was considered within the framework of percolation theory. Mathematical modelling makes it possible to understand the role of irregular morphology in non-steady solid-state reactions and diffusion processes taking place in disordered materials whose spatial-structure complexity evolves in time. Percolation theory enabled us to establish the relationship between the volume content of the new phase and its fraction connected with the external surface of the sample ('open porosity'). The gaseous products of reaction may migrate to the sample surface using diffusion pathways available in this phase.

The main attention in mathematical modelling was paid to the percolation threshold, the value of the critical index, as well as to the investigation of the distribution of reaction products in the proximity of the percolation threshold. Contrary to the formal kinetics approach, the percolation theory approach makes it possible to explain a number of experimentally observed effects, such as:

- the threshold of gas escape from the thermally decomposed solids;
- the loss of sample compactness and the grain-size distribution of the reaction products; and
- the disagreement between experimentally observed TG/DTG and EGA curves and the formal kinetics curves of the solid-state process corresponding to the reaction mechanism assumed.

The lattice percolation model requires the existence of gas flow through 'bonding' which connects neighbouring sites in a regular lattice. Lattice disorder can be introduced in several ways. The most common statistical assumptions are known as the 'bond percolation' and the 'site percolation' models [10]. In the first model, a known fraction of the randomly distributed bonding is missing in the lattice, which means that the gas cannot pass through there. In the second

model, a known fraction of sites is assumed to be missing. The absence of sites implies that no gas can pass through any of the bonds which join that site to its neighbours. This is the general description of the percolation threshold, α_c . The percolation threshold of a system determines the volume fraction of the newly produced phase at which an ‘infinite’ cluster appears (i.e. where the breakdown of material takes place).

To demonstrate this general picture of the percolation threshold, we shall describe a lattice containing N sites, where N is a large number. Quantities relevant to percolation theory are defined in the limit $N \rightarrow \infty$, and will depend on α_2 , where α_2 is the concentration of the ‘allowed’ sites for the passage of gas, as well as on the geometry of the lattice. When the value of α_2 is low enough ($\alpha_2 \ll \alpha_c$), the allowed sites occur individually or in small isolated clusters adjacent to allowed sites. As the value of α_2 increases, large clusters occur, and the mean size of a cluster increases monotonically. As α_2 approaches α_c from below, the larger clusters begin to merge, creating a few extremely large clusters, so that, in the limit $N \rightarrow \infty$, the mean cluster size diverges at α_c . For any finite N , this implies that there is a completed path of adjacent allowed sites crossing the system, and thus macroscopic flow through the system becomes possible.

In a given system, a new phase can exist:

- (i) in isolation, or in clusters that are surrounded by initial phase, or
- (ii) in sample spanning regions that allow passage of gas through the new phase from one side of the sample to another, without leaving it [10].

As soon as $\alpha_2 > \alpha_c$ it appears that, if N is sufficiently large, only one large cluster remains along with many small clusters. The ratio of the number of sites in an infinite cluster to the number of sites in the lattice tends to a sharply defined function of α_2 when N is very large, with $\alpha_2 > \alpha_c$. This ratio, called the ‘site percolation probability’, $P(\alpha_2)$, is a parameter to be used in the description of transport in the system. As the value of α_2 increases above α_c , the infinite cluster grows rapidly, absorbing smaller clusters. Correspondingly, the value of $P(\alpha_2)$ rises sharply from zero just above the percolation threshold, tending asymptotically to α_2 , when $\alpha_2 \gg \alpha_c$ and isolated clusters become rare. $P(\alpha_2)$ near the

threshold can be characterized by a simple power law [10,11]:

$$P(\alpha_2) \propto (\alpha_2 - \alpha_c)^S \quad (1)$$

where the critical index S is approximately the same for all regular lattices: $0.3 \leq S \leq 0.4$.

A uniform two-dimensional grid consisting of sites and links was considered in the modelling. The coordination number was determined by the number of links per site. The properties of the phases present in the sample were assumed to be determined by mutual relationships between sites and links. Changes in the properties of the sites and the links during the solid-state reaction were also assumed. In order to characterize the sample morphology at any one time, the geometry (form) and topological structures (links) existing between the two phases (components) of the heterogeneous solid were calculated.

2.3. Parameters describing the thermal decomposition of a heterogeneous sample

The following parameters that determine the properties of the solid medium were calculated:

- the volume fraction of new phase (which in special cases can be taken to be the porosity);
- the volume fraction of initial phase;
- the density of the interface surface, the width of clusters of the new and initial phases;
- the volume fraction of the isolated clusters of the sample components (which in a special case can be taken for ‘closed porosity’);
- the volume fraction of the new phase connected with the surface of sample (which in a special case can be taken for ‘open porosity’);
- the volume fraction of the sample components, the surface of which is interconnected (in a special case considered as ‘through porosity’);
- the percolation threshold and critical index; and
- the diffusion conductivity factor (taking into account winding diffusion pathways of the new and initial phases), and the presence of impassable ways.

In addition to the above-mentioned properties, the value of the following characteristics of the sample were calculated – the skeleton fraction (i.e. the set of

pathways which can be used by the gaseous products to migrate out from the sample):

- the impassable fraction (i.e. the pathways which prevent the gaseous products from the skeleton part from reaching the sample surface or connecting with separate pathways of the skeleton); and
- the volume of the elastic skeleton fraction (i.e. the part of the shortest pathways which can be used by the gaseous product to migrate out).

Statistical distributions of the site clusters, according to their dimensions, to their volume and their surface area, were calculated in order to obtain additional characteristics of the material investigated. Fractal geometry methods were used in the characterization of the heterogeneous material [12].

The percolation threshold and material distributions under conditions near threshold play a crucial role in the modelling of thermal decomposition reactions. In most cases, the decomposition reactions occur at material boundaries. Under dynamic conditions of sample heating the morphology will change with time. The main advantage of the use of percolation theory in the modelling of thermal analysis results is the possibility of establishing the relationships between the degree of conversion and experimentally measured parameters, e.g. the mass of sample, the flux of gaseous reaction products released, etc.

Different mechanisms for solid-state reactions can be considered in the interpretation of the thermal analysis results.

3. Results of the modelling

In Fig. 1(a–c), the spatial distributions of the reaction components (both solid and gaseous) at the surface and bulk of the sample are demonstrated as the result of the modelling. The following characteristics of the thermal decomposition kinetics were calculated during the modelling:

- the time dependence of the volume fraction of the initial phase, $\alpha_1(t)$;
- the time dependence of the portion of the newly formed, highly disordered phase enabling the evolved gases to be released was considered as

$$\alpha_2(t) = \alpha_{2,\text{open}}(t) + \alpha_{2,\text{closed}}(t)$$

where $\alpha_{2,\text{open}}(t)$ is the portion of ‘open porosity’, $\alpha_{2,\text{closed}}(t)$ the portion of ‘closed porosity’, and $\alpha_1 + \alpha_2 = 1$;

- the time dependence of sample mass changes, $M(t)$ (TG parameter);
- the time dependence of the flux $J(t)$ of the gaseous reaction products released from the sample (EGA parameter);
- the time dependence of the release of inert gases previously introduced into the sample $J_{\text{ig}}(t)$ (ETA parameter); and
- the time dependence of the release of inert gases $E(t)$, from samples labelled with the parent nuclides of inert gases, ensuring a permanent source of inert gases in the sample. (In ETA terminology, the E value is called the emanation release rate or the emanating power.)

In the two-dimensional model presented in Fig. 1, a mechanism of random nucleation of the new phase throughout the volume of the initial phase, accompanied by the production of gases, was considered. The decomposition of the initial phase is described by first-order kinetics. It was assumed that diffusion of gaseous products in the initial phase is not possible ($D_1 \approx 0$), while in the newly formed phase diffusion occurs easily ($D_2 \gg D_1$).

From the results of the two-dimensional distribution of the reaction components presented in Fig. 1, it is evident that during the first stage of thermal decomposition (Fig. 1(a)) the fraction of ‘open-porosity new phase’, $\alpha_{2,\text{open}}$, represents only a small part of the total fraction of the newly produced phase, α_2 . Therefore, in spite of the fact that the thermal decomposition proceeds in the sample, the release of gaseous reaction products cannot be observed.

During the further course of the reaction, isolated regions of the newly produced phase are formed (Fig. 1(b)). After a certain stage of decomposition, a ‘breakdown’ of the sample takes place, accompanied by escape of the gaseous products (this time corresponds to the percolation threshold).

As the solid-state reaction proceeds, the volume of the newly formed phase becomes larger, representing a larger volume cluster, whereas the initial phase is represented by small volume inclusions present in the newly formed phase (see Fig. 1(c)). During the final stage of the decomposition, the

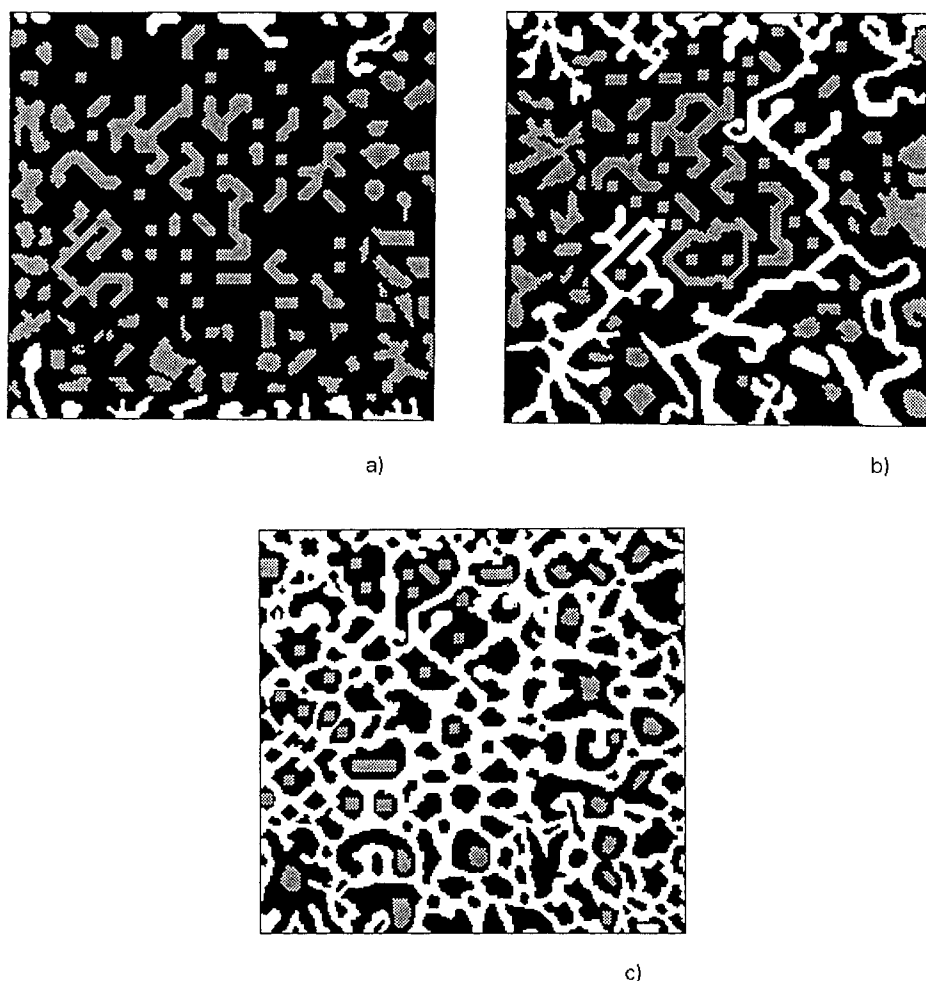


Fig. 1. Statistical modelling of a solid-state decomposition using a two-component model and assuming a mechanism of random nucleation. (a) The initial period of thermal decomposition when the new phase is formed by random nucleation. Clusters of the new phase are totally surrounded by the old phase, not permitting the migration of gaseous reaction products to the sample surface. (b) The next step of the thermal decomposition when the new phase regions are mutually interconnected products at the surface. (c) The period of the thermal decomposition corresponding to the stage when the clusters of the initial 'non-reacted' phase are surrounded by the new phase. Key: solid black, initial (old) phase; white, interconnected clusters of the new phase (or 'opened porosity'); and hatched, clusters of the new phase totally surrounded by the old phase (or 'closed porosity').

newly formed phase represents a very small cluster.

In Fig. 2, the time dependence of the decreasing amount of the initial phase, $\alpha_1(t)$, during its thermal decomposition, as calculated from the first-order reaction mechanism (curve 1), a TG curve (curve 2) and the evolved gas analysis, EGA, (curve 3) are shown.

It can be seen from curve 2 in Fig. 2, that the amount of the released gaseous product (a model

TG curve) is not proportional to the amount of the reacted material, but only to that part of the sample representing pathways for the migration of the gaseous product out of the sample. The kinetics of the thermal decomposition are represented by curve 1, Fig. 2.

From a comparison of curve 2 and curve 1 in Fig. 2, it is obvious that, at the beginning of the thermal decomposition, the TG curve does not reflect the thermal decomposition as it would correspond to

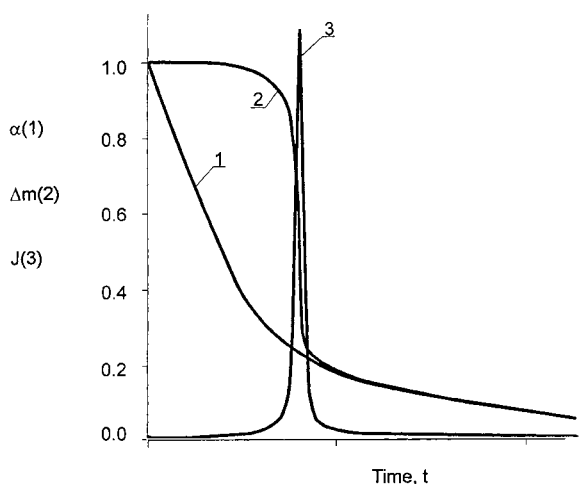


Fig. 2. Time dependence of the model thermal-decomposition reaction, assuming a mechanism of random nucleation of the new phase: curve 1 demonstrates the decrease of the initial phase $\alpha_1(t)$ in the sample volume; curve 2 the mass change $M(t)$ of the sample, representing a theoretical TG curve; and curve 3 the flux $J(t)$ of gaseous reaction products released from the sample, (the curve represent the EGA curve as well as the DTG curve).

first-order kinetics (see curve 1, Fig. 2). Moreover, from the model TG curve (curve 2, Fig. 2) it follows that the decrease of sample mass due to the release of the gaseous reaction products begins after the decomposition of $\approx 30\%$ of the initial sample mass. Only after the decomposition of $\approx 60\%$ of the sample mass do curves 1 and 2 in Fig. 2 become identical. Consequently, in this case, the results calculated from the reaction kinetics law do not give information corresponding to the real process of thermal decomposition of the solid.

Curve 3 in Fig. 2 represents the EGA curve (or the DTG curve). The position of the peak coincides with the time interval when the percolation threshold is attained (and it also coincides with the interval to reach maximum rate of decomposition, as shown by the DTG curve). As the reaction develops, unification of material occurs in different regions of the newly produced phase and, at some moment, there is a 'breakdown' of the sample accompanied by strong ejection of gaseous products of reaction (percolation threshold). Only from this moment on does the $d\alpha/dt$ curve coincide with the EGA (or DTG) curve. A similar shape can also be expected for the ETA curve

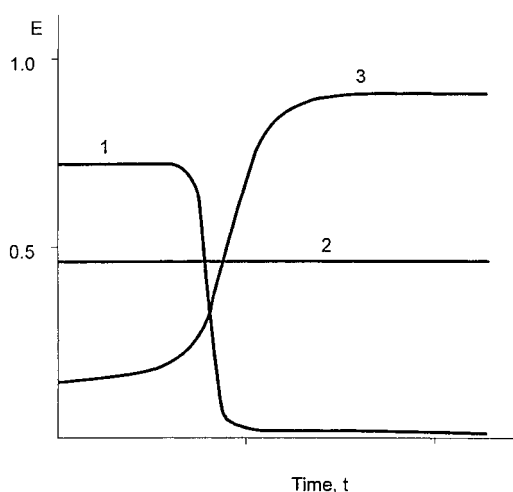


Fig. 3. Results of the modelling of ETA curves. Time dependence of the emanation power $E(t)$ from samples labelled with Th-228 as the inert-gas parent radionuclide. Curve 1 corresponds to the case when the value of the emanation power of the initial phase E_1 is higher than the value of the emanation power of the final solid phase E_2 , $E_1 > E_2$ ($E_1=0.69$, $E_2=0.01$). Curve 2 corresponds to the case when $E_1=E_2$. Curve 3 corresponds to the case when $E_1 < E_2$ ($E_1=0.14$, $E_2=0.90$).

when the inert gas was introduced homogeneously into the whole sample volume (e.g. by a diffusion technique or during sample preparation in an inert gas medium).

In ETA where the sample is labelled by the introduction of inert-gas parent radionuclide, serving as a quasi-permanent source of the inert gas, the ETA curves differ from those mentioned above and are discussed on the basis of Fig. 3.

In Fig. 3, we present the ETA curves obtained during the thermal decomposition of the samples labelled by the parent nuclides of the inert gas (e.g. for radon-220 by the radionuclides of Th-228 and Ra-224), which differ from curve 2 in Fig. 2. ETA curves presented in Fig. 3 reflect changes of the sample microstructure during thermal decomposition.

Model ETA curves are presented in Fig. 3 assuming three different values of the radon diffusion coefficients of the two components considered in the solid sample during its thermal decomposition. In modelling ETA curves, we have assumed that both the initial phase and the newly formed phase differ in their chemical and physical properties and in their radon diffusion coefficients. For curve 1, it was assumed that

the value of the emanation power E_1 of the initial (old) phase was higher than the value of E_2 of the reaction product (final phase), i.e. $E_1 > E_2$. Curve 2 corresponds to the case when values of E_1 and E_2 are comparable, i.e. $E_1 = E_2$, and curve 3 to the case when $E_1 < E_2$.

The results of modelling, demonstrated in Fig. 3, make it possible to understand the high sensitivity of ETA to changes of sample morphology taking place during the thermal decomposition of solids. For example, when a solid reaction product of relatively high surface area and porosity results from the decomposition, curve 3 in Fig. 3 models the characteristic ETA curve. Curve 1 models the characteristic ETA curve for formation of a relatively dense decomposition product and curve 2 the case when thermal decomposition is not accompanied by any change of morphology or surface area of the sample.

Numerous examples of experimental ETA results corresponding to the model described above have been presented in a monograph [5] and a review paper [13]. ETA has been used in the characterisation of changes of surface area and porosity of sorbents, catalysts, etc., during heating [5].

4. Conclusion

From the above discussion, it follows that experimental TG curves may not reflect the true kinetics of the thermal decomposition process, which may lead to an incorrect determination of the rate equation and to false conclusions about the mechanism of the solid-state reaction. Consequently, correction of the experimental TG curve is necessary. It has been demonstrated that EGA and ETA curves are able to represent the true kinetics of thermal decomposition reactions.

The sensitivity of ETA to morphology changes taking place during the thermal decomposition of solids has been demonstrated for three modelling cases. ETA can be recommended as a tool for obtaining supplementary information about development of

the morphology of both porous and non-porous solids during their preparation by thermal decomposition.

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