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Solid decomposition reactions induced by laser: The use of a non-isothermal kinetics model *

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Abstract

The authors presented earlier some results concerning the kinetics of the decomposition reactions of inorganic substances irradiated with a CW CO_2 laser. All these processes were characterized by a unique step, probably due to the high heating rate which is developed within the impact region of the laser beam.

A more precise description seems to be possible using the analysis of the decomposition processes induced by controlled heating. Thus we observed that the reaction occurs in several steps, and not in a single one. The kinetics of these steps may be investigated using non-isothermal methods. The present paper underlines some advantages and limitations to the use of non-isothermal kinetics models for a more complete description of laser-induced reactions.

INTRODUCTION

There are several instances in which the decomposition of a solid inorganic salt can be induced by a CW CO_2 laser, according to the general chemical reaction [1]

$$\text{Solid} \rightarrow \text{Solid} + \text{Gas} \qquad (1)$$

In order to analyse the kinetics of these reactions, a non-isothermal kinetics model of the heterogeneous reaction model was chosen [2]. A simple experimental device, shown schematically in Fig. 1, was used to perform the experiments. The cell which contains the salt uniformly distributed as a layer of known thickness, is driven at constant speed through a laser beam whose power is measured by a PM powermeter; the cell was weighed after each passage. The decomposition was followed until no weight change was

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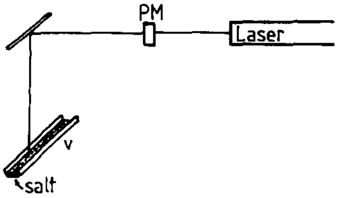

Fig. 1. The experimental system.

recorded for two consecutive passages. The temperature of a specific area of the experimental cell was recorded with an optical pyrometer and the curves shown in Fig. 2 were obtained.

The highest temperature reached during the experiment depends on the power of the laser, the absorptivity of the substance, etc. In our experiments it ranged from 1000 to 1500 K for a 25 W laser. After each passage the temperature of the area decreases until a new interaction is reached. The model is assumed to be representative of the whole cell. The number of the spikes in Fig. 2 is equal to the number of passages of the cell through the laser beam. The temperature of the peaks is, for simplicity, assumed constant.

It is supposed that the high heating rates involved in laser experiments (the steep slope in Fig. 2) hide the intermediate reactions which occur before formation of the final product. This may explain the one-step-like decomposition reactions which are observed when laser-induced reactions are followed.

In order to better describe the decomposition reactions and to confirm the existence of the different steps, low heating rates and constant experimental parameters have to be used. Therefore thermal gravimetric experiments were used. The acquired experimental data (the decrease in weight of the material and the corresponding time period) for both laser and thermally induced reactions may be calculated using the usual kinetics equation [3]

$$d\alpha/dt = f(1-\alpha)k(T) \tag{2}$$

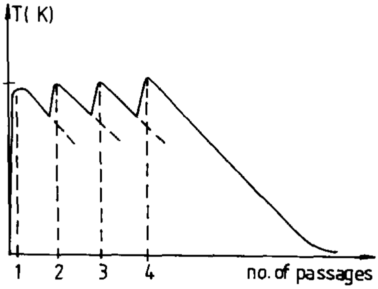

Fig. 2. Typical temperature evolution curve during laser experiments.

where α is the degree of conversion given by

$$\alpha = \frac{m_t - m_0}{m_\infty - m_0} \tag{3}$$

where m_t is the mass of substance at time t, m_0 is the mass of substance at the beginning of the experiment, m_∞ is the mass of substance at the end of the experiment, $f(1-\alpha)$ is the conversion function and $k(T)$ is assumed to obey an Arrhenius-type relationship:

$$k(T) = A \exp(-E/RT) \tag{4}$$

The time variable t may be replaced by temperature using

$$b(T) = \mathrm{d}T/\mathrm{d}t \tag{5}$$

if the dependence of the heating rate b on the temperature T is known (during thermogravimetric experiments the equipment has a fixed b). The following equation is then obtained [4]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{1}{b} f(1-\alpha) A \exp(-E/RT) \tag{6}$$

The definitions of the terms in the above equations require some comment.

Mechanism

The term $f(1-\alpha)$ is a function of the conversion whose analytical form is closely related to the mechanism of the rate-determining step. There are many forms given in the literature [2] for $f(1-\alpha)$, some of which are listed in Table 1. The last form

$$f(1-\alpha) = (1-\alpha)^n \tag{7}$$

where n is the reaction order, is used when our knowledge is not sufficient for an exact description of the process. The advantage of the use of eqn. (7) is that a complex process may be fitted with the simplest polynomial form.

In fact the form determined for $f(1-\alpha)$ requires additional confirmatory experimental evidence, e.g. microscopy or X-ray diffraction. In order to determine $f(1-\alpha)$ from thermogravimetric experiments, eqn. (6) may be used in the integral logarithmic form [5]:

$$\ln \int_0^\alpha \frac{\mathrm{d}x}{f(1-x)} = -\frac{E}{RT} + \ln \frac{AE}{bR} \tag{8}$$

A plot of $\ln \int_0^\alpha \mathrm{d}x/f(1-x)$ vs. $-1/RT$ leads to a straight line whose slope and intercept give E and A respectively; the best correlation coefficient is obtained for the most suitable $f(1-\alpha)$ and if the same result is obtained for 3–4 different heating rates the values of E, A and $f(1-\alpha)$ may be considered as valid kinetic parameters for the process.

Equation (6) cannot be used for the same purpose when experimental laser data are to be analysed because temperature cannot be adequately

TABLE 1

The conversion functions and mechanisms

Mechanism	Conversion function, $f(1-\alpha)$
Nucleation and nuclei growth	
Random nucleation	$1-\alpha$
Avrami–Erofeev nuclei growth	
two-dimensional growth	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
three-dimensional growth	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
Prout–Tompkins branching nuclei	$\alpha(1-\alpha)$
Avrami–Erofeev general equation	$\frac{1}{r}(1-\alpha)[-\ln(1-\alpha)]^{1-r}$
Diffusion	
Parabolic law (one-dimensional transport process)	α^{-1}
Valensi law (two-dimensional diffusion)	$[-\ln(1-\alpha)]^{-1}$
Jander law (three-dimensional diffusion)	$(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}$
Anti-Jander (three-dimensional counter-diffusion)	$(1+\alpha)^{1/3}[1-(1+\alpha)^{-1/3}]^{-1}$
Brounshtein–Ginstling (three-dimensional diffusion)	$[(1-\alpha)^{-1/3}-1]^{-1}$
Phase boundary movement	
One-dimensional (zero order)	Const.
Contracting cylinder (two-dimensional)	$(1-\alpha)^{1/2}$
Contracting sphere (three-dimensional)	$(1-\alpha)^{2/3}$
Power law	$\frac{1}{r}\alpha^{1-r}$
Reaction order	$(1-\alpha)^n$

controlled during the experiment. Because the temperature of the peaks in Fig. 2 is more or less the same for a decomposition process, $k(T)$ in eqn. (6) may be considered a constant. Equation (2) may then be used in its logarithmic form:

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln f(1-\alpha) + \ln k(T) \tag{9}$$

and a plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ against α for each peak gives a straight line for the correct $f(1-\alpha)$ function only (the best correlation coefficient method may also be used).

In order to compare the kinetics of laser-induced reactions with those induced by thermal heating, it is necessary to assume that the intermediate steps are identical for both types of reactions. A demonstration of the validity of this assumption is obtained from a consideration of the results of the decomposition of $LiOH \cdot H_2O$. This salt decomposes thermally according to the scheme [1]

$$2LiOH \cdot H_2O \xrightarrow[-2H_2O]{} 2LiOH \xrightarrow[-H_2O]{} Li_2O \tag{10}$$

The absorptivity of LiOH at 10.6 μm is almost nil, whilst that of the initial salt is about 30%. If the laser-induced decomposition follows the same route the reaction should stop at the LiOH stage according to the absorptivity law (negative feedback) [6]. Analysis of the final product demonstrated the presence of LiOH [1]. Moreover, we obtained only one conversion function for the laser-induced reactions, probably a result of the overlapping of the individual functions describing each step in the mechanism. Because of our lack of knowledge, the reaction order model (eqn. (4)) is the best model we have found to fit the results.

In many experiments we have obtained $n = 1$. When the decomposition of $MgSO_4 \cdot 7H_2O$ or $LiOH \cdot H_2O$ was studied, the result $n = 0.7$ was obtained. The latter value, as Table 1 shows ($n = 2/3$) suggests that a three-dimensional phase boundary movement mechanism governs the two decomposition reactions. As our observations showed, the diffusion of the evolved gas must also be considered in all the reactions studied. It appears, therefore, that the real form of $f(1 - \alpha)$ for the laser-induced reactions is a problem requiring further investigation; the formulation of a model for solid decomposition reactions deserves further attention.

To summarize, we consider that both laser and thermally induced reactions follow the same decomposition route but with different kinetic functions.

Arrhenius parameters

The two parameters E and A cannot be calculated for the laser-induced experiments. In this case we obtained only one complex function, $k(T)$, which does not offer much information. It has to be related somehow to the values of E and A (the Arrhenius-type relationship) for the intermediate steps and also to the IR absorptivity of the intermediate compounds.

Some experiments on the decomposition of nickel salts pointed out clearly that the value of E for intermediate steps calculated from TG experiments and the absorptivity of laser quanta by the initial salt play an important role in the final physical form of the nickel oxides obtained and in their stoichiometry. For example, we have observed that the sum of the E values for the intermediate steps influences the stoichiometry of the nickel oxides obtained [7].

We may conclude, therefore, that even if E and A are considered to be only fitting parameters, at least E has some further relationship with the energies of the processes.

The heating rate

The heating rate b is constant or is a given function of T for the thermally induced reactions. It is known that if the linear heating rate

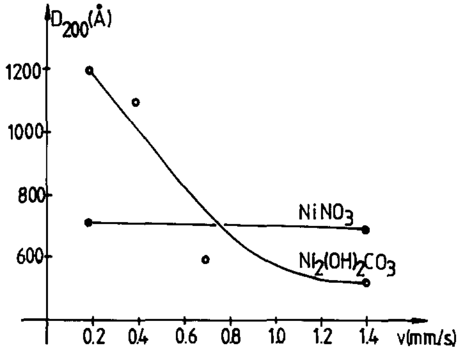

Fig. 3. The dependence of the mean size of NiO_x on the speed of passage through the laser beam.

increases (higher values of b), the temperature of the maximum value of the conversion rate shifts to higher temperatures [8]. Some theoretical considerations led us to the conclusion that if b is nonlinear (a function of temperature) it influences the form of $f(1-\alpha)$ itself [5]. It appears that b is an important experimental parameter. The heating rate of the laser-induced reactions is strongly related to the number of quanta absorbed by the substance, i.e. to the absorptivity of the salt at 10.6 μm, the power of the source, the speed of the cell through the laser beam etc. Obviously the heating rate for the laser experiments is a non-linear function of temperature and, according to the above discussion, different heating rate functions (i.e. different powers, speeds etc.) will lead to different physical forms of the final products.

Two different nickel salts, a hydroxycarbonate and a nitrate, were used to obtain a proof of the above supposition. The first salt has an absorptivity of about 42% whilst that of the second is only 2%. It is expected that a change in the speed of the cell through the laser beam will lead to a more significant change in heating rate for the salt which has a higher absorptivity. The results of the experiments are given in Fig. 3. The results plotted above support the theoretical dependence of $f(1-\alpha)$ on the heating rate function.

Other factors

The use of the thermogravimetric device and non-isothermal kinetics model to analyse the results of the laser-induced reactions indicate that there are other experimental parameters whose importance should be analysed. These factors which are known to influence the conversion function during thermal experiments are [2] the shape of the crucible, the thermal properties of the crucible material, the composition of the atmosphere and the partial pressures above the cell. Their effect was observed in a qualitative manner during our experiments, but a deeper analysis has yet to be done.

CONCLUSIONS

The advantages and limitations of the use of a non-isothermal kinetics model to analyse the decomposition reactions induced by a laser may be summarized below.

Limitations. Laser phenomena involve not only thermal problems but also the absorptivity, resonance, directionality of the laser beam etc., which are only indirectly included in the non-isothermal kinetics model and the results, at this stage at least, are only qualitative. The questions raised by the physical meaning of non-isothermal kinetics parameters for heterogeneous reactions remain unsolved. Moreover, eqn. (2) used for the analysis of the laser-induced reactions leads to two complex functions, $f(1-\alpha)$ and $k(T)$ which are not clearly defined. Each of them is probably a combination of E, A and $f(1-\alpha)$ (obtained by thermogravimetric methods for the intermediate steps) and some other parameters such as absorptivity, resonance etc., as mentioned above.

Advantages. Non-isothermal kinetics models allow a better understanding of the laser-induced decomposition route and stress the importance of positive and negative feedback. The knowledge of the intermediate steps and the absorptivity of the intermediate compounds allows a more precise description of the decomposition process.

Finally, the same model may be used to analyse the inverse chemical reaction, i.e.

$$\text{Solid} + \text{Gas} \rightarrow \text{Solid} \tag{11}$$

Such reactions are met when deposition on a given solid support from a given atmosphere are investigated. Some results published recently by Bali and Nánai [9] concerning the laser-induced oxidation of tantalum in air atmosphere seem to support this assumption.

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