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Gamma irradiation effects on the electrical conductivity behaviour and thermal decomposition induction period in nickel oxalate

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Abstract

The effects of pre-irradiation with γ-rays prior to thermal decomposition on the induction periods of nickel oxalate have been investigated. The results indicated that the induction period of the investigated salt does not appear to be reduced systematically with the γ-ray dose in the range $10^3 < \phi < 10^6$ Gy where ϕ is the γ-ray dose absorbed by nickel oxalate. The pre-irradiation changed the kinetics of propagation and growth of the decomposition centres in highly irradiated samples attributed to radiation damage of the crystals. Electrical conductivities of γ-irradiated samples were measured during the thermal decomposition of nickel oxalate and the results were evaluated.

Keywords: DTA; Electrical conductivity; Gamma irradiation; Nickel oxalate; TGA; Thermal decomposition induction period

1. Introduction

Most often, studies on irradiated materials have been performed with the aim of investigating whether radiation can modify one or more properties of the material in some important way. For example, irradiation may introduce lattice defects or trapped charges which modify any subsequently measured process such as thermal stability. Detailed description of isothermal chemical decomposition kinetics is given in the literature [1, 2]. Studies of the thermal analysis and kinetics of thermal decomposition of metal oxalates have attracted the interest of several investigators. Quite often

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radiolysis and thermal decomposition of such materials result in a product (e.g., oxide or metal) which possesses pores, lattice imperfections as a reactive solid; some oxalates have been considered as economic catalyst precursors.

Our previous [3] study on the thermal decomposition of nickel oxalate showed that the decomposition was controlled by Avrami–Erofeev nucleation growth. The present study deals with an investigation of the effect of γ-irradiation on the thermal decomposition induction period in nickel oxalate and whether the previous relationship between the isothermal induction period, t_i, and the radiation dose, ϕ,

$$t_i = C_1 - C_2 \log \phi$$

(where C_1 and C_2 are constants) derived for the thermal decomposition of γ-irradiation of inorganic solids [4] is applicable to nickel oxalate. The electrical conductivities of γ-irradiated solid samples of nickel oxalate were also measured in order to find a correlation between the conductivities of the γ-irradiated nickel oxalate samples and their thermal decomposition.

2. Experimental

Hydrated nickel oxalate was obtained commercially (α-inorganic) and used without further purification. Four samples of hydrated NiC_2O_4 were subjected to γ-rays in different dosages ranging from 1×10^3 to 1×10^6 Gy (samples II to V). The samples were encapsulated in glass vials and were exposed to successively increasing doses of radiation at constant intensity using a Co-60 γ-ray source at a dose rate of 1.1 Gy s^{-1}. The source was calibrated against a Fricke ferrous sulphate dosimeter and the dose rate in the irradiated samples was calculated by applying appropriate corrections on the basis of photon mass attenuation and energy absorption coefficients for the sample and dosimeter solution [5].

TGA and DTG of unirradiated and irradiated nickel oxalate were obtained using a DuPont thermal analyzer 2000 with a heating rate of 10°C min^{-1}. The study of isothermal kinetics of the samples was carried out with the aid of a Sartorius electrobalance. The sample (100 mg) was placed in a quartz basket suspended from the arm of the balance by means of a quartz wire. The sample temperature was adjusted at 345°C using a Gallenkamp temperature controller.

The electrical conductivity measurements accompanying the thermal decomposition of the samples were carried out using a method which has been described previously [6].

3. Results

TG and DTG curves of non-irradiated (sample (I)) and nickel oxalate irradiated with a total γ-ray dose of 1×10^6 Gy (sample (V)) are shown in Fig. 1 (a and b, respectively). The TG curves show that the dehydration of $NiC_2O_4 \cdot 2H_2O$ takes place in one step in the temperature range 200–255°C, and corresponds to elimination of two water

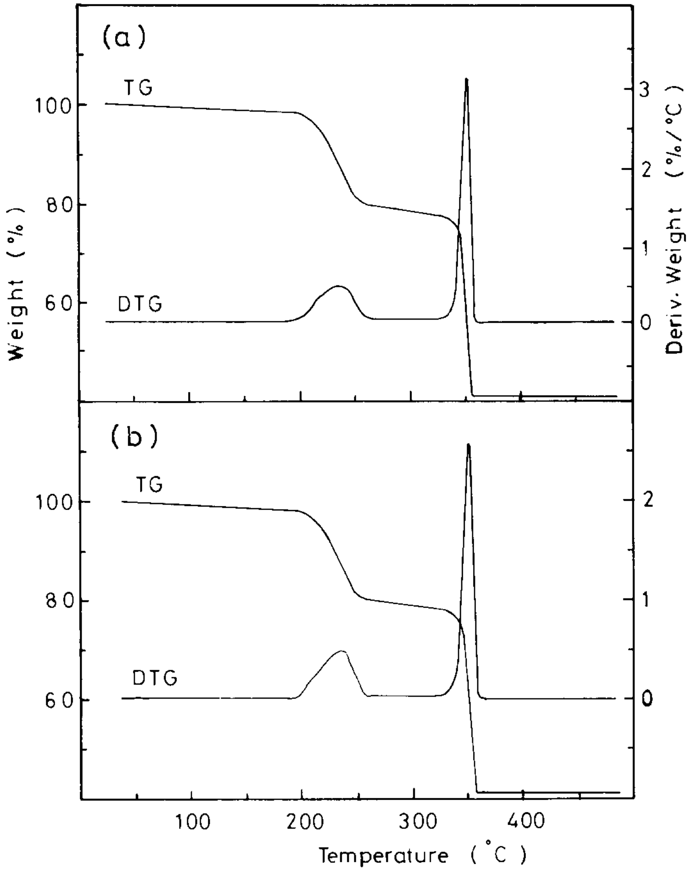

Fig. 1. TG and DTG curves of (a) non-irradiated hydrated nickel oxalate and (b) γ-irradiated hydrated nickel oxalate (γ-ray dose 1 × 10^6 Gy).

molecules. The weight loss observed was 19.5% which is in agreement with the theoretically calculated value (19.7%). Decomposition commences at 350°C. These processes correspond to the following equations:

$$NiC_2O_4 \cdot 2H_2O \xrightarrow{200\text{–}255\,C} NiC_2O_4 + 2H_2O$$

$$NiC_2O_4 + O_2 \xrightarrow{350\,C} NiO + 2CO_2$$

Fig. 2 shows α vs time plots for the isothermal decomposition at 345°C for samples (II–V) of irradiated nickel oxalate, where α is the fraction decomposed at time *t*, together with comparative data for the non-irradiated salt. The results show that the characteristic shape of the α vs *t* decomposition curves was not detectably

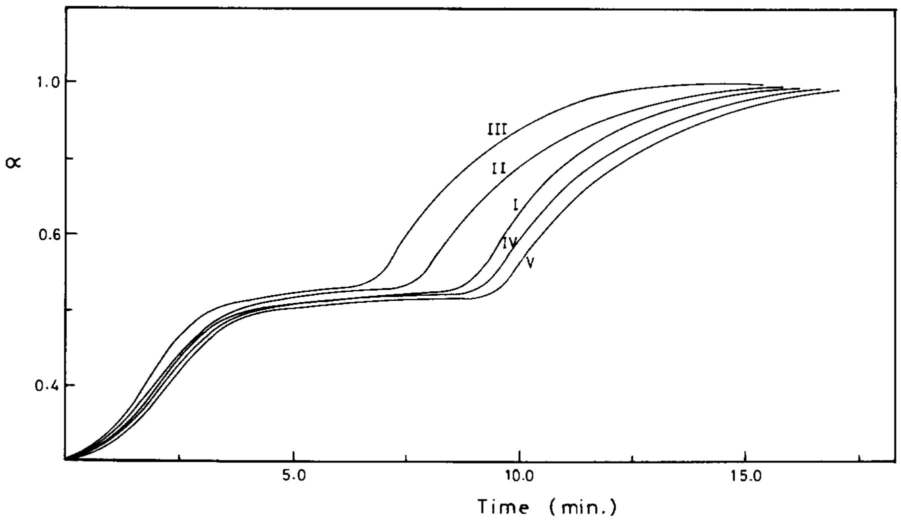

Fig. 2. Fractional decomposition vs. time for the isothermal decomposition at 345°C of non-irradiated hydrated nickel oxalate (I) and γ-irradiated nickel oxalate with γ-ray dose 1×10^3 Gy (II), 1×10^4 Gy (III), 1×10^5 Gy (IV) and 1×10^6 Gy (V).

changed, i.e. the decomposition curves remain almost sigmoid over the entire dose investigated.

The results plotted in Fig. 2 show also that the induction periods of the γ-irradiated samples at the given decomposition temperature do not appear to be systematically reduced by the γ-ray dose. For relatively low irradiated samples (II and III) with total γ-ray dose 1×10^3 and 1×10^6 Gy, respectively, the induction period appears to be shortened with increasing γ-ray dose, ϕ, whilst for the other highly irradiated samples (IV and V) with total γ-ray dose 1×10^5 and 1×10^6 Gy, respectively, the induction period was lengthened with an increase in the γ-ray dose, ϕ, absorbed.

The electrical conductivity of sample (I) and of pre-irradiated samples (III and V) of nickel oxalate have been measured during their thermal decomposition. The variations of $\log \sigma$ with $1/T$, where σ is the electrical conductivity, in the temperature range $30° < t < 400°$C under air atmosphere are shown in Fig. 3, curves a, b and c, respectively. From these curves some trends and conclusions can be drawn as follows:

(1) In region (A) there is a continuous decrease in the electrical conductivity with increasing temperature; this reaches a minimum in the temperature range 200–240°C.

(2) On increasing the temperature, an increase in electrical conductivity was observed; this reaches a maximum in the temperature range 340–360°C region (B).

(3) Regions (A) and (B) shifted to lower temperatures with increasing irradiation dosages.

(4) In the decomposition region (C), there is a decrease in the conductance of all samples under investigation. The decomposition of low irradiated sample (III)

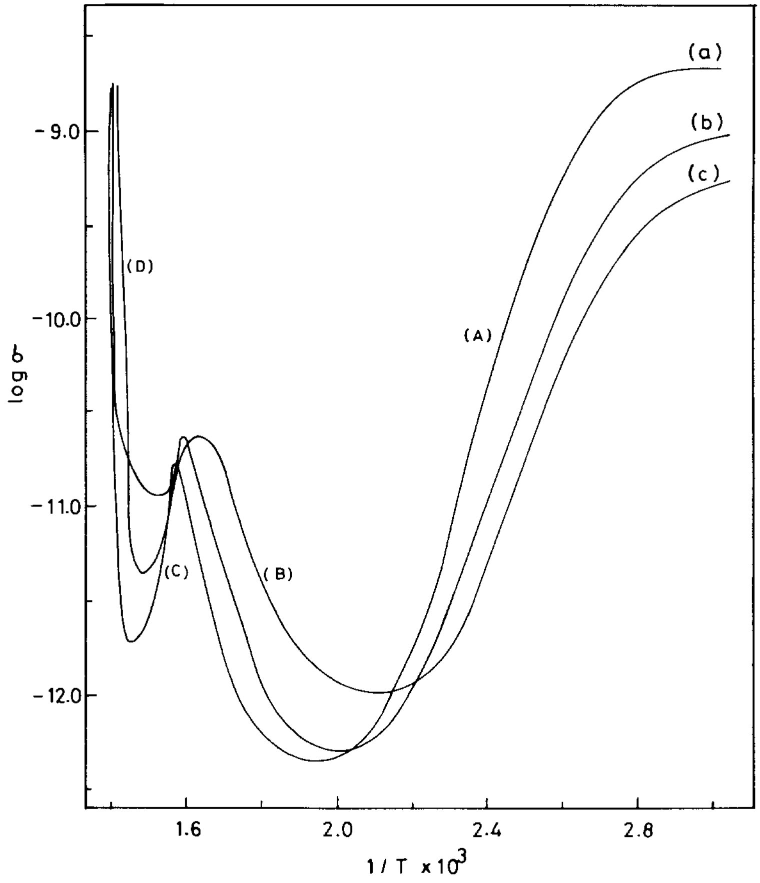

Fig. 3. Variation of log σ with $1/T$ for non-irradiated hydrated nickel oxalate (a) and γ-irradiated nickel oxalate with γ-ray dose 1×10^4 Gy (b) and 1×10^6 Gy (c) during their thermal decomposition in air.

was observed at a lower temperature ($\simeq 375$°C) and the version sample at higher temperature ($\simeq 415$°C).

4. Discussion

The principal conclusion reached from the results plotted in Fig. 2 is that the induction period does not appear to be reduced systematically with γ-ray dose until $\phi = 1 \times 10^6$ Gy. This result accords well with the pattern of kinetic behaviour qualitatively perceived from Fig. 2. For the relatively low irradiated sample (III), t_i constitutes ca 40% of the time required for complete decomposition ($\alpha = 1.00$). The values of t_i for the two most highly irradiated samples (IV and V) increased systematically with γ-ray dose absorbed and the non-irradiated material occupied an intermediate position. This is entirely consistent with the view that at low dosages γ-irradiation generates prenucleation imperfections that exhibit identical reactivity with the sites of onset of reaction in non-irradiated salt. However, at high dosages high radiation damage in the crystals was obtained [7, 8]. The experimentally obtained results indicated also that linear nucleation growth is not subsequently combined with exponential growth during heating.

Most often, it is assumed that the physical process occurring during the induction period is the formation of new decomposition nuclei or the growth of a fixed number of nuclei from a relatively small initial size to a considerably large size. For the present purpose we identify t_i as the time required for the precursors to nucleus generation to be transformed into fully active growth nuclei to obedience to the Avrami–Erofeev equation which describes the kinetics of the thermal decomposition [3] and also the time required for completeness of the dehydration step.

The change of the induction period with γ-ray dose could be explained according to the following mechanism:

$$\mathrm{NiC_2O_4} \overset{\gamma\text{-ray}}{\rightleftharpoons} \mathrm{NiC_2O_{4-n}}\Box n + n\mathrm{O} \qquad (1)$$

where $\Box$ refers to oxygen vacancy and n is the number of oxygen vacancies. According to this mechanism the number of oxygen vacancies produced in the lattice will increase with an increase in the γ-ray dose absorbed. At low dosages these oxygen vacancies lead to formation of additional sites of potential nucleation and help to shorten the induction period and promotion of decomposition, whilst for high dosages γ-irradiation generates high crystal defects (radiation damage) and formation of unreactive radicals and centres inside the crystals which lead to a decrease in the number of decomposition centres. More extensive irradiation hinders the onset of reaction, this is envisaged as being due to the involvement of a small amount of damage products which advance the transformation of some precursor specialized sites into inactive growth nuclei and the kinetics of propagation and growth of the decomposition centres at high dosages are expected to be changed.

In order to find out if there is any correlation between decomposition reactions and electron transfer reactions we have measured the bulk electrical conductivity of the solid samples of nickel oxalate irradiated with different γ-ray doses together with the conductivity of version sample during their thermal decomposition; the results are plotted in Fig. 3. It is seen that the conductivity of the investigated samples in region (A) decreases with increasing the temperature, behaviour attributed to elimination of molecules of water of crystallisation and rearrangement of the bonds inside the molecules. From the radiation point of view we observed that there is a decrease in conductivity with increasing γ-ray dose, attributed to creation of point defects inside the crystals which act as trapping centres for electrons. In region (B), the conductivity of the investigated nickel oxalate samples increases with increasing the temperature which indicates that the dehydration process is accompanied by an increase in charge carriers. Also, it can be seen that the conductivity of the samples increases with increasing γ-ray dose. This behaviour may be attributed to the formation of impurity centres of charge different from that of the corresponding ion in the host lattice. These impurity centres act as donor levels in the crystals, giving rise to an increase in the electron depth and hence to an increase in conductivity. The decrease in the conductivity values on increasing the temperature as shown in region (C) is attributed to the decomposition of the nickel oxalate to nickel oxide. In this region, we observed that the relatively low irradiated sample (III) decomposed at a lower temperature than the highly irradiated sample (V); this was attributed to the formation of additional sites of nucleation and growth (reactive centres), as we mentioned above, which leads to an increase of electrical conductivity.

Electrical conductivity measurements give a good indication of the number of free charge carriers, the number and energy distribution of electron trapping sites, the depth of traps and the ability of free charge carriers to transfer energy to the surrounding molecules. If the decomposition is controlled by electron-transfer reactions, then it is expected that the decomposition reactions will depend on the measured electrical conductivity and we would expect that the conductivity of the highly irradiated sample (V) starts to increase at higher temperature than those of the non-irradiated sample and the relatively low irradiated sample (III). It is noticed that the electrical conductivities of the samples under investigation lie in the semiconductor range and hence it must be expected that electron-transfer reactions are of relatively little importance and that atomic displacement (Eq. (1)) and diffusion in the crystal are the main processes which control the decomposition process.

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