

Kinetics of the thermal decomposition of γ -irradiated cobaltous acetate

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Abstract

Kinetics of the thermal decomposition of un-irradiated (pristine) and pre- γ -irradiated dehydrated cobaltous acetate was studied within the temperature range (538–563 K) and in air using isothermal and dynamics thermogravimetric techniques. The data were analyzed using various solid state reaction models. Integral method using Coat–Redfon equation was applied in dynamic data analysis. The results showed that the kinetic of isothermal decomposition for acceleratory stage was governed by diffusion-controlled process while in non-isothermal (dynamic) decomposition the kinetic was controlled by phase boundary process. The activation energies for pristine and pre-irradiated samples were calculated and the results of the isothermal and dynamic decomposition integral methods were compared and discussed. The change in texture and crystal structure of the investigated cobaltous acetate by γ -irradiation was studied using scanning electron microscopy and X-ray diffraction technique. Thermodynamic values of the main decomposition process were calculated and evaluated. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal decomposition of solids is an important field of solid state chemistry with wide technical applications [1]. Pre exposure to ionizing radiation (γ -ray or UV light) was found to accelerate the isothermal decomposition of solids. However, details of the kinetics were not reported [2]. Previous work on the thermal decomposition of metal acetates indicated that the isothermal decomposition kinetics could be effected markedly by prior exposure to ionizing radiation [3]. In general the effects with increasing dose are a shortening of the induction period followed by an

overall decrease in time required to complete the reaction [4]. Metal acetates represent an important class of the compounds with wide technical and biological applications.

In the present investigation, the kinetics of the thermal decomposition of dehydrated cobaltous acetate before and after γ -irradiation was studied by isothermal and dynamic thermogravimetry.

2. Experimental

Cobaltous acetate tetrahydrate was obtained commercially (BDH, UK) and used without further purification. The sample used for investigation was dried at 200°C in a muffle furnace to ensure complete dehydration.

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The decomposition of cobaltous acetate in air yields Co_3O_4 and some volatile products and within experimental error the process eventually goes to completion [5]. The investigated sample weights were in the range of 100 mg. The decomposition was followed in air using isothermal and dynamic thermogravimetric techniques in the temperature range (538–563 K) using Netzsch STA 429, thermal analyzer (Germany). For isothermal measurement the heating rate was (5°C/min). Under non-isothermal conditions three different heating rates 2, 5 and 10°C/min were applied.

For irradiation, samples were encapsulated under vacuum in glass vials and were exposed to successively increasing doses of radiation at constant intensity using Co-60 γ -ray cell 220 (Nordion INT-INC, Intario, Canada) at a dose rate of 10^4 Gy/h. The source was calibrated against 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 coefficient for the sample and the dosimeter solution [6].

3. Results and discussion

3.1. Isothermal decomposition

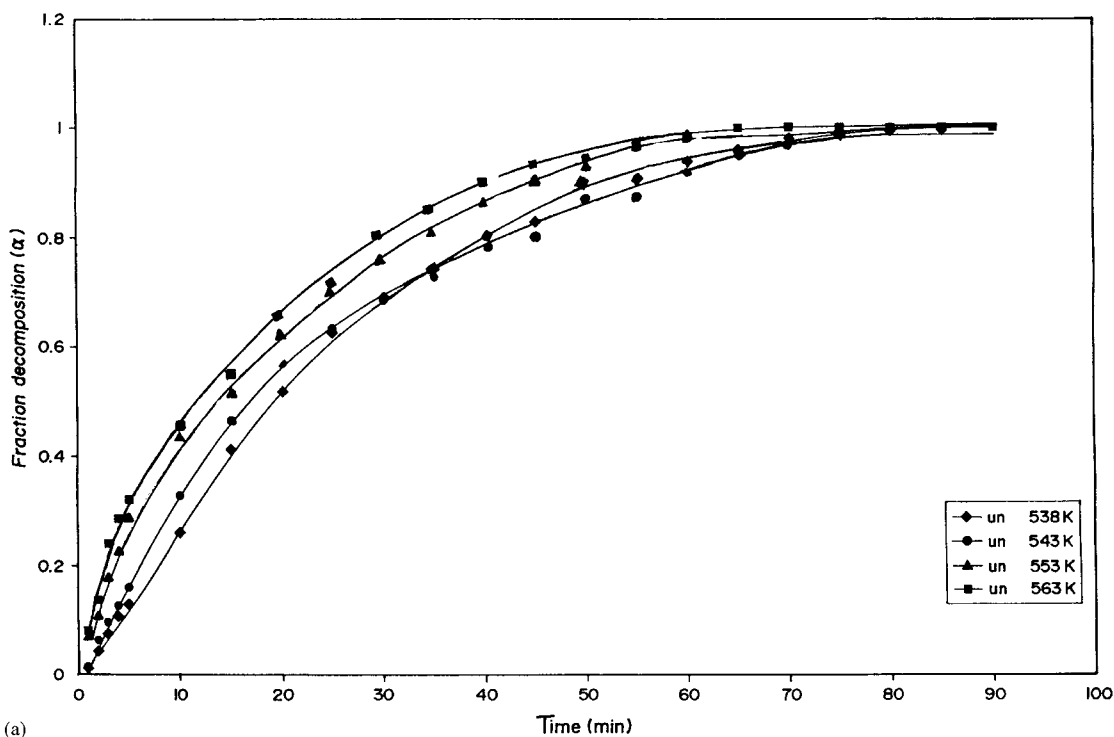
Fig. 1a and b shows α - t curves of the isothermal decomposition of un-irradiated and pre- γ -irradiated cobaltous acetate (total dose 6.07×10^6 Gy) at four different decomposition temperatures (538, 543, 553 and 563 K), where α is the fraction decomposed at decomposition time t . The curves show an increase in the fraction decomposed α with an increase in the

decomposition time up to a maximum value (α_{max}) depending on the temperature investigated. In general the isothermal decomposition of both un-irradiated and pre- γ -irradiated material produces sigmoid α versus t curves in the range (538–563 K). Shortening of the induction period and acceleration in time required to reach α_{max} at a given temperature was observed markedly in the decomposition γ -irradiated sample of cobaltous acetate. This behaviour could be attributed to the formation of additional nucleation sites. The additional nucleation centers enhance all of the decomposition stages (induction period, acceleratory region and decay stage).

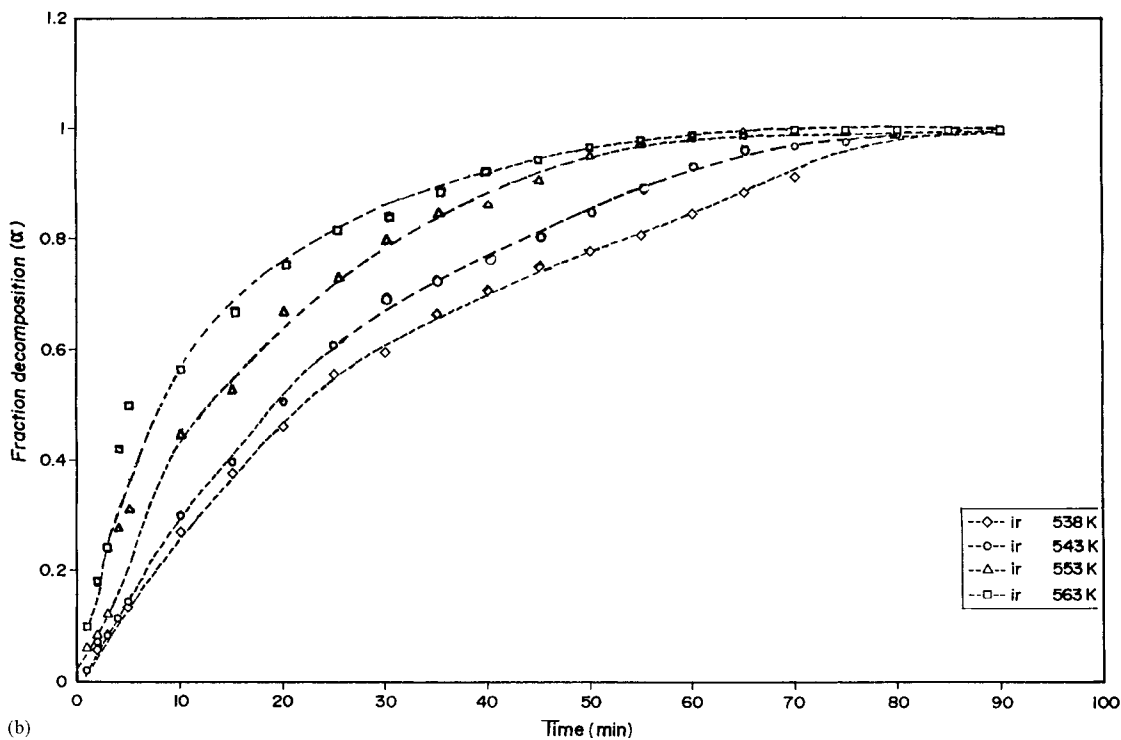
The isothermal α/t data for the main process, i.e. the acceleratory region of cobaltous acetate decomposition ($0.13 < \alpha < 0.968$) was analyzed according to the various kinetic mechanisms and cited in Table 1 [4]. Under isothermal conditions, the rate constant k , is independent of the reaction time and so $kt = g(\alpha)$. A plot of $g(\alpha)$ versus t should give a straight line if the correct form of $g(\alpha)$ versus t is reached. The function $g(\alpha)$ depends on the mechanism controlling the reaction, the size and shape of the reacting particles [7]. In a diffusion-controlled reaction: D is the function for a one-dimensional diffusion process governed by a parabolic law, with constant diffusion coefficient; D_2 is for a two-dimensional diffusion-controlled process into a cylinder; D_3 is Jander's equation for diffusion-controlled reaction in a sphere and D_4 is a function for a diffusion-controlled reaction starting on the exterior of a spherical particle. In phase-boundary-controlled reactions, the reaction is controlled by movement of an interface at constant velocity and nucleation occurs virtually instantaneously, then, the equation relating α and t is the R_2 function for a

Table 1
Mechanistic equation examined in this work

Equation	Function	Function
One-dimensional diffusion	α^2	D_1
Two-dimensional diffusion	$(1 - \alpha) \ln(1 - \alpha) + \alpha$	D_2
Jander equation, three-dimensional diffusion	$[1 - (1 - \alpha)^{1/3}]^2$	D_3
Ginstling-Brounshtein equation, three-dimensional diffusion	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$	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 kinetic	$\ln(1 - \alpha)$	F_1
Avrami equation, random nucleation	$-\ln(1 - \alpha)^{1/2}$	A_2
Erofe'ev equation, random nucleation	$-\ln(1 - \alpha)^{1/3}$	A_3



(a)



(b)

Fig. 1. Fractional decomposition α vs. t curves for the isothermal decomposition of cobaltous acetate, (a) un-irradiated and (b) γ -irradiated.

circular disc reacting from the edge inward and the function R_3 for a sphere reacting from the surface inward. If the solid-state reaction follows first-order kinetic (F_1 function) then the rate-determining step is the nucleation process and there is an equal probability of nucleation at each active site. In phase-boundary reaction, it is assumed that the nucleation step occurs instantaneously, so that the surface of each particle is covered with a layer of the product. Nucleation of the reactant, however, may be a random process, not followed by rapid surface growth. As the nuclei grow larger they must eventually impinge on one another, so that growth ceases where they touch. This process has been considered by Avrami and Erofe'ev, who have given the function A_2 and A_3 , respectively [8]. Our results show that isothermal data of cobaltous acetate samples obey two-dimensional diffusion (D_2) model (Fig. 2). Kinetic energy of the main decomposition processes, i.e. the acceleratory region for pristine and pre-irradiated material was calculated by applying the least square method using Arrhenius equation. The results are tabulated in Table 2.

3.2. Non-isothermal decomposition

Non-isothermal decomposition of un-irradiated and pre- γ -irradiated cobaltous acetate sample is shown in (Fig. 3). The rate is set to a constant value β and the function $g(\alpha)$ is given by Doyle's equation [9]:

$$g(\alpha) = \left(\frac{A}{B}\right) \int_0^T \exp\left[\frac{-E}{RT}\right] dT = \frac{AE}{R\beta} p(x)$$

The fraction $p(x)$ has been defined as

$$p(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-\mu} d\mu}{\mu}$$

Where $\mu = E/RT$ and x is the corresponding value of μ at which a fraction α of material has decomposed. In the Coats–Redfon method, the function $g(\alpha)$ is approximated to the form

$$\frac{\log g(\alpha)}{T^2} = \log \frac{AR}{E\beta} - \frac{E}{2.3RT}$$

Accordingly $\log(g(\alpha)/T^2)$ is to be calculated and plotted against $1/T$ for all possible mechanisms and

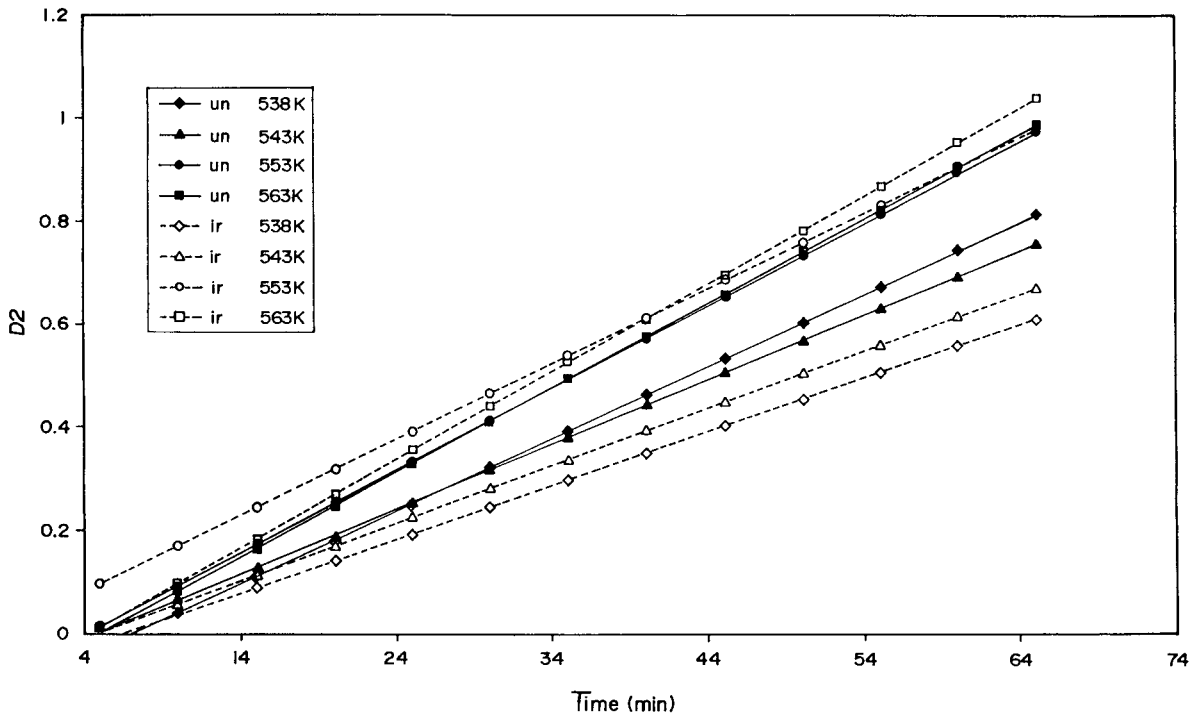


Fig. 2. Isothermal decomposition reaction for cobaltous acetate according to two-dimensional diffusion.

Table 2
Kinetic parameters of the isothermal and non-isothermal decomposition of cobaltous acetate

Kinetic parameters	Isothermal technique	(Non-isothermal technique)		
		Heating rate ($^{\circ}\text{C}/\text{min}$)		
		2	5	10
E_a (kJ/mol) un-irradiated	49.78	72.27	78.81	84.6
γ -irradiated (6.07×10^6 Gy)	65.48	76.27	84.81	95.12
$\ln A$ (min^{-1}) un-irradiated	1.77	–	–	–
γ -irradiated (6.07×10^6 Gy)	7.16	–	–	–

the best straight line determines the operating mechanism. E_a and A values are calculated from the slope and intercept [10]. Fig. 4 shows the results of data analysis performed according to Coats–Redfern equation. The results indicate that the best fit of dynamic data of cobaltous acetate was achieved using two-dimensional phase-boundary reaction model (R_2). The calculated kinetic parameters using dynamic isothermal techniques are tabulated in Table 2. It should be mentioned

that in non-isothermal (dynamic) technique the calculated E_a values for γ -irradiated salt show relatively higher values compared with the values calculated for un-irradiated (pristine) salt. This difference in activation energy values was significantly observed in the isothermal measurements. Creation of trapped holes, electron and radicals in the host lattice of γ -irradiated cobaltous acetate retard the decomposition process and reduce the number of reactive sites available

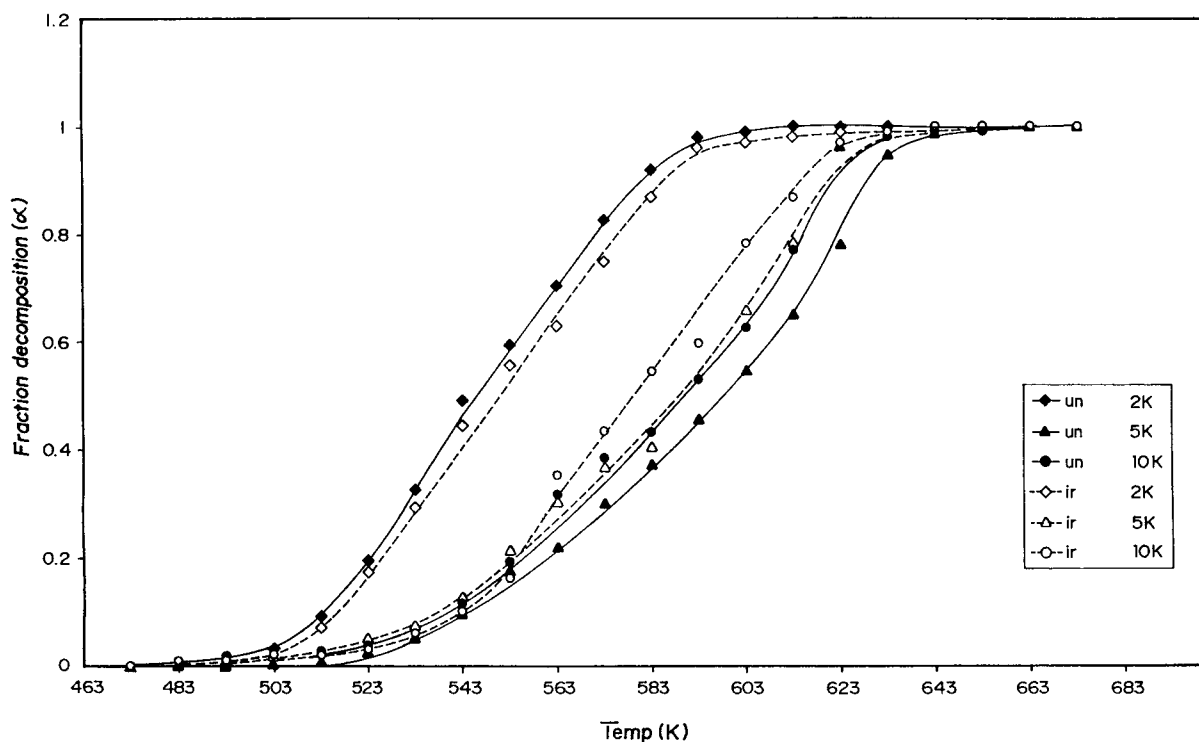


Fig. 3. Dynamic measurements for cobaltous acetate thermal decomposition.

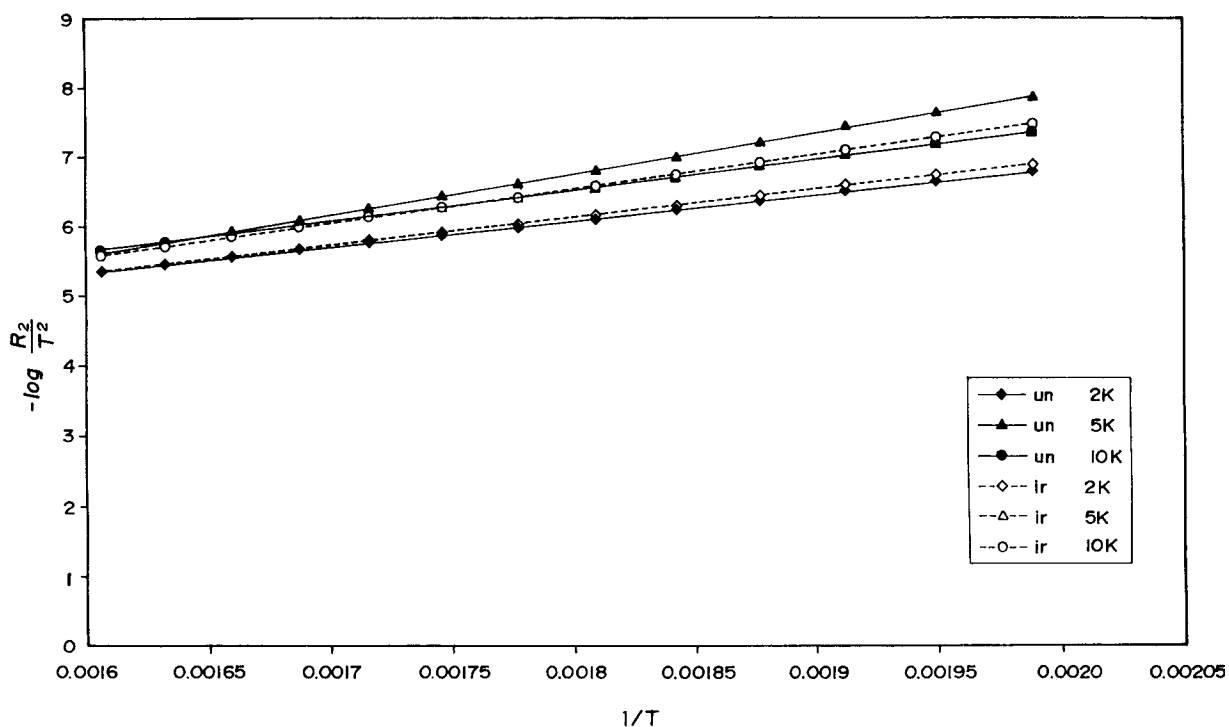


Fig. 4. Isothermal decomposition of cobaltous acetate according to the two-dimensional phase-boundary reaction.

for the decomposition. The changes in the textural and morphological structure of the investigated samples before and after γ -irradiation were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis and the results are presented in Fig. 5a and b. The crystallinity changes by γ -irradiation was also tested using X-ray diffraction powder pattern (XRD) technique as shown in Fig. 6a and b. The results of kinetic parameter calculations, SEM and XRD measurements for pristine and pre-irradiated cobaltous acetate showed that the irradiated sample up to $(6.07 \times 10^6 \text{ Gy})$ γ -ray dose has largely maintained its crystallographic identity and stability in spite of the relatively high γ -ray dose absorbed by the sample.

Entropy and enthalpy values of the main decomposition process were calculated using the following equation [11]:

$$\ln \frac{k}{T} = \frac{-\Delta H^{\#0}}{RT} + \ln \frac{R}{Nh} + \frac{\Delta S^{\#0}}{R}$$

Where k is the rate constant, R gas constant, T absolute

temperature, N Avogadro's number and h is the Planck constant. Plotting $\ln k/T$ against $1/T$ the slope and intercept give $\Delta H^{\#0}$ and $\Delta S^{\#0}$ respectively. The calculated values are included in Table 3.

4. Role of irradiation

Upon irradiation with ^{60}Co γ -ray, the Compton effect has the largest cross-section in very light elements and diminishes to zero around atomic number 125 [12]. The possibility of displacement of cobalt (atomic weight 58.9) by Compton electrons is very low. Generation additional sites of potential

Table 3
 $\Delta H^{\#0}$ and $\Delta S^{\#0}$ values for isothermal decomposition of cobaltous acetate

Cobaltous acetate	$\Delta S^{\#0}$ kJ/mol K	$\Delta H^{\#0}$ kJ/mol
un-irradiated	-0.251	45.21
γ -irradiated ($6.07 \times 10^6 \text{ Gy}$)	-0.198	60.90

nucleation are produced by γ -ray. These may be crystal defects or reactive radicals that are not necessarily identical with intrinsic nucleation sites but are of comparable reactivity and or more probably evolve by a similar sequence of steps into growth nuclei. More

extensive irradiation advances the onset of decomposition; this is envisaged as being due to the involvement of a small amount of decomposition products, which advance the transformation of all precursor-specialized sites into active growth nuclei. The

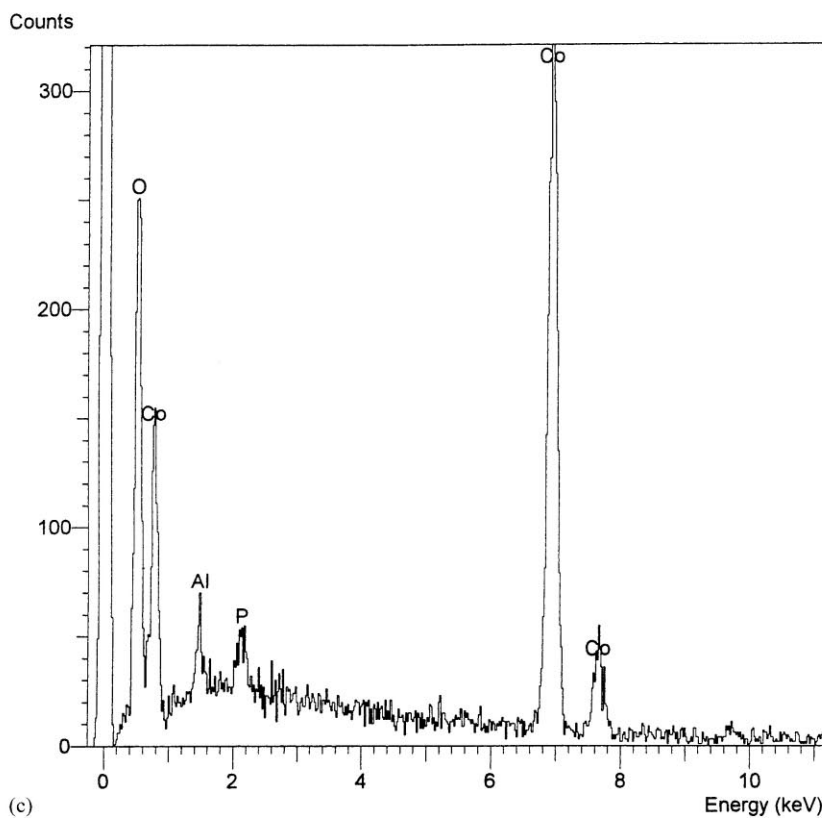
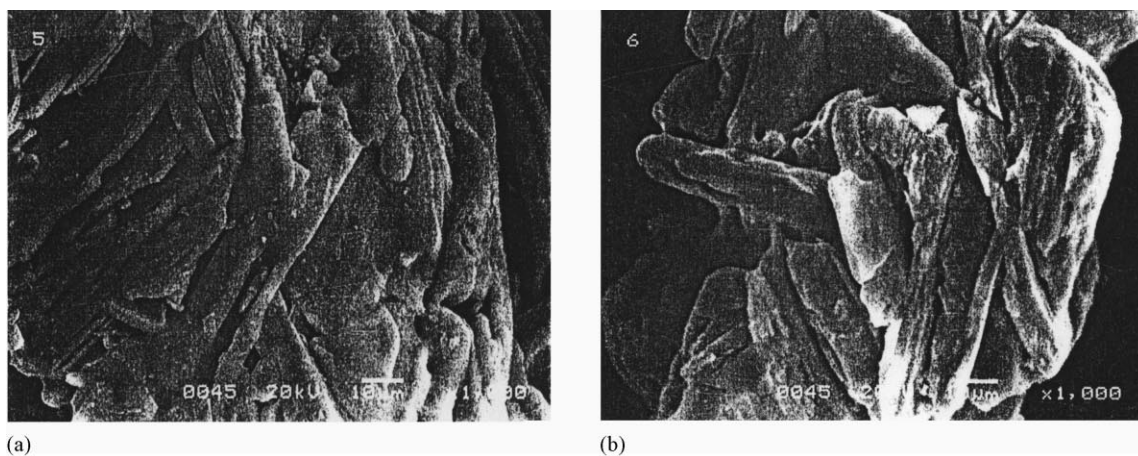


Fig. 5. SEM and EDX for cobaltous acetate (a) un-irradiated and (b) γ -irradiated (6.07×10^6 Gy).

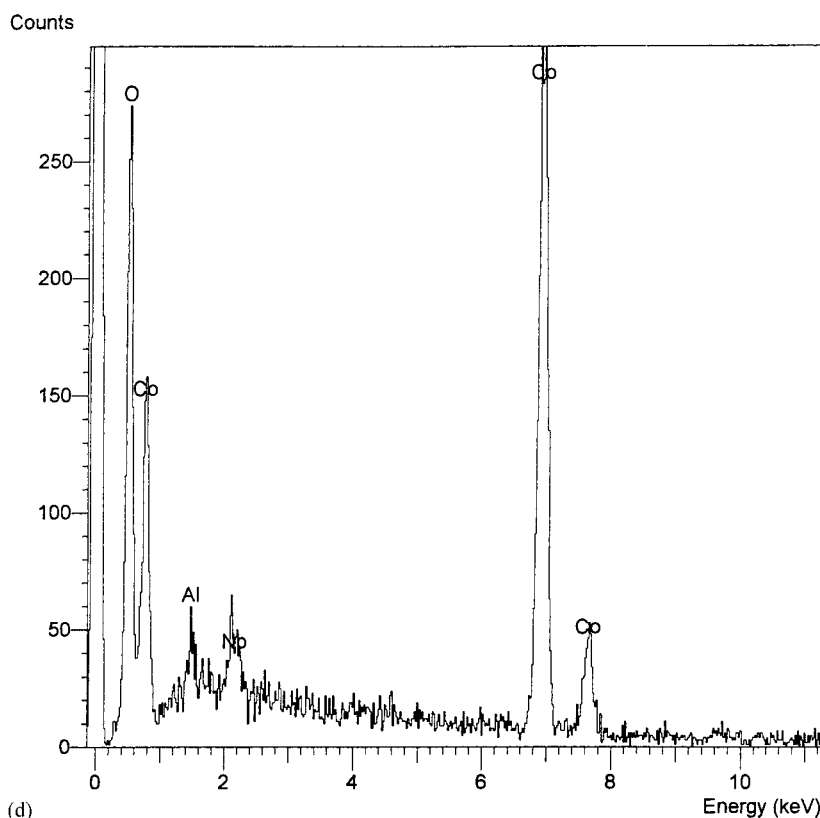


Fig. 5. (Continued).

kinetics of growth of all nuclei are identical. The observed increase in reaction rate for γ -irradiated samples is ascribed to a direct relationship between the extent of salt γ -irradiation and number of nuclei developed on subsequent decomposition [13].

5. Conclusion

In the present investigation γ -irradiation effects on the thermal decomposition of dehydrated cobaltous acetate was studied in air using both isothermal and dynamic techniques. Different theories of solid state reactions and models were applied to choose the best model or solid state reaction, which control the decomposition of cobaltous acetate. The effects of γ -irradiation on the decomposition process were studied by irradiating the investigated cobaltous acetate sample to different γ -ray doses ranging from

1×10^4 – 6.07×10^6 Gy. The kinetic parameters of the decomposition before and after γ -irradiation using isothermal and non-isothermal techniques were calculated and evaluated. The general conclusion of the present study could be summarized in the following observations:

1. Under isothermal condition the decomposition of both pristine and pre-irradiated dehydrated cobaltous acetate was controlled by diffusion controlled process.
2. Under non-isothermal (dynamic) condition the decomposition of the investigated cobaltous acetate was controlled by phase-boundary model.
3. The kinetic and thermodynamics values of the decomposition process of γ -irradiated cobaltous acetate were higher than the corresponding values calculated for un-irradiated salt with no change in the applied kinetic function $g(\alpha)$. The radiation

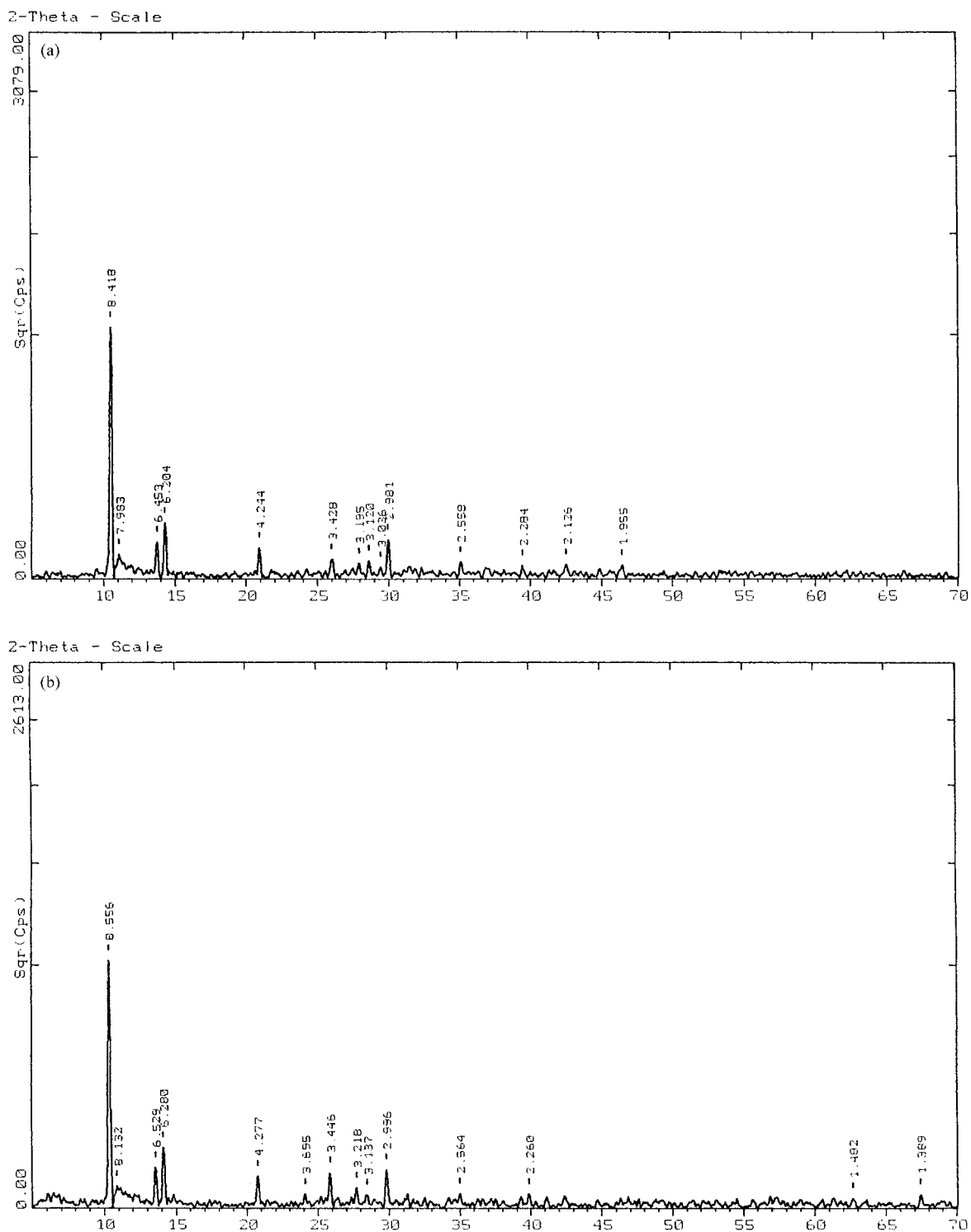


Fig. 6. XRD for cobaltous acetate (a) un-irradiated and (b) γ -irradiated (6.07×10^6 Gy).

retard the thermal process and inhibit the rate of decomposition due to the formation of long lived trapped radicals and holes in the host lattice. The kinetic function used $g(\alpha)$ for isothermal decomposition of un-irradiated and γ -irradiated cobaltous acetate was however different from the function used for dynamic decomposition. The general disadvantage of dynamic thermal analysis is the fact that in many cases more than one function from $g(\alpha)$ fits the experimental results. The selection of a proper model is then practically impossible leading to inability to estimate the real kinetic parameters (E , A). Recently the view that the combined use of isothermal and non-isothermal methods for kinetic determination is the proper solution has been more and more frequently expressed.

4. The results of the SEM, EDX and XRD measurements indicated that the crystal structure of the material was not significantly alternated by exposure to γ -ray up to 6.07×10^6 Gy. The shortening of the induction period and acceleration of the decomposition process, i.e. the decrease in time required to complete the reaction in case of the pre-irradiated material were attributed to the formation of additional nucleation sites and reactive centers.

5. The following mechanism could be suggested to explain the decomposition process and the formation of gaseous products. The main step in the suggested mechanism is the rupture of C–O and C–C bonds followed by electronic rearrangement.

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