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Isothermal decomposition of γ-irradiated uranyl acetate

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Abstract

Isothermal decomposition of un-irradiated and pre-γ-irradiated dehydrated uranyl acetate has been investigated at different temperatures between 573 and 593 K. Irradiation enhances the rate of decomposition without modification of the mechanism of thermal decomposition which has been shown to proceed by a nucleation and growth mechanism, both for un-irradiated and pre-γ-irradiated samples of uranyl acetate. The enhancement of the decomposition was found to increase with an increase in the γ-ray dose applied to the sample and may be attributed to an increase in the number of point defects and formation of additional nucleation centers generated in the host lattice. © 1998 Elsevier Science B.V.

Keywords: Isothermal decomposition; γ-irradiated; Uranyl acetate

1. Introduction

Thermal decomposition of solids is an important field of solid-state chemistry with wide technical applications [1]. Many recent studies on the isothermal decomposition of inorganic solids have included measurements on samples that were exposed to radiation prior to heating. These measurements were performed for one or both of the following reasons. First, the material may have been irradiated to investigate one or more features of the decomposition process. Second, it may have been included in a 'radiation damage' study to determine whether radiation can modify one or more properties of the material in a significant way by creating point defects or increasing the number of nucleation forming sites [2]. Thermal decomposition of uranium compounds has not been studied sufficiently, especially in compounds which have been subjected to pre-irradiation [3,4].

In this investigation, the kinetics of the thermal decomposition of dehydrated uranyl acetate before, and after, γ-irradiation have been studied by isothermal thermogravimetry. No previous study of this type has been made for uranyl acetate.

2. Experimental

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

The decomposition of uranyl acetate in air yields U_3O_8 and volatile products and, within experimental error, eventually goes to completion [5]. The decomposition was followed using isothermal thermogravimetric technique in the 573–593 K range, using Netzsch STA 429 (Germany) thermal analyzer. The heating rate was (5°C/min). The sample weights were in the around 200 mg. For the irradiation, samples

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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

Thermal decomposition of un-irradiated and pre-irradiated sample of uranyl acetate with total γ-ray dose of 6.07×10^6 Gy was studied in the 573–593 K range. The general form is sigmoidal for both, un-irradiated and pre-irradiated samples with a gradual approach to the acceleratory region (see Fig. 1). The α-time curves for pre-irradiated sample showed that the time required to reach the maximum rate proceeds faster, the value of α at the point of inflection, i.e. $\alpha_{\max}$ is reduced and the induction period shortened by irradiation. The observed promotion of decomposition by pre-irradiation is ascribed to the generation of additional sites of potential nucleation as crystal defects, or long-lived reactive radicals, may be of different kinds compared to intrinsic nucleation sites but are of comparable activity. Morphological and textural investigations of the sample before, and after, γ-irradiation are presented in (Fig. 2). The figure clearly shows the nucleation growth in the pre-irradiated sample of uranyl acetate and formation of additional sites of nucleation as a result of the decomposition. The isothermal α/t data for the main

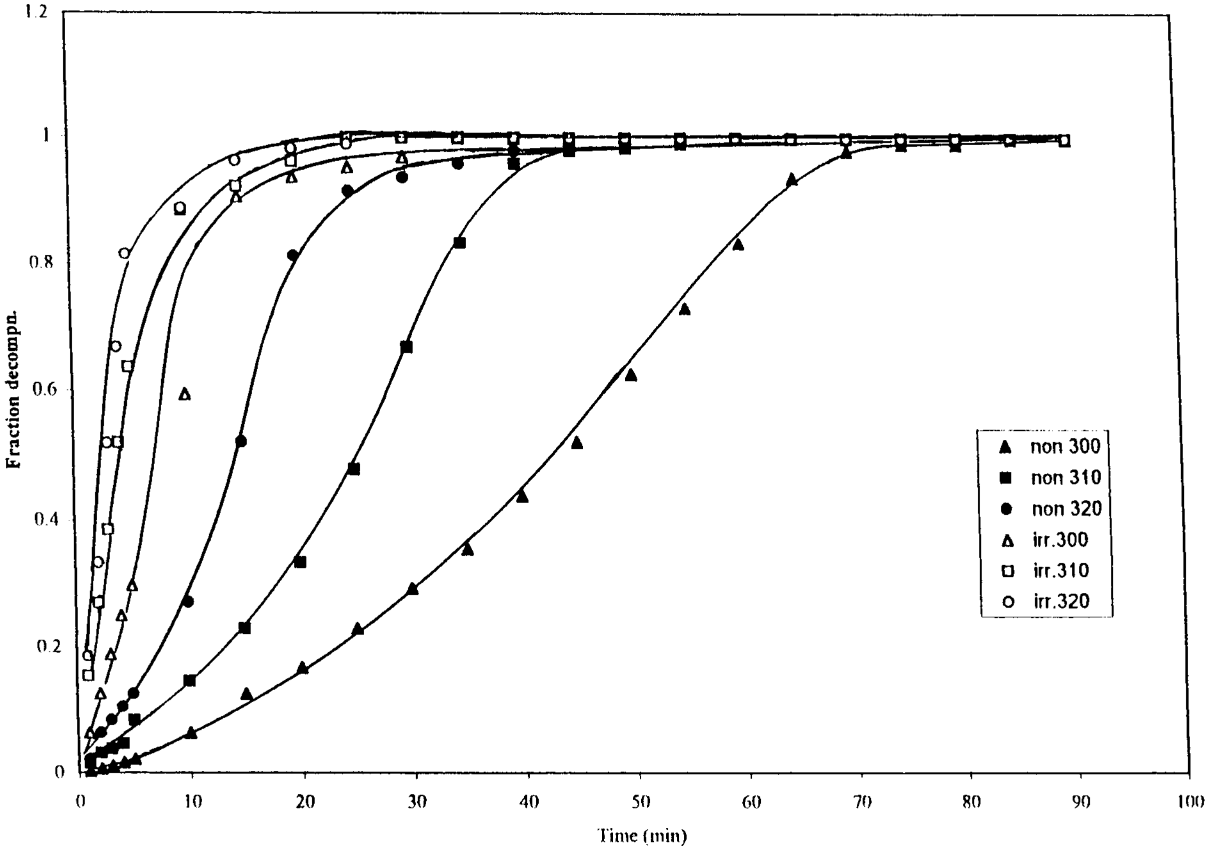

Fig. 1. Fractional decomposition α vs. time curves for the isothermal decomposition of uranyl acetate.

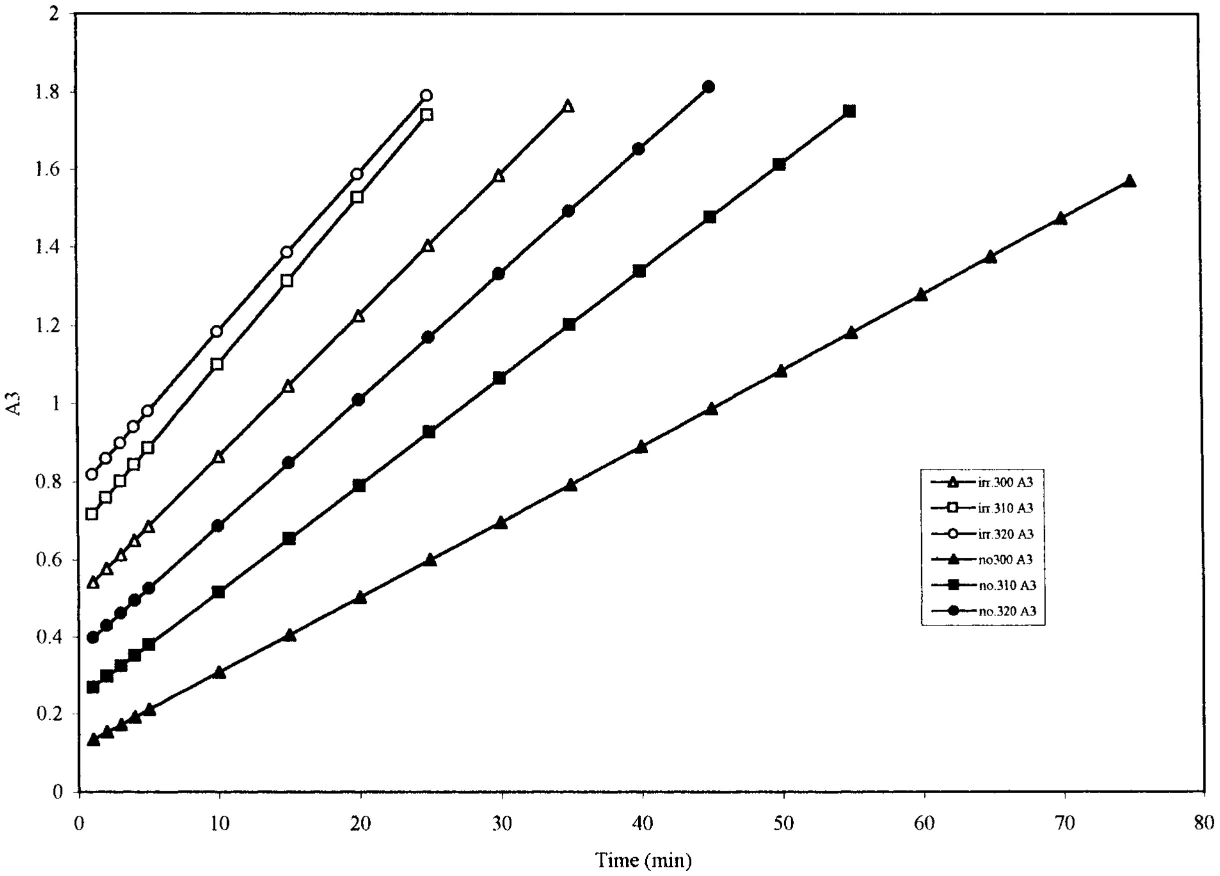

Fig. 2. Isothermal decomposition curves for uranyl acetate.

process, i.e. the acceleratory region of dehydrated uranyl acetate decomposition ($0.06<\alpha<0.95$) were analyzed according to the various kinetic mechanisms cited in Table 1 [7]. Under isothermal conditions, the rate constant K, is independent of reaction time and, hence, $Kt=g\ (\alpha)$. A plot of $g(\alpha)$ vs. t should give a straight line if the correct form of $g(\alpha)$ vs. t is reached. The function $g(\alpha)$ depends on the mechanism controlling the reaction and on the size and shape of the reacting particles [8]. 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 for a two-dimensional diffusion-controlled process into a cylinder; D_3 is the Jander equation for a diffusion-controlled reaction in a sphere and D_4 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 a constant velocity and nucleation occurs virtually instantaneously, then the equation relating α and 7 is the R_2 function for a 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 the first-order kinetics (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 reactions, 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

Table 1
Mechanistic equation examined in this work

Equation	$g(\propto)$	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	$[1-\ln(1-\alpha)^{1/2}]$	R_2
Three-dimensional phase-boundary reaction	$[1-\ln(1-\alpha)^{1/3}]$	R_3
First-order kinetic	$[-\ln(1-\alpha)]$	F_1
Random nucleation: Avrami equation	$[-\ln(1-\alpha)^{1/2}]$	A_1
Random nucleation: Erofe'ev equation	$[\ln(1-\alpha)]^{1/3}$	A_2

they touch. This process has been considered by Avrami and Erofe'ev, who have given the functions A_2 and A_3, respectively. Our results show that both sets of data for the un-irradiated and pre-γ-irradiated samples obey the Avrami and Erofe'ev equation, i.e. random nucleation followed by growth of three-dimensional nuclei, (Fig. 2). For the γ-irradiated material, some radiolysis of uranyl acetate occurs. The gas produced is evolved, in part, into the capsule during irradiation and, in part, on first heating to the decomposition temperature. This may create additional numbers of potential nucleation forming sites, help to shorten the induction period and accelerate the decomposition process. The reaction begins at the surface from a number of potential nuclei, which become active by thermal fluctuation. Growth then proceeds three-dimensionally into the crystalline, probably along preferred planes. Irradiation appears to increase the number of potential nuclei, but does not enhance the growth rate. The activation energy of the main decomposition process, i.e. the acceleratory region was calculated from least-squares method using Arrhenius equation as shown in (Fig. 3), and the values were found to be E=71.15 and E=26.31 kJ mol^{-1} for the un-irradiated and pre-irradiated sample, respectively. It can be seen that γ-irradiation brings about a significant change in the activation energy values of the decomposition reaction. The radiolytic products formed in case of pre-irradiated sample allow the decomposition to proceeds easily, thereby lowering the activation energy.

Further studies concerning application of α-irradiated uranyl acetate as catalyst are in progress in our laboratory.

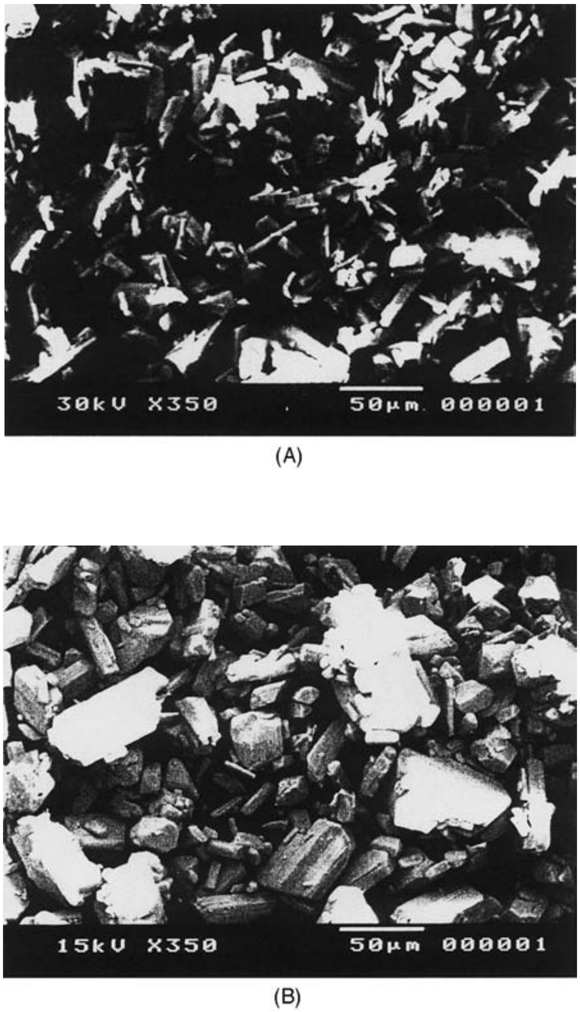

Fig. 3. SEM for (a) un-irradiated and (b) pre-irradiated uranyl acetate.

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