KINETICS OF ISOTHERMAL ANNEALING OF γ-IRRADIATED EUTECTIC MIXTURE OF $NaNO_3$-KNO_3

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A considerable amount of work has been reported on isothermal annealing of pure alkali and alkaline earth metal nitrates. In the present work, initially, the eutectic of $NaNO_3$-KNO_3 was prepared by mixing $NaNO_3$ (45%) and KNO_3 (55%) fused at 225 ^{0}C and cooled naturally. The samples of a eutectic of $NaNO_3$-KNO_3 were irradiated in ^{60}Co – gamma source. The radiation decomposition of the eutectic mixture takes place. Present work mainly deals with the study of isothermal annealing of radiation damage in a eutectic mixture of $NaNO_3$-KNO_3. This data has been analyzed by using conventional kinetics and the Waite model. Results of annealing show that a significant fraction of annealing obeys second order kinetics except in the initial short period. The energies of activation are calculated by two methods and are found to agree.

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INTRODUCTION

A considerable amount of research results has been reported on isothermal annealing of pure alkali and alkaline earth metal nitrates,[1-7] however, only limited data are available on the annealing of eutectics.

It is well established that defect concentration in solids increases after irradiation as compared to the thermal equilibrium level. These defects are responsible for different property changes in solids. These defects react to reduce the free energy of the system. When the temperature of irradiated solids is raised sufficiently, the property reverts to its original value. This general process of decay of property-change by temperature is known as annealing.

Several workers carried out the experiments on the thermal annealing process in alkali and alkaline earth nitrates.[8-10]. The kinetic analysis showed that the order of reaction varied concerning the nature of nitrates. Bedekar et. al[2] reported 100 % annealing of damage in ammonium nitrate crystals and about 35 % annealing to take place in KNO_3-$Sr(NO_3)_2$ eutectic at 200 ^{0}C.

The process of annealing is generally formulated using equations similar to those of chemical kinetics. Various diffusion-controlled models have been proposed such as Fletcher-Brown model and Waite model[11,12] to explain the characteristics of annealing kinetics. The energy of activation for the annealing reaction is computed. An appropriate mechanism of annealing consistent with the observed results is proposed.

EXPERIMENTAL

The eutectic mixture of $NaNO_3$ (45 %)-KNO_3(55 %) was fused at 225^0 C and cooled naturally.[13] The irradiation of samples of eutectic was carried out in 2.5 kCi ^{60}Co γ-source at ambient temperature. The results of the radiolytic decomposition of a eutectic mixture of $NaNO_3$-KNO_3 are already reported in terms of $G(NO_2^-)$ values.

After irradiation, the samples of the eutectic mixture of $NaNO_3$-KNO_3 were subjected to isothermal annealing at various temperatures for different time intervals using an electric furnace.

The annealed samples of the eutectic mixture after removal from thermostat or furnace were analyzed to estimate the amount of nitrite [$G(NO_2^-)$] left after annealing by using Shinn's method.[14]

RESULTS AND DISCUSSION

The fraction annealed, ø, after heating for time *t*, is defined by an expression

$$ø = (NO_2^-)_0 - (NO_2^-)_t/(NO_2^-)_0$$

where, $(NO_2^-)_0$ and $(NO_2^-)_t$ are the concentrations expressed in a number of NO_2^- molecules per gram of the eutectic mixture present initially and after time *t*, respectively.

A plot of fraction annealed ø, as a function of annealing time at various temperatures, are shown in Fig. 1. The examination of the annealing curves obtained reveals that there is an abrupt recovery of damage in the initial period of annealing followed by a slow rate of annealing at every temperature.

For example, the extent of annealing in a eutectic mixture of $NaNO_3$-KNO_3 at 200 ^{0}C is found to be 45 % in 10 h, while only 10 % of annealing takes place during the next 20 h.

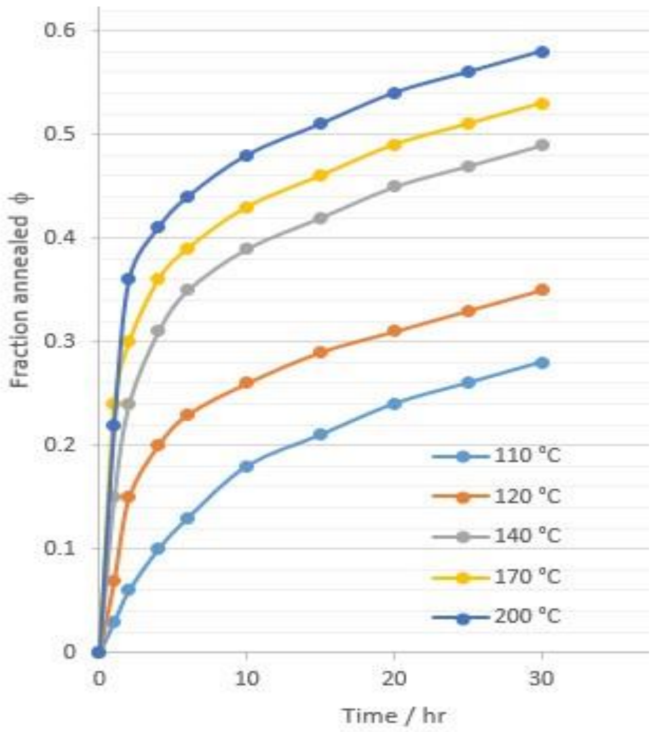

Figure 1. A plot of fraction annealed ø, as a function of annealing time at various temperatures

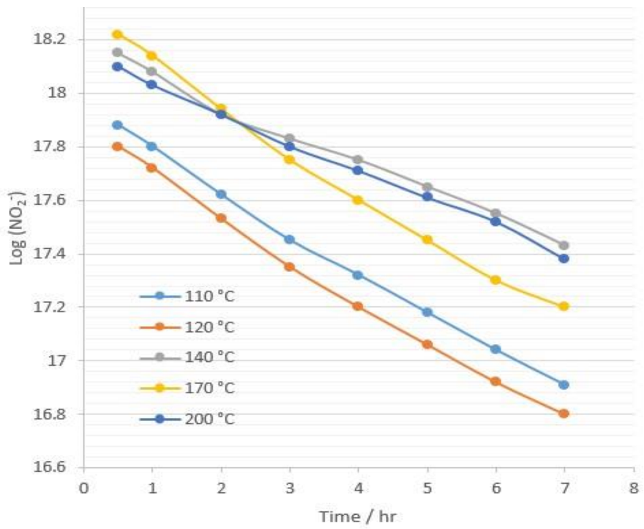

Figure 2. First order plots for annealing of nitrite in γ–irradiated $NaNO_3$-KNO_3 eutectic.

Analysis of data of annealing obtained at various temperatures by conventional kinetics[5] showed that the annealing occurs by a combination of the first and the second order processes. The first order process taking place in the initial stages is attributed to the germinate recombination of fragments in the damaged zone. The first order disappearance of the nitrite is the recovery of closely correlated NO_2^- and O pairs in the form of NO_3^- (Fig. 2).

While, the occurrence of the second order is explained on the basis of a random combination of NO_2^- and O or O_2 fragments which have diffused farther apart in the crystal lattice. (Fig. 3)

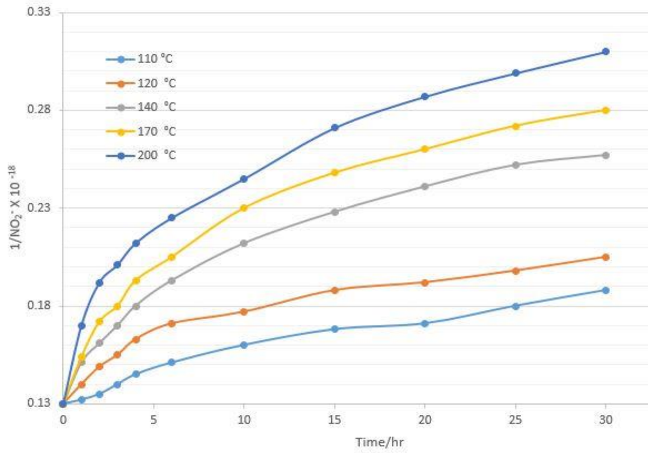

Figure 3. Second order plots for annealing of nitrite in γ–irradiated $NaNO_3$-KNO_3 eutectic.

The energy of activation for the first and the second order processes computed from the Arrhenius plot are found to be 8.0 kJ. mol^{-1} and 14.4 kJ mol^{-1} respectively. The kinetics of annealing is also explored by using the Waite Model which considers the annealing as a diffusion-controlled reaction. This model envisages a spread in the separation of an interstitial from the corresponding vacancy and a random distribution of pairs concerning one another. The resulting expression for short time of annealing is

$$ø = K\{D_0 e^{-E/RT}\}^{1/2} t^{1/2}$$

where,

D_0 is the diffusion coefficient and

E is the energy of activation for diffusion.

The energy of activation of annealing from this is found to be 13.7 kJ mol^{-1} which is in reasonable agreement with the value obtained for the second order process using the conventional method.

CONCLUSIONS

The present investigations revealed that the recovery of damage in irradiated samples of the eutectic mixture of $NaNO_3$-KNO_3 occurs due to thermal reactions as well as reactions accompanying phase transformations in the damaged crystals.

The isothermal annealing process is formed to consist of a fast first-order reaction in addition to a slow predominant second order reaction.

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