# The Effects of the Crystal-structural Transformation on the Chemical Behavior of $^{64}$Cu Recoil Atoms in $\alpha$-Copper Phthalocyanine

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The Stage-II annealing process of $^{64}$Cu recoil atoms in neutron-irradiated $\alpha$-copper phthalocyanine was carefully examined. The isothermal annealing curve above 270°C showed anomalous inflection point. It was found that the Stage-II annealing process of the $\alpha$-crystal consisted of a "normal" monotonous annealing process and a "delayed" process caused by the crystal-structural transformation. The results of a kinematic analysis suggested that the fluctuation of the matrix and the change in the crystalographic factors due to the structural transformation play a triggering role in the delayed annealing reaction.

Despite a number of studies of the annealing reaction of $^{64}$Cu recoil atoms in neutron-irradiated copper phthalocyanine,[1–12] the details of the mechanism of the reaction do not appear to have been completely elucidated. Yoshihara and Ebihara[9] found striking effects of the crystal structure on the thermal annealing of the $^{64}$Cu recoil atoms produced by (n, $\gamma$) and ($\gamma$,n) reactions. The recoil atoms in the irradiated $\beta$-copper phthalocyanine were very easily annealed, while those in the $\alpha$-crystal were relatively insensitive. The thermal annealing process could be separated into two stages in both the $\alpha$- and $\beta$-crystals; Stage I below 200°C and Stage II above 250°C.

$\beta$-Copper phthalocyanine is the most stable crystal modification, and its crystal structure has been reported in detail by Robertson.[13] At least two other crystal forms, designated as the $\alpha$- and $\gamma$-form, have been characterized by a study of their X-ray powder diffraction patterns and by infrared or visible spectroscopy.[14–21] The $\alpha$-modification (a metastable crystal) is converted into the $\beta$-form by treating it in various organic suspension media, by sublimating it *in vacuo*, or simply by heating it above 250°C.[22–27]

It is known that the behavior of the recoil atom in solids depends on such crystallographic factors as the surface activities, the grain size, and the concentration of defects.[12,28] These factors will inevitably be affected by the crystal-structural transformation. An investigation of the effect of the crystal-structural transformation on the thermal annealing process can be expected to give further information on the chemical fate of the $^{64}$Cu recoil atoms in neutron-irradiated $\alpha$-copper phthalocyanine, especially for the Stage-II annealing process. This effect has, however, attracted little attention during the study of the annealing process in $\alpha$-copper phthalocyanine.[9]

The aim of the present work is to investigate the effect of the crystal-structural transformation on the Stage-II annealing of $^{64}$Cu recoil atoms in neutron-irradiated $\alpha$-copper phthalocyanine. In fact, the isothermal annealing curve above 270°C showed an anomalous inflection point, while no anomaly was observed in the curve below 250°C. The results are discussed in terms of the crystal-structural transformation during the thermal treatment.

## Experimental

*Target Materials.* $\alpha$-Copper phthalocyanine from Dai-nihon Ink and Chemicals Inc. was carefully purified by recrystallization from sulfuric acid. $\beta$-Copper phthalocyanine was obtained by heating the $\alpha$-crystal for 5 hr at 300°C. The X-ray powder diffraction pattern, the electron micrograph, and the thermogram of the materials were recorded.

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*Irradiation.* The neutron irradiation of copper Phthalocyanine was performed at the temperature of dry ice ($-78°C$) for 10 sec by means of a pneumatic tube in the nuclear reactor, JRR-2, of the Japan Atomic Energy Research Institute. The thermal neutron flux at the irradiation position was $5.5 \times 10^{13}$ n/cm$^2$/sec, and the $\gamma$-ray dose rate was about $10^8$ R/hr.

*Chemical Separation and Radioactivity Measurements.* The analytical technique consisted of the dissolution of the target and the separation of the radioactive products by a method described in the literature.[9] After irradiation, the target was dissolved in cold sulfuric acid ($<0°C$). The solution was slowly poured into a mixture of ice and water to prevent any exchange reaction provoked by a sudden rise of the temperature. The precipitate of copper phthalocyanine was filtered out, and the radioactivity of $^{64}Cu$ both in the precipitate and in the filtrate was measured by a Baird Atomic single-channel $\gamma$-ray spectrometer connected to the NaI(T1) crystal (well type, $1.75'' \phi \times 2''$).

*Thermal Annealing.* The irradiated sample was heated in a constant-boiling bath with an accuracy of $\pm 0.5°C$ ($<200°C$) or in an electric furnace with its temperature controlled within $\pm 1\%$ ($>200°C$). No thermal decomposition in a gross amount was observed at any temperature.

## Results and Discussion

Figure 1 shows the carefully observed isothermal annealing curves of $^{64}Cu$ recoil atoms in neutron-irradiated $\alpha$-copper phthalocyanine. As has been described in Ref. 9, the annealable portion in Stage I (below 200°C) is very small, so the State-II process (above 250°C) appears predominant in this system. One can find anomalies in the annealing curves. The isothermal annealing curve of Stage II has an inflection point which moves to the left on the time axis with an increase in its temperature.

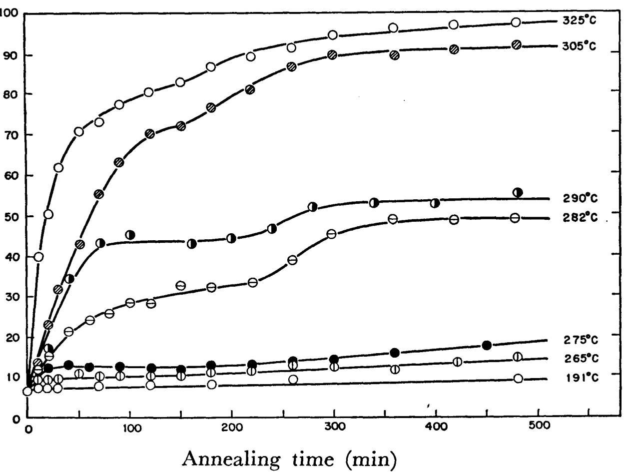



Fig. 1. Isothermal annealing curves of $^{64}Cu$ recoil atoms in the neutron irradiated $\alpha$-copper phthalocyanine.

Figure 2 illustrates the isothermal annealing curves of $\beta$-copper phthalocyanine. The neutron irradiation and the thermal treatment were carried out under the same condition as those used for the $\alpha$-crystal. Figure 2 clearly shows the difference between two annealing curves. The annealing process of the $\beta$-crystal shows a normal monotonous curve, whereas

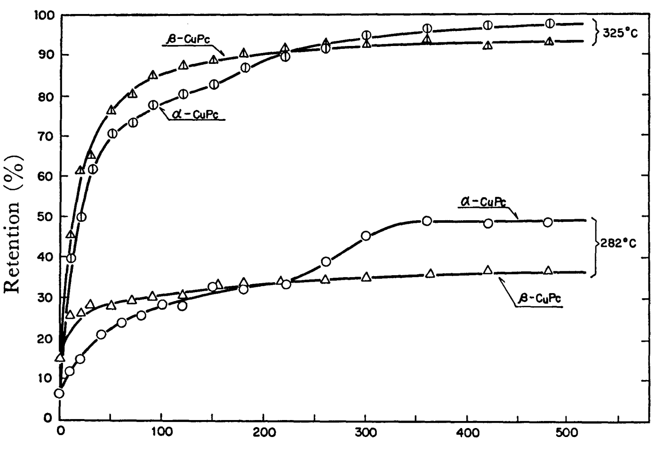



Fig. 2. Comparison of the isothermal annealing curves between $\alpha$- and $\beta$-copper phthalocyanine.

the curve of the $\alpha$-crystal is not so simple. It can also be pointed out that, although the rate of the annealing reaction of the $\alpha$-crystal seems somewhat slower than that of the $\beta$-crystal at the beginning, the curve for the former reaches a plateau higher than that of the latter, showing a rapid rise around the inflection point. One may attribute these results to the superimposing effect of the crystal-structural transformation in the Stage-II annealing.

The annealing process of the $\alpha$-crystal appears to consist of the "normal" monotonous annealing process and the "delayed" process which is to be ascribed to the structural transformation. An attempt was made to decompose the curve into two components by assuming that the normal annealing curve can be represented by the first-order rate law. Figure 3 presents two components of the isothermal annealing process of $^{64}Cu$ recoil atoms in $\alpha$-copper phthalocyanine. The solid and dotted lines represent the normal annealing process (Component 1) and the other process (Component 2) respectively. Although the magnitude of the annealable portion is not large, the factors determining the features of the curve will hopefully supply

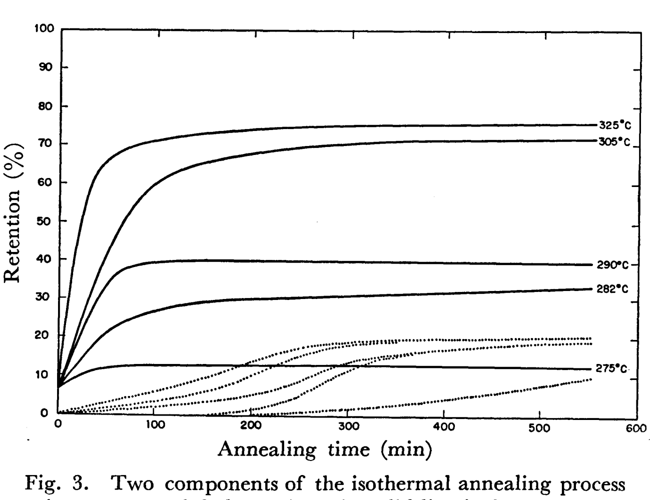



Fig. 3. Two components of the isothermal annealing process in $\alpha$-copper phthalocyanine; the solid line is the "normal" process (the component 1) and the dotted line is the "delayed" process (the component 2).

information on the mechanism of the delayed annealing process.

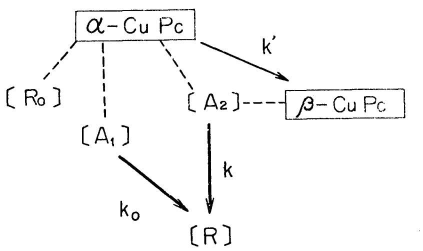
A kinematic analysis was undertaken, with special attention being paid to the delayed annealing process. It was found that the following equations could explain all the features of the annealing reaction:

$$[R] = [C_1] + [C_2], \quad (1)$$

where: $$[C_1] = [A_1]\{1-\exp(-\boldsymbol{k}_0 t)\} \quad (2)$$

and $$[C_2] = [A_2]/\{1+1/\boldsymbol{a}\exp(-\boldsymbol{k}t)\}. \quad (3)$$

Here, [R] is the experimentally-observed value of retention; $[C_1]$, $[A_1]$, and $\boldsymbol{k}_0$ are the retention, the annealable portion, and the rate constant associated with the normal annealing process; $[C_2]$, $[A_2]$, and $\boldsymbol{k}$ are the corresponding quantities of the other process, and $\boldsymbol{a}$ is a parameter. The mechanism proposed above is depicted schematically in Fig. 4, where $\boldsymbol{k}'$ is the rate constant of the structural transformation of α-copper phthalocyanine to the β-form.




Eig. 4. The possible schematic explanation of annealing process in α-copper phthalocyanine.

As is illustrated in Fig. 5, the curve calculated by the use of Eq. (3) with appropriate values of the $\boldsymbol{a}$ parameter and the $\boldsymbol{k}$ rate constant can satisfactorily explain the delayed annealing reaction. Equation (3) has been derived in the sense of an autocatalytic reaction[29] by assuming that the crystal-structural transformation plays a catalytic role in the course of the delayed process. The parameter $\boldsymbol{a}$ in Eq. (3) determines the induction period, $\tau$, of the delayed process and is closely related to the concentration ratio of the β-modification to the α-crystal in the target under heat treatment. The magnitude of the parameter $\boldsymbol{a}$ becomes smaller with a decrease in the temperature.

The slope of the linear part of the delayed annealing process depends principally on the value of $\boldsymbol{k}$. The value of $\boldsymbol{k}$ estimated based on the proposed mechanism was found to be of the same order of magnitude as the value of $\boldsymbol{k}'$ associated with the structural transformation of α-copper phthalocyanine. This may indicate that the delayed process is evoked by the crystal-structural transformation.

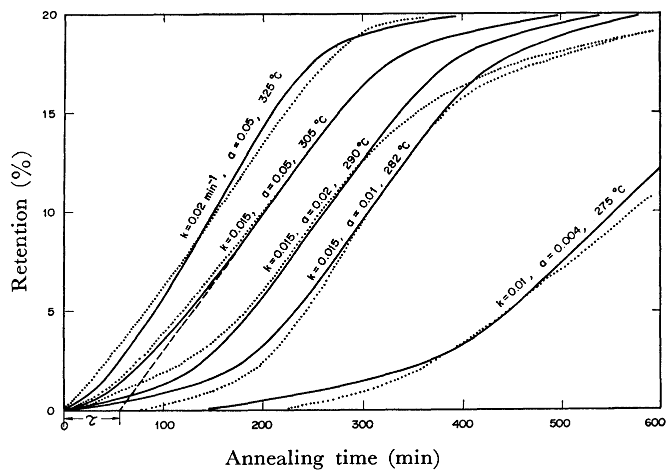



Fig. 5. The calculated curve of the delayed annealing process in α-copper phthalocyanine; the dotted line is the calculated curve and the solid line is the component 2 in Fig. 3.

It is known[30] that the nucleation of a β-particle in a pure α-crystal occurs in the earlier stage of the crystal-structural transformation. After nucleation has begun, the transformation enters the growth stage, the rate of which is controlled by the diffusion process. The electron-micrographic observation revealed that these processes were also involved in the α–β structural transformation of copper phthalocyanine.[31] Consequently, the delayed annealing reaction may be interpreted in terms of the spontaneous fluctuation of the matrix and the change in the crystalographic factors, such as the surface activity and the concentration of defects, due to the structural transformation. These factors probably play a triggering role in the delayed annealing reaction.

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31) The detailed observation of the crystal structural transformation of copper phthalocyanine by means of the electron microscope will be published elsewhere.