The Effects of Pre-irradiation Treatments on the Chemical Behavior of ^{64}Cu Recoil Atoms in Neutron-irradiated Copper Phthalocyanine

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The chemical behavior of ^{64}Cu recoil atoms was studied in copper phthalocyanine which had been quenched from an elevated temperature or exposed to ^{60}Co γ-rays before the neutron irradiation. In the quenched β-crystal, the initial retention was found to increase with an increase in the temperature of pre-irradiation heating, while the plateau retention of the post-neutron annealing reaction decreased. These results were compared with those for cadmium phthalocyanine and were understood in terms of "dislocation" in the crystal, the recoil atoms being assumed to be trapped and stabilized in the "dislocation." Although the variations were small, the irradiation with ^{60}Co γ-rays caused a change in the chemical behavior of the recoil atom. The role of some radiation-induced species were discussed.

A series of studies[1-5] have reported that the bulk properties of the target crystal have a marked influence on the chemical consequence of ^{64}Cu recoil atoms in neutron-irradiated copper phthalocyanine. Both the initial retention and the thermal-annealing process depended on the crystal structure, the size and shape of grains, and the concentration of defects in the solids.

The pre-irradiation treatments, involving quenching and irradiation with ionizing radiation, are well known to sensitize the material to the thermal-annealing reaction.[6-11] In the previous studies concerned with the chemical behavior of ^{115}Cd recoil atoms in cadmium phthalocyanine,[12,13] it was suggested that the central metal vacancies introduced in the target by quenching had a strong effect on the subsequent course of the thermal-annealing reaction of the recoil atom.

The present investigation was undertaken in order to see if a similar effect was observed for ^{64}Cu recoil atoms in copper phthalocyanine. The experiment was expected to provide some useful information for the understanding of the detailed scope of the chemical behavior of recoil atoms in the crystalline metal phthalocyanines.

Experimental

Target Material. α-Copper phthalocyanine from Dainippon Ink and Chemicals was carefully purified by recrystallization from sulfuric acid. The β-copper phthalocyanine was obtained by suspending the α-crystal in benzene at 80°C for 2 hr. The X-ray powder diffraction pattern, the electron micrograph, and the thermogram of the materials were recorded.

Irradiation. The neutron irradiation of copper phthalocyanine was performed at the temperature of dry ice (−78°C) for 10 sec in the nuclear reactor, JRR-2, of the Japan Atomic Energy Research Institute. The thermal neutron flux at the irradiation position was 5.7×10^{13} n/cm^2/sec, and the γ-ray dose rate was 1×10^{8} R/hr.

For the pre-irradiation treatments with γ-rays, the target was irradiated by means of a 16 kCi ^{60}Co γ-ray source to a dose of 1.1×10^{7} R or 1.0×10^{8} R at temperatures of −78 and 20°C. The target was then irradiated in JRR-2 for 10 sec at the temperature of dry ice.

Chemical Treatments and Radioactivity Measurements. The procedures of the chemical separation and the thermal treatments used here were virtually identical with those described in the previous paper.[4)]

In the quenching experiment, the targets were heated to a specified temperature for 5 hr in an electric furnace and then cooled quickly in liquid nitrogen. The target was stored in dry ice until the neutron irradiation.

The radioactivity was measured by means of a Baird Atomic single-channel γ-ray spectrometer, using the NaI(Tl) crystal as the detector.

Results

It has already been reported that the initial retentions[14)] of ^{64}Cu recoil atoms in neutron-irradiated copper phthalocyanine are 5.5% for the α-crystal and 13.5% for the β-crystal,[1,2,4)] and that the α-crystal is converted to the β-crystal by heating above 250°C.[4,15,16)] The influence of heating the α-crystal prior to the neutron irradiation was examined. The results presented in Fig. 1 show that the initial retention increased, as would be expected, when the target was subjected to

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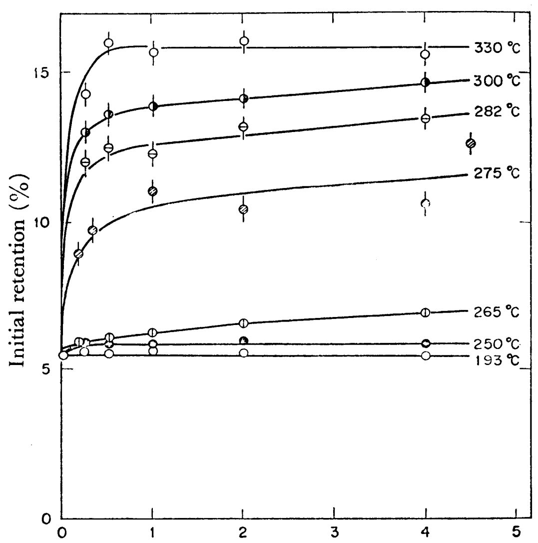

Fig. 1. The change in the initial retention of ^{64}Cu recoil atoms in α-copper phthalocyanine which has been heated before the neutron irradiation.

pre-irradiation heating (pre-heating) above 250°C, reflecting the α-β crystal structural transformation of copper phthalocyanine. The initial retention of the target pre-heated at 330°C reached a slightly higher value than that of the untreated β-crystal. This will be discussed further in the following section.

Table 1 lists the initial retentions of β-copper phthalocyanine pre-heated for 5 hr at various temperatures. It was found that the value increased with an increase in the temperature of pre-heating. Table 2 lists the thermal-annealing data of the pre-heated target in comparison with those of the untreated target. The annealing time of 5 hr was chosen because of the time at which the retention had reached the plateau. The data for the pre-heated α-crystal were the same as those observed for the pre-heated β-crystal. This may be attributed to the fact that the α-crystal has been completely transformed to the β-crystal by pre-heating, as is shown in Fig. 1.

TABLE 1. THE INITIAL RETENTION OF β-COPPER PHTHALOCYANINE HEATED FOR 5 hr BEFORE THE NEUTRON IRRADIATION

Pre-heating temperature (°C)	Initial retention (%)
Untreated	13.5±0.2
195	13.7±0.2
300	14.6±0.4
330	16.0±0.3
350	17.2±0.5

TABLE 2. COMPARISON OF THE THERMAL ANNEALING DATA BETWEEN THE QUENCHED AND THE UNTREATED COPPER PHTHALOCYANINE

Target	Retention (%)		
	Initial retention	Annealed at 196°C for 5 hr	Annealed at 300°C for 5 hr
α-Crystal			
Untreated	5.5±0.4	7.8±0.3	88.7±1.3
Quenched[a)]	14.6±0.3	19.9±0.3	25.5±0.5
β-Crystal			
Untreated	13.5±0.4	24.2±0.5	75.8±1.5
Quenched[a)]	14.6±0.2	19.8±0.4	24.2±0.5

a) The target was heated for 5 hr at 300°C and quenched before the neutron irradiation.

TABLE 3. THE INITIAL RETENTION OF α- AND β-COPPER PHTHALOCYANINE EXPOSED TO ^{60}Co γ-RAYS BEFORE THE NEUTRON IRRADIATION

Target	γ-Ray irradiation		Initial retention (%)
	Irradiation temperature (°C)	Radiation dose (R)	
α-Crystal	−78	1.1×10^7	5.3±0.5
	−78	1.0×10^8	5.4±0.5
	20	1.1×10^7	5.3±0.5
	20	1.0×10^8	5.3±0.5
		Untreated	5.5±0.3
β-Crystal	−78	1.1×10^7	13.2±0.3
	−78	1.0×10^8	15.2±0.3
	20	1.1×10^7	11.8±0.3
	20	1.0×10^8	11.0±0.3
		Untreated	13.5±0.3

The initial retentions of α- and β-copper phthalocyanine, which has been exposed to the ^{60}Co γ-rays before the neutron irradiation, are listed in Table 3. One can find almost the same initial retentions for the α-crystal between the untreated and the γ-irradiated targets. For the β-crystal, however, the initial retention was found to increase or decrease depending on the irradiation temperature of the γ-rays; the initial retention was a little higher at −78°C and lower at 20°C. Figure 2 shows the isothermal-annealing curve of ^{64}Cu recoil atoms in β-copper phthalocyanine which has been irradiated with γ-rays to dose of 1.0×10^8 R before the

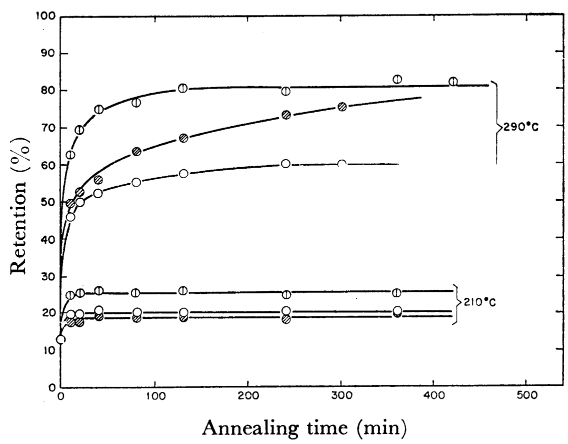

Fig. 2. The isothermal annealing curves for β-copper phthalocyanine which has been exposed to ^{60}Co γ-rays before the neutron irradiation.

○: Untreated sample; ⦶: irradiated at −78°C to dose of 0.97×10^8R; ●, irradiated at 20°C to does of 1.0×10^8R.

neutron irradiation, unlike the untreated target. The annealing curve at 290°C (Stage II) showed a different pattern from that of the untreated target—an increase in the plateau value of the retention. Only a small change in the annealing process was observed at 210°C (Stage I).

Discussion

As is shown in Tables 1 and 2, the heat treatment before the neutron irradiation (pre-heating) raised the initial retention and lowered the plateau of the post-neutron annealing curve in both Stage I and Stage II. It has been reported for tris-acetylacetonatocobalt(III) and -chromium(III) complexes[17] that heating the crystals before the neutron irradiation decreased the initial retention and reduced the thermal annealing reaction. In the case of pre-heating for cadmium phthalocyanine,[13] the initial retention was found to decrease, while the annealable portion increased. These results have been interpreted in terms of defects in the solids, but the role of the defects may vary from one compound to another.

The results obtained for cadmium phthalocyanine, from which the central metal was easily removed, were interpreted in terms of the central vacancy in the crystal, but this interpretation is not valid in the case of copper phthalocyanine, in which the bond strength between the central metal and the ligand is very strong. The central metal of copper phthalocyanine is quite stable under thermal treatment,[18-20] and the metal can not be removed from the central position of the complex. For ionic crystals[10,11] effects similar to those of copper phthalocyanine have been reported. The pre-irradiation heating raised the initial retention and decreased the annealable portion. These results were explained in terms of the thermal removal of defects from the lattice, suggesting that a small fraction of (n,γ)-activated recoils were stabilized only in a reduced state in the lattice by interaction with a "reducing" inherent crystal defect. However, this explanation does not seem applicable to the molecular crystal of copper phthalocyanine.

For copper phthalocyanine it seems possible that the effective crystal imperfection is not a point defect, as has been described for the ionic crystals, but a "dislocation" (a line defect) or a disorder of the molecular configuration, introduced through the recrystallization. Dislocations are thermodynamically unstable, since the enthalpy change associated with the formation of a dislocation is extremely large and since the entropy change is very small.[21] This kind of crystal imperfection can be removed from solids by heat treatment. In the electron micrograph of the α-crystal used here, a large number of "gaps" (separated from one another by some 100's of Å) were observed, while these gaps disappeared in the β-crystal which had been transformed from the α-crystal by heat treatment above 250°C. Dislocations being assumed to trap and stabilize the recoil atom, the results presented in Table 1 may be explained in connection with the "dislocation" in crystalline copper phthalocyanine. The decrease in the "dislocation" with the increase in the temperature of pre-heating should raise the initial retention of ^{64}Cu recoil atoms and reduce the annealable portion in copper phthalocyanine because of the reduction of diffusion processes controlled by the dislocation.

Contrary to the case of cadmium phthalocyanine,[13] the ionizing radiation caused a change in the chemical behavior of ^{64}Cu recoil atoms in copper phthalocyanine. Although the variations were small, the effect of irradiation with ^{60}Co γ-rays for β-copper phthalocyanine seems dependent upon the irradiation temperature of γ-rays. The irradiation at −78°C raised the initial retention and enhanced the thermal-annealing reaction. On the other hand, the initial retention of the target exposed to the ^{60}Co γ-rays at 20°C decreased slightly. The pattern of the isothermal annealing curve was different from that of the other case. An increase in the annealable portion in the Stage-II process (290°C) was seen in both cases.

The temperature dependence observed here may imply that the species produced by the ionizing radiation are different depending on whether the target is irradiated at 20°C or −78°C. The intermediate oxidized species might be produced in the solid under the γ-ray irradiation at 20°C. The intermediate species can be reversed to the parent complex by heat treatment,[22] so that the retention increases in the Stage-II annealing process. The decrease in the initial retention may be ascribed to the fact that the intermediate species stabilize the recoil atom placed in the interstitial position.

In the case of γ-ray irradiation at −78°C, the species which affect the behavior of recoil atoms may be some radiation-induced acceptor which can raise the initial retention. A previous investigation[5] has already revealed that the electron acceptor in the crystalline phthalocyanine is effective in increasing the initial retention of recoil atoms in the complex. However, more experimental data must be accumulated to clarify the effect of ionizing radiation, especially the radiation-induced acceptor.

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