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The Thermal Annealing Behavior of Recoil Manganese Atoms Produced in Alkali Metal Permanganates by (n, 2n) and (n, γ) Reactions*1

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The thermal annealing behavior of recoil manganese atoms produced in alkali metal permanganates by $^{55}Mn(n,2n)^{54}Mn$ and $^{55}Mn(n,\gamma)^{56}Mn$ reactions was studied. In the case of potassium permanganate, the thermal annealing of ^{54}Mn proceeded faster than that of ^{56}Mn. The retention of ^{54}Mn in the annealing curve decreased after an initial increase when it was treated at 180°C, whereas this anomaly was not observed in the case of ^{56}Mn. These differences in the annealing behavior of the two nuclides were ascribed to the effects of background gamma radiation during the neutron irradiation and also to the differences in recoil energies. An effect of the counterpart cations of permanganate was also observed in the thermal annealing behavior, and was interpreted in terms of the ionization potential of alkali metal.

It is well known that the chemical behavior of recoil atoms of the same element produced in a crystal by different nuclear processes is often not exactly the same. However, very little work has been carried out on their thermal annealing behaviors.

Aten and his co-workers[1] studied the thermal annealing of iodine atoms produced in potassium iodate by $^{127}I(n,2n)^{126}I$ and $^{127}I(n,\gamma)^{128}I$ reactions and observed that the thermal annealing of both recoils proceeded at the same rate, while the initial retention of ^{128}I recoils is higher than that of ^{126}I recoils. Jach and Harbottle[2] found that the thermal annealing of ^{82}Br recoils in bromate crystal irradiated with thermal neutrons proceeded faster than that of ^{80m}Br recoils. These isotope effects on thermal annealing behavior have been ascribed to the differences in the initial recoil energies of the various isotopes and also to differences in the electric charge of the recoil atoms. However, more detailed investigations are necessary in order to elucidate the effect of the recoil energy on thermal annealing.

This paper will deal with the thermal annealing behavior of recoil manganese atoms produced in alkali metal permanganates by $^{55}Mn(n,2n)^{54}Mn$, and $^{55}Mn(n,\gamma)^{56}Mn$ reactions from the point of view of the influences of the recoil energy and the effect of the alkali metal cation. The initial kinetic energy of ^{54}Mn recoils produced by the (n,2n) reaction is about 1000 times that of ^{56}Mn recoils produced by the (n,γ) reaction. The differences in the thermal annealing behavior of the two recoil atoms will be discussed in relation to the effects of the recoil damage and of gamma radiation during the neutron irradiation. Further, a remarkable effect of counterpart cations in the permanganate on the thermal annealing of the manganese recoils will be interpreted in terms of the electrostatic character of the alkali metal ion.

Experimental

Sample. The alkali metal permanganates were prepared by the method described in a previous paper.[3] All the samples were sealed in quartz or glass ampoules for neutron irradiation after the ampoules had been evacuated to a pressure below 10^{-4} mmHg.

Neutron Irradiations and Thermal Annealing Procedure. For the $^{55}Mn(n,2n)^{54}Mn$ reaction, about 500 mg of the sample was irradiated with 14 MeV neutrons for 5 hr at room temperature. The neutron flux at the irradiation position was 1×10^{7} n/cm^2/sec, and the gamma dose rate was about 5 R/hr.

On the other hand, for the $^{55}Mn(n,\gamma)^{56}Mn$ reaction, a few mg of the sample were irradiated for 6 min at the reactor temperature (*ca.* 40°C) with thermal neutrons in a pneumatic tube of the KUR at Kyoto University. The thermal neutron flux was 4×10^{12} n/cm^2/sec, and the gamma dose rate was estimated to be 2×10^{7} R/hr.

After irradiation, all the samples were stored at the temperature of dry ice. The thermal annealing ex-

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1) A. H. W. Aten, Jr., M. Lindner and L. Lindner, "Chemical Effects of Nuclear Transformations," Vol.II, IAEA (1965), p. 125. G. A. Dupetit and A. H. W. Aten, Jr., *Radiochim. Acta*, **7**, 165 (1967).

2) J. Jach and G. Harbottle, *Trans. Faraday. Soc.*, **54**, 520 (1958).

3) T. Shiokawa, M. Yagi and T. Sasaki, *Radiochim. Acta*, **12**, 54 (1969).

periment was carried out by using an oil bath, its temperature controlled within ± 1°C.

Analytical Procedure for Chemical Species. The irradiated samples were dissolved into redistilled water at room temperature. The chemical species of radioactive manganese were separated into three fractions ($*Mn^{2+}$, $*MnO_2$ and $*MnO_4^-$ ions) by employing a simplified adsorption method based on an earlier worker's.[4] The radioactive permanganate ion was separated from the reduced species by shaking with 200 mg of manganese dioxide, followed by filteration through a glass filter. This procedure was repeated three times, each time using fresh manganese dioxide. Then the manganese dioxide which contained radioactive manganese dioxide and manganous ions was washed with neutral water until the purple color of the permanganate ion disappeared completely. The radioactive manganous ion was then eluted with 20 m*l* of a 10% manganous nitrate solution and 10 m*l* of 3N nitric acid from the manganese dioxide fraction. Finally, the latter was reduced into a solution by hydrochloric acid containing a small amount of hydrogen peroxide.

Radioactivity Measurements. The radioactivity was measured by means of a multi-channel pulse-height analyzer connected with a well-type NaI (Tl) detector (2in × 1¾in). The intensities of 0.84 and 0.85 MeV gamma rays were counted for ^{54}Mn and ^{56}Mn respectively.

Results and Discussion

No radiolytic decomposition of the samples through fast or reactor neutron irradiation was observed, except that the lithium salt was decomposed slightly as a consequences of the $^6Li(n,\alpha)^3H$ reaction in the case of reactor irradiation.

The $*MnO_2$-yield in each of the three fractions described above was independent of the type of nuclear reaction and was 4—8% for all samples except the potassium permanganate annealed at 180°C.

The retentions for the samples irradiated with fast neutrons are listed in Table 1. The tabulated values are the means of at least two determinations. The results of isothermal annealing for the samples irradiated with reactor neutrons are given in Table 2. As may be seen in this table, the yield depends slightly on the heating time when it is longer than 90 min. It is noticeable that the retentions for ^{54}Mn recoils in every permanganate treated at room temperature are higher than those for the ^{56}Mn recoils which were reported in the previous paper.[3]

TABLE 1. CHEMICAL DISTRIBUTIONS OF ^{54}Mn RECOILS IN ALKALI METAL PERMANGANATES TREATED AT ROOM TEMPERATURE

Compound	Yield (%)		
	$^{54}Mn^{2+}$	$^{54}MnO_2$	$^{54}MnO_4^-$
$LiMnO_4$	69.0±2.2	15.7±2.0	15.3±1.7
$NaMnO_4$	70.1±2.1	7.0±1.5	22.9±1.9
$KMnO_4$	61.3±2.5	10.6±2.8	24.5±2.2
$RbMnO_4$	53.7±2.5	13.5±2.0	32.8±2.4
$CsMnO_4$	46.4±0.9	11.2±0.5	43.1±0.6

The isothermal annealing curves of the manganese recoils produced in the potassium permanganate are shown in Figs. 1 and 2. The rapid increase in retention by heating corresponds to the decrease in the $*Mn^{2+}$-yield for both nuclides. In treatment at 180°C, the retention for ^{54}Mn recoils decreased after a rapid initial increase, while the $^{54}MnO_2$-yield increased slowly with the heating time. Nothing similar was observed in the case of ^{56}Mn recoils.

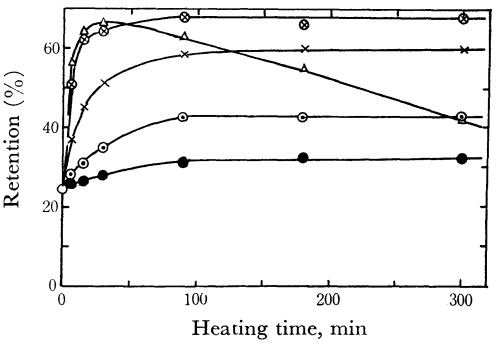

Fig. 1. Isothermal annealing curves for ^{54}Mn recoils in potassium permanganate.
●: 70°C ⊙: 100°C ×: 130°C
⊗: 150°C △: 180°C

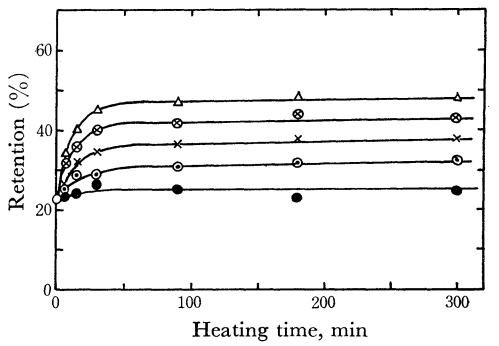

Fig. 2. Isothermal annealing curves for ^{56}Mn recoils in potassium permanganate.
●: 70°C ⊙: 100°C ×:130°C
⊗: 150°C △: 180°C

Figure 3 shows isochronal annealing curves obtained by 5 hr heating, together with the results of the thermal decomposition of the samples which had been irradiated with 14 MeV neutrons for 5 hr before heating. Although, for both nuclides, the difference in retention was not very large in room-temperature treatment, at a higher temperature the thermal annealing of ^{54}Mn recoils proceeded more rapidly. In other words, the thermal annealing

4) For example, D. J. Apers and G. Harbottle, *Radiochim. Acta*, **1**, 189 (1963).

Table 2. Chemical distributions of ^{56}Mn recoils in alkali metal permanganates annealed at various temperatures for 90 and 180 min

Compound	Chemical species*	Yield (%) 100°C 90 min	100°C 180 min	130°C 90 min	130°C 180 min	150°C 90 min	150°C 180 min
$LiMnO_4$	A	78.5±0.8					
	B	9.9±1.3					
	C	11.6±2.1					
$NaMnO_4$	A	67.6±2.3		56.7±1.5	54.5±1.3		
	B	12.8±2.5		14.2±2.0	15.1±2.2		
	C	19.6±1.4		29.1±1.2	30.4±0.9		
$KMnO_4$	A	64.4±1.3	63.2±1.1	57.5±1.3	56.2±1.2	53.0±1.0	49.3±0.9
	B	4.0±2.2	4.8±1.7	5.7±0.8	5.8±1.3	4.0±0.8	7.0±1.2
	C	31.6±1.5	32.0±0.9	36.8±0.9	38.0±0.9	42.2±2.1	43.7±1.7
$RbMnO_4$	A	48.6±1.4			33.9±1.8	30.8±1.8	
	B	6.5±1.1			4.9±0.3	5.4±1.2	
	C	44.9±0.7			61.2±1.5	63.9±2.0	
$CsMnO_4$	A	37.7±1.5		22.1±1.5		22.6±1.9	
	B	6.0±1.8		5.3±0.9		5.1±0.9	
	C	58.3±1.2		72.6±1.8		72.9±2.3	

* A: $^{56}Mn^{2+}$, B: $^{56}MnO_2$, C: $^{56}MnO_4^-$

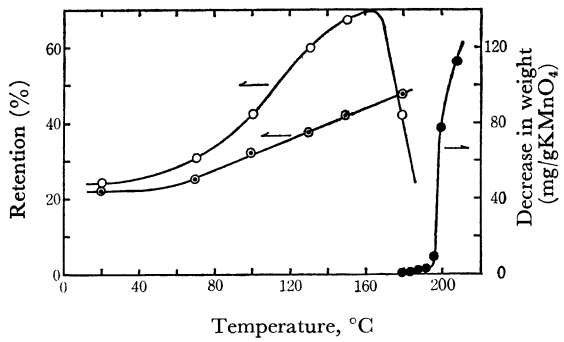

Fig. 3. Isochronal annealing curves (heating time: 5 hr) and the results of thermal decomposition of potassium permanganate irradiated with fast neutrons.
○: ^{54}Mn recoils ⊙: ^{56}Mn recoils
●: results for thermal decomposition

of ^{56}Mn recoils seems to be somewhat prevented at temperatures under 160°C, this tendency becomes more remarkable with the increase in the annealing temperature. On the other hand, the anomalous behavior in the thermal annealing of ^{54}Mn recoils at 180°C was not due to either thermal or radiolytic decomposition, because a macroscopic decomposition of the samples occurred over 190°C.

As is shown in Tables 1 and 2, the retentions of the samples treated at the same temperature increase in the order of the atomic number of the alkali metal in the permanganate. Because the retention values are very low[3,5],*3 in the lower-temperature treatment of the permanganates, the tabulated values may be considered to indicate the fractions annealed at the respective temperatures. These do not depend on any steric character of the crystal,

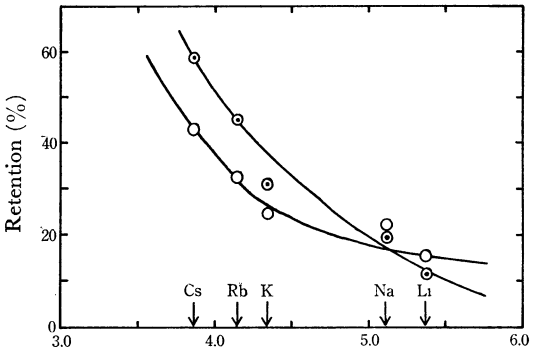

Fig. 4. The relationships between retention and the ionization potential of alkali metal.
○: retention for ^{54}Mn recoils at room temperature
⊙: retention for ^{56}Mn recoils at 100°C (heating time: 90 min)

5) S. R. Veljković and G. Harbottle, *J. Inorg. Nucl. Chem.*, **23**, 159 (1961); **24**, 1517 (1961).

*3 For potassium and rubidium permanganates which were irradiated with thermal neutrons at −196°C and then dissolved in cold acetone of −78°C, the retention values were 5.8±2.1 and 2.0±1.8% respectively.

such as the crystal configuration or the crystal free space of permanganate, but on the electrostatic character of the alkali metal ion. The relationships between the retention and the first ionization potential of alkali metal are shown in Fig. 4. The trends in this figure show that the thermal annealing is promoted by the decrease in the ionization potential of alkali metal or by the increase in the electron density of the inactive permanganate ion. These findings imply that the thermal annealing of manganese recoils proceeds by means of a mechanism similar to the transfer annealing suggested for potassium chromate crystal doped with chromic ions,[6] through interaction between the permanganate ion and the reduced species of those manganese recoils which are positively-charged.

The assumptions listed above may be supported by the experimental results on the thermal annealing of bromine recoils produced in alkali metal bromate crystals,[2,7,8] in which a decrease (ΔR) in annealed fractions was observed with an increase in the first ionization potential of alkali metal. The contradictory results are presumably due to the fact that the reduced species in the permanganate is detected as positive, while that in the bromate is detected as nagative. Thus, it is clear that the electrostatic characteristics of the lattice constituents influence the thermal annealing of the recoils.

These processes are different for each nuclide, as is shown in Fig. 3. In the case of iodine recoils in iodates, Aten and his coworkers[1] have ascribed the isotope effects observed in the thermal annealing to the differences in the de-excitation processes of the compound nucleus and the composite nature of the reduced species of the recoils. However, the following noticeable fact, which may account for the different annealing behavior of the manganese recoils, was found in correlated investigations.

The potassium permanganate which had been irradiated with 14 MeV neutron was exposured to gamma rays of a ^{60}Co source for 1 hr (total gamma dose: 2.0×10^6R) and then heated for 90 min at 130°C. These gamma rays caused the retention to decrease from 58.7 ± 1.4 to 33.7 ± 2.2%, almost the same as for the samples irradiated with reactor neutrons (36.8 ± 0.9%). These findings for permanganate are peculiar compared with the findings for the other oxianion salts, such as chromate,[9] bromate[10] and phosphate,[11,12] in which the retentions increased upon exposure to gamma radiation. As no macroscopic decomposition of the samples was observed, the present results suggest that the thermal annealing processes in the permanganate crystals are prevented by gamma irradiation. Therefore, the different annealing behavior in the two nuclides at temperatures under 150°C probably resulted from the different total gamma dose, which were 25 and 2.0×10^6 R, respectively, in the fast neutron and in the reactor neutron irradiations.

On the other hand, the anomalous behavior in the thermal annealing of ^{54}Mn recoils observed at 180°C arose from the peculiar properties of the recoil site, because a thermal decomposition of the sample began to occur over 190°C. By approximate calculation, the initial kinetic energy of the recoils is estimated to be 370 keV for the ^{55}Mn(n,2n)^{54}Mn reaction and 330 eV for the ^{55}Mn(n,γ)^{56}Mn reaction. The linear range of ^{54}Mn recoils in the potassium permanganate crystal is calculated to be 6900 Å according to the range-energy relations proposed by Nielsen;[13] hence, a recoil damage of a few ten Å at least may be created. It is well known[14,15] that the temperature of thermal decomposition is lowered when potassium parmanganate contains a small amount of an impurity such as carbon dioxide or manganese dioxide. Therefore, the rapid decrease in retention may be explained as follows: the recoil site of ^{54}Mn acts as an impurity in the crystal, thus promoting catalytically the localized thermal decomposition in the post-thermal treatment, even at a temperature lower than that of thermal decomposition. These conclusions may be supported also by the experimental finding that the $^{54}MnO_2$-yield increased with the lapse of the time of thermal annealing at 180°C. Thus, the recoil energy strongly influences the thermal annealing behavior in the temperature region of thermal decomposition.

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