CHEMISTRY LETTERS, pp. 1377-1380, 1993.


# Ion Beam Induced Phase Change in $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ Bombarded by 40 keV $He^+$ Ions

Yasuyuki ARATONO, Masami NAKADA, Chiaki SAGAWA,
Mikio NAKASHIMA, and Masakatsu SAEKI
Department of Chemistry, Japan Atomic Energy Research Institute,
Tokai, Ibaraki 319-11

Phase change induced by 40 keV $He^+$ ion bombardment in $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ was studied by conversion electron Mössbauer spectroscopy. From the similarity of ion bombardment effect and thermal annealing behavior, the significant role of thermochemical process after the propagation of the collision cascade for the final fate of the bombarded entity was suggested.

The chemical effect induced by high energetic atoms for the solid has been interesting from viewpoints of basic research on hot atom chemistry and its application to modification of the physicochemical properties of the solid or to creation of new functional material.[1-4] The research on the surface phenomena has been developed with the progress of the instruments such as XPS, AES, and so on. However, the works on the reaction occurring inside the solid have not been so much carried out compared to the surface reaction due to the difficulty of non-destructive analysis of the reaction products.

The authors have been studying the ion bombardment chemistry of iron compounds by Mössbauer Spectroscopy, which is a non-destructive technique.[5] In the present study, the Conversion Electron Mössbauer spectroscopy(CEMS) was applied because its detection depth is comparable to the range of 40 keV $He^+$ ion. From the comparison of the bombardment effects studied by CEMS with thermal annealing effects, phase diagram of Fe-O system,[6] and the energy-loss processes calculated by TRIM code,[7] the authors obtained suggestive results on the reaction induced by energetic $He^+$ ions.

The materials were target grade sintered $\alpha$-$Fe_2O_3$ and $Fe_3O_4$ with a 95% of theoretical density purchased from Furuuchi Chemicals Co.. They were cut into 1.5 x 1.5 x 0.05 $cm^3$ and mechanically polished with 200,

30 and 5 μm-diamond disks and 1 and 0.3 μm-alumina abrasives.

Ion bombardment was carried out by 40 keV $He^+$ ions with a beam current density of 100 μA $cm^{-2}$. The sample was chilled by ice bath when irradiated at room temperature and temperature rise during the bombardment was less than 25 ℃. After the bombardment, the sample was removed from the accelerator and mounted onto a gas flow conversion electron detector. The Mössbauer spectra were measured with about $10^7$ Bq of $^{57}Co/Rh$ source by a constant acceleration at room temperature. The thermal annealing experiments were done in vacuo in a quartz-made reaction vessel at 1173, 1273, and 1373 K for 30 min.

Figure 1 shows the effects of the ion bombardment and the thermal annealing behavior. At $1.8x10^{17}$ ions $cm^{-2}$ bombardment, the spectrum was almost the same as that of $\alpha$-$Fe_2O_3$. More than 99 % of $\alpha$-$Fe_2O_3$ was reduced to $Fe_3O_4$ at the fluence of $2.2x10^{18}$ ions $cm^{-2}$(Fig. 1A). The similar phase change from $\alpha$-$Fe_2O_3$ to $Fe_3O_4$ was observed under the thermal annealing between 1273 and 1373 K(Fig. 1B). On the other hand, in the case of $Fe_3O_4$, the phase change to FeO by ion bombardment did not take place under the same irradiation condition as $\alpha$-$Fe_2O_3$ but proceeded at 773 K for 1 h bombardment(Fig. 1C). New small doublet peaks at the center were identified as FeO from Mossbauer parameters. From the comparison of areal intensity, FeO content was estimated to be 6%.

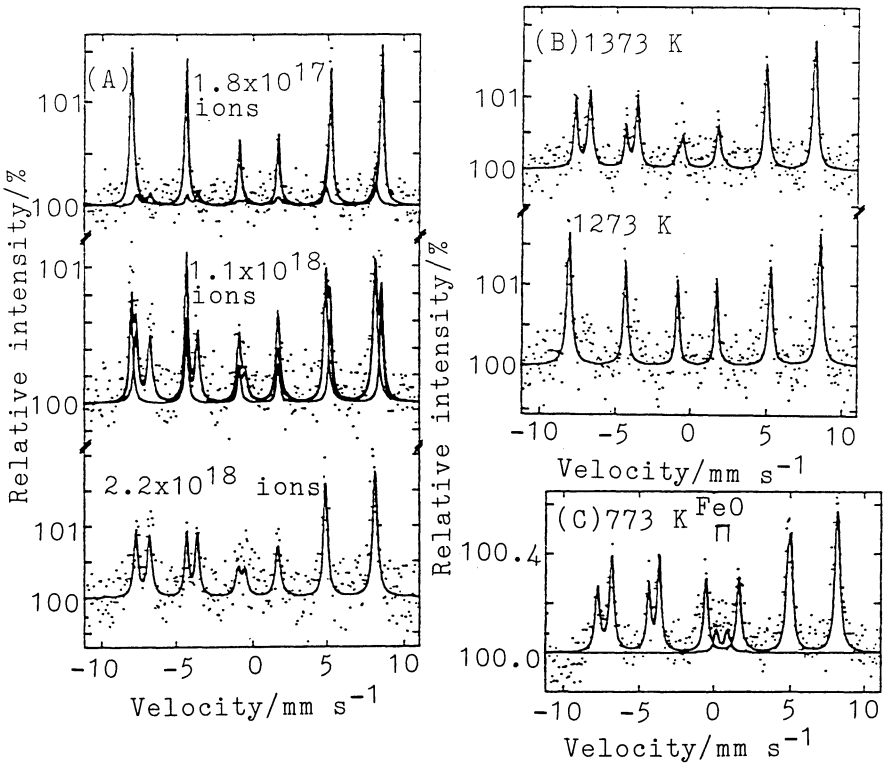


Fig. 1. Comparison of bombardment effect and thermal annealing behavior.
(A) $\alpha$-$Fe_2O_3$ : Bombardment at room temp.
(B) $\alpha$-$Fe_2O_3$ : Thermal annealing.
(C) $Fe_3O_4$ : Bomardment at 773 K for 1 h.

According to the phase diagram,[6] the higher temperature is necessary for reduction of $Fe_3O_4$ to FeO than that of $\alpha$-$Fe_2O_3$ to $Fe_3O_4$ under the same oxygen pressure. The bombardment results in Fig. 1A and C, agree

with the prediction from the phase diagram. The apparent agreement in reduction behavior in the bombardment with the thermochemical treatment and higher bombardment-reduction temperature for $Fe_3O_4$ than for $\alpha$-$Fe_2O_3$ suggest the important role of thermal spike in the bombardment-induced phase change. Thus, the temperature and the duration time of the thermal spike formed in $\alpha$-$Fe_2O_3$ were estimated with the assumption of the cylindrical one along the track.

According to the model proposed by Mozumder,[8] the excess temperature, $T_{ex}$, can be expressed as a function of the distance from the center of the track ,r, elapsed time after passage of the ion, t, and size parameter of the track, $r_0$, as follows

$$T_{ex}=T_0(1+4\delta t/r_0^2)^{-1}\exp[-r^2/(r_0^2+4\delta t)]$$

where, $T_0$ and $\delta$ are the initial excess temperature at the center of the track and the thermal diffusivity and expressed as,

$$T_0=s/(\rho c_v r_0^2) \quad \text{and} \quad \delta = k/\rho c_v$$

where s, $\rho$, k, and $c_v$ denote the average stopping power from the surface to the detection depth of the conversion electron, the density, the heat conductivity and the specific heat respectively. As the detection depth of the conversion electron is estimated to be 100 nm, which corresponds to about one-third of the maximum projected range of 40 keV $He^+$ ion, the s value was found to be 220 eV $nm^{-1}$ by TRIM calculation. Though the radius of the track formed in $\alpha$-$Fe_2O_3$ by 40 keV $He^+$ ion has not been reported, 1-1.5 nm was supposed to be most probable. Thus, by taking $\rho$ =5.24 g $cm^{-3}$, $c_v$=1.6x$10^{-1}$ cal $g^{-1}$ $K^{-1}$ and k=1.44x$10^{-2}$ cal $s^{-1}$ $cm^{-1}$ $K^{-1}$,[9] the initial excess temperatures at the center of the track were estimated to be 3200 K for $r_0$=1 nm and 1400 K for $r_0$=1.5 nm, respectively.

Figure 2 shows the excess temperature at the distance of 0.7, 1.0, and 1.5 nm from the center of the track for $r_0$=1.0 nm and 1.5 nm. It has been reported that the collision cascade propagates entirely within $10^{-13}$ s for ions in the energy range 10-100 keV and the reformation proceeds after completion of the collision cascade.[10] If the phase change due to ion bombardment occurs at the similar temperature to thermal annealing, 1273-1373 K, the result in Fig. 2

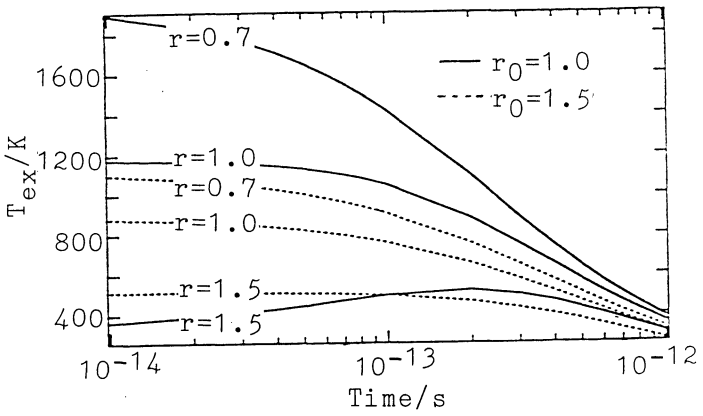


Fig. 2. Excess Temperature(Tex) against time after passage of incident ion at various distances from the center of the track. ($T_{ex}$=actual temp - 300)

implies that the phase change from $\alpha$-$Fe_2O_3$ proceeds between $10^{-13}$ and $10^{-12}$ s within the radius of about 0.7-1 nm from the center of the track.

Generally, the ion-induced reaction proceeds under non-equilibrium conditions. The similarity of the ion-induced phase change to the phase diagram obtained in the present experiment indicates that final chemical reaction may be controlled by thermodynamic equilibrium process. Some authors have reported the important role of the thermal spike in desorption[11] and grain growth[12] induced by bombardment. The correlation of the ion-induced surface phenomena such as sputtering,[1-3] trapping of $O_2$ or $N_2$ on various metals by $Ar^+$ bombardment[13,14] with thermodynamic parameters has been also reported. The present results suggest that the reformation process which occurs inside the solid after collision cascade is also controlled by thermodynamic process.

References

1) R. Kelly, " Materials Modification by High-fluence Ion Beams," ed by R. Kelly and M. Fernanda da Silva, NATO ASI series, Kluwer Academic Publishers, Dordrecht/Boston/London (1987), p. 305.
2) R. Kelly, Nucl. Inst. Meth. Phys. Res., **B39**, 43(1989).
3) R. Kelly, Materials Sci. Eng., **A115**, 11(1989).
4) "Handbook of Hot Atom Chemistry," ed by J. P. Adloff, P. P. Gasper, M.Imamura, A. G. Maddock, T. Matsuura, H. Sano and K. Yoshihara, Kodansha, Tokyo(1992).
5) Y. Aratono, C. Sagawa, M. Nakashima, M. Nakada, K. Hojou, and M. Saeki, Hyperfine Interactions, **70**, 905(1992).
6) "Phase Diagram" ed by A. M. Alper, Academic Press, New York, San Francisco, London (1976) vol. 5, p. 195.
7) J. P. Biersack, L. G. Haggmark, Nucl. Inst. Methods, **174**, 257(1980).
8) A. Mozumder, "Advances in Radiation Chemistry" ed by M. Burton and J. L. Magee, Wiley-Interscience (1969) vol. 1, p. 1.
9) The k value for $Fe_3O_4$ in the following literature was used for the lack of the reported one for $\alpha$-$Fe_2O_3$. "Thermophysical Properties of Matter, vol. 2, Thermal Conductivity-Nonmetallic Solids," ed by Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klements, IFI/Plenum, New York, Washington (1970) p. 154.
10) Hj. Matzke, Radiation Effect, **64**, 3(1982).
11) R. R. Lucchese, J. Chem. Phys., **86**, 443(1987).
12) D. E. Alexander and G. S. Was, ANL/CP-73384(1991).
13) Y. Baba, T. A. Sasaki, and I. Takano, Surf. Sci., **221**, 609(1989).
14) T. A. Sasaki, Y. Baba, and H. Yamamoto, Vacuum, **41**, 15(1990).

(Received May 7, 1993)