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State analysis related to zinc and manganese components in hopeite crystals of zinc phosphate films by XANES and EXAFS

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Using Hopeite crystals as zinc phosphate films formed on zinc coated steel sheets of automobile body, EXAFS methods were applied to analyze the local structure of heavy metal components contained in these crystals. The relationship between these spectral data and the modified crystal structure of Hopeite was discussed. Analysis was done by observing XANES spectra and Fourier transformation of EXAFS for two kinds of powdered Hopeite crystals formed in zinc phosphating bath. XANES and EXAFS spectra for Zn–K and Mn–K absorption edge of the Hopeite containing a manganese component were compared with those of the manganese free sample. Both spectra showed almost the same value of the absorption edge with 9.662–9.663 keV, but the amplitude of XANES and EXAFS spectra for the former was smaller than that for the latter. And, though Mn–K absorption edges were 6.545–6.546 keV for the modified Hopeite crystals and MnO, that of MnO_2 showed a higher value by 5–6eV than the former samples. The peak position of EXAFS relating to first neighbouring atom showed the same difference as in XANES. These facts support that manganese exists as Mn^{2+} in the modified Hopeite crystals. XANES spectra and Fourier transformation of EXAFS provided a conclusion that the modified Hopeite crystal has a structure of $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$.

1. Introduction

Hopeite crystal films are formed on zinc coated steel sheets of automobile body. Conventional Hopeite films have a property of poor adhesiveness between paint films and the zinc coated steels, but developments of zinc phosphate solution enabled to improve the adhesiveness sufficiently [1].

Characterization of Hopeite films has been investigated to ensure the mechanism by means of X-ray diffraction, X-ray photoelectron spectroscopy, Ion micro analysis, Auger electron spectroscopy and Electron spin resonance [2–8]. As the results, it was found that Hopeite films are modified by an action of Mn^{2+} or Ni^{2+} in zinc phosphate solution, and that these modified Hopeite films are possible to be expressed as $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$ or $Zn_{3-y}Ni_y(PO_4)_2 \cdot 4H_2O$ compared to $Zn_3(PO_4)_2 \cdot 4H_2O$ of conventional Hopeite structure. That is, manganese or nickel component in Hopeite films has useful function. And it was cleared that the action of manganese component was more remarkable than that of nickel component [9].

Then in this paper, the modification of Hopeite crystal films by manganese component was investigated and discussed by X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS).

2. Experimental procedure

2.1. Steel sheet material

Galvannealed steel sheet with a coating mass of $45\,\mathrm{gm}^{-2}$, mainly as the δ_1 phase of $FeZn_7$, was studied.

2.2. Degreasing and zinc phosphating

Before zinc phosphating, alkaline degreasing was carried out at 55° C for 120 s. And then zinc phosphating under the conditions given in Table I was performed.

2.3. Preparation of specimens

Zinc phosphate films of Hopeite on the galvannealed steel sheets were scraped out from the substrate with a knife carefully. Before analysing by EXAFS, the metal contents of the films were determined by atomic absorption using a Hitachi 180–60 instrument.

The reference samples of MnO and MnO_2 were analyzed too. MnO (99.9% pure of Rare Metallic Co. Ltd) MnO_2 (99.9% pure of Rare Metallic Co. Ltd).

2.4. EXAFS analysis

2.4.1. Instrument of EXAFS

The instrument of EXAFS belonging to National Laboratory for High Energy Physics was applied.

2.4.2. Conditions for EXAFS measurement

Measurement system is shown in Fig. 1. The detail conditions are as follows.

(1) Absorption edges – Zn–K and Mn–K crusts
(2) Monochromator
    Channel cut – Si(311)
    Type of monochromator – Dual crystal type
    Lattice constants : $d = 0.163747\,\mathrm{nm}$
    Plane spacing : $D = 9.5\,\mathrm{mm}$
(3) Measurement – Penetration system at R.T.

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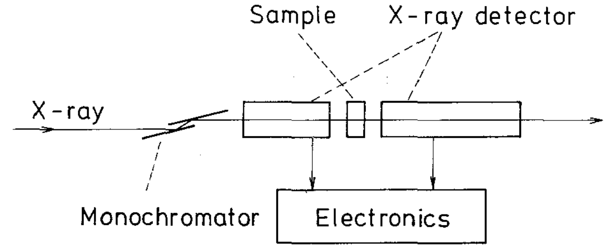


Figure 1 Measurement system of EXAFS.

(4) Analysis methods
(4)-1 Analysis by XANES spectrum
(4)-2 Analysis by Fourier transformation of EXAFS

3. Results and discussion

Metal contents of two kinds of Hopeite films formed in zinc phosphating conditions given in Table I were as follows:

Hopeite films from solution A – Zn : 42.6 wt %
Hopeite films from solution B – Zn : 38.0 wt %, Mn : 4.8 wt %

3.1. Analysis by XANES and Fourier transformation of EXAFS spectra for zinc component

XANES spectra related to Zn–K absorption edges for Hopeite powdered samples of $Zn_3(PO_4)_2 \cdot 4H_2O$ formed in solution A and powdered samples of modified Hopeite formed in solution B were shown in Fig. 2. Absorption edges were 9.663 keV for the former and 9.662 keV for the latter, and these spectra showed the same patterns. It was confirmed that the electron binding energy of zinc component in the modified Hopeite crystals is the same in the conventional Hopeite crystals.

However, the vibration amplitude of the modified Hopeite crystals in high energy region beyond an absorption edge, is smaller than that of the conventional Hopeite crystals. It was thought that the decline of vibration amplitude was caused by a structural disorder of zinc component and the disorder was generated by a trapping of manganese component into the modified Hopeite crystals.

TABLE I Specific values of zinc phosphating conditions

Item		Solution A	Solution B
Chemical composition (p.p.m.)	Zn^{2+}	1000	1000
	Mn^{2+}	0	1000
	PO_4^{3-}	20000	20000
	F^-	0	500
	ClO_3^-	500	0
Temp. (°C)		53	43
Time (sec)		120	120

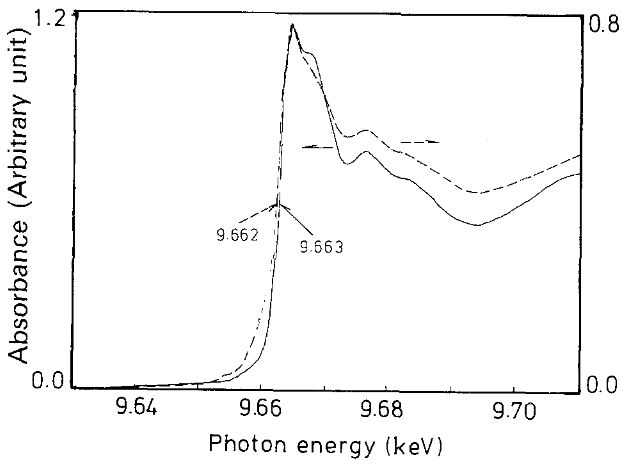
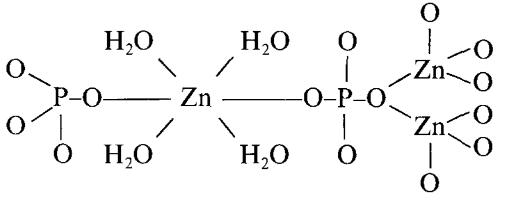


Figure 2 XANES spectrum showing Zn–K absorption edge of Hopeite crystals formed in solutions A and B. —— : Hopeite from solution A, - - - : Hopeite from solution B.

Fourier transformation of EXAFS implies a radial distribution of an atom and provides information about environmental conditions for the atom. Fourier transformations of EXAFS related to the zinc component in the conventional Hopeite crystals and the modified ones were shown in Fig. 3. The spectra indicated first neighbouring atoms at 0.146 nm distance for the former and at 0.144 nm distance for the latter. $Zn_3(PO_4)_2 \cdot 4H_2O$ of Hopeite crystals are consisted of the tetrahedron structures of $[ZnO_4]$ and $[PO_4]$, and the octahedron structure of $[ZnO_2(H_2O)_4]$ [10, 11] as follows:



Accordingly, the first neighbouring atom of zinc component is thought to be oxygen. The absolute peak value of the first neighbouring atom in the modified Hopeite crystals showed a tendency of declining compared to that in the conventional ones. It was thought that a local structure disorder of the zinc component was caused by the manganese trapping action into the crystal structure. Since the ion radii of Mn^{2+} and Zn^{2+} are 0.096 nm and 0.089 nm respectively [12]. It is possible to interpret that a crystalline strain was generated by the substitution of the Mn^{2+} for the Zn^{2+} in the modified Hopeite crystals.

3.2. Analysis by XANES and Fourier transformation of EXAFS spectra for manganese component

XANES spectrum for the manganese component of

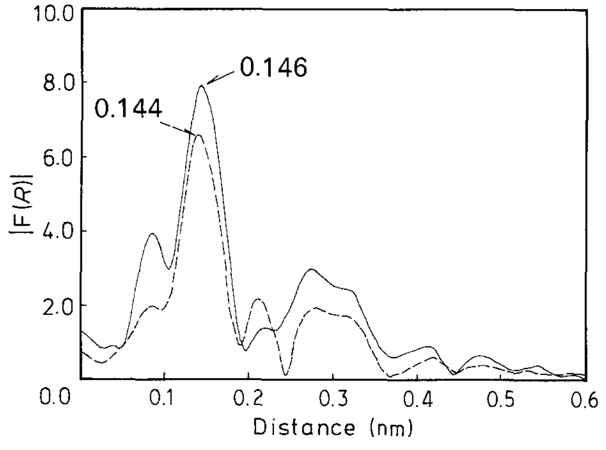


Figure 3 Fourier transformation of EXAFS showing Zn–K absorption edge of Hopeite crystals formed in solutions A and B. —— : Hopeite from solution A, - - - : Hopeite from solution B.

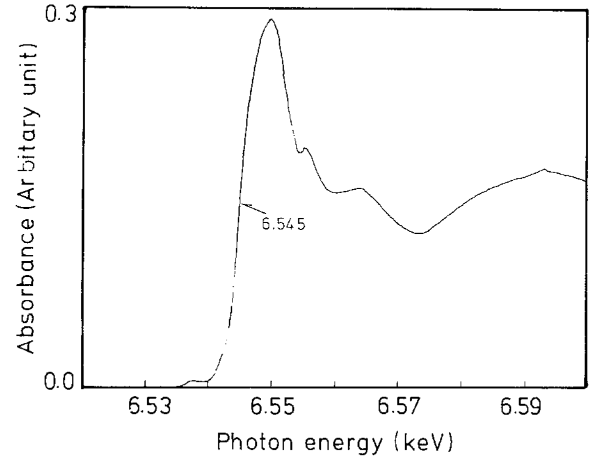


Figure 4 XANES spectrum showing Mn–K absorption edge of Hopeite crystals formed in solution B.

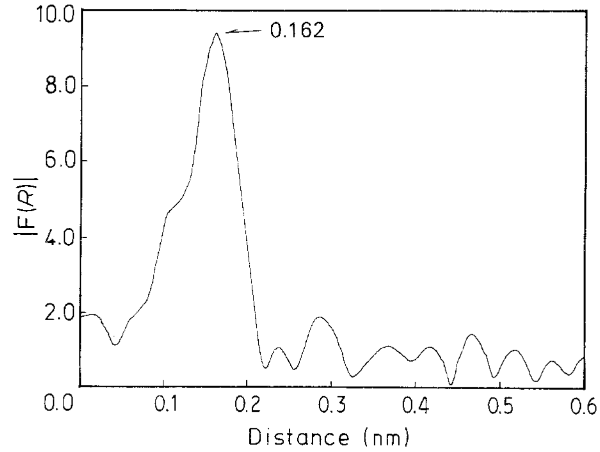


Figure 6 Fourier transformation of EXAFS showing Mn–K absorption edge of Hopeite crystals formed in solution B.

the modified Hopeite crystals was investigated and shown in Fig. 4. For the purpose of clearing a structure state of the manganese component, the reference samples of MnO and MnO_2 were measured and shown in Fig. 5. All the spectra correspond to Mn–K absorption edge. The absorption edges were 6 545 keV for the modified Hopeite crystals, 6.546 keV for the MnO and 6.551 keV for the MnO_2. Therefore, the value of manganese component in the modified Hopeite crystals was consistent with that of MnO, but that of MnO_2 showed higher energy by 5–6 eV than the others.

In general, a value of absorption edge depends on a valence of atom. The data supported that the manganese component in the modified Hopeite crystals is divalent. However, the spectrum pattern of the manganese component in the crystals was different from that of MnO. The fact means that the manganese component in the crystals does not have a structure of oxide, but it coordinates into the crystals with a chemical structure of $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$.

Fourier transformation of EXAFS related to the manganese component in the modified Hopeite crystals was shown in Fig. 6. It showed a radial distribution with the first neighbouring atom at 0.162 nm distance. In the same way, Fourier transformations of EXAFS for MnO and MnO_2 were measured and shown in Fig. 7. The radial distribution of MnO had the first neighbouring atom at 0.168 nm distance and that of MnO_2 had it at 0.140 nm. These first neighbouring atoms are oxygens. Through the distance values of the first neighbouring atoms that mean the binding distance for the manganese components, the value of the modified Hopeite crystals was similar with that of MnO. That of MnO_2 showed shorter distance than the others. The reason is that the ion radius of Mn^{4+} is 0.068 nm and it is smaller than that of Mn^{2+}. Fourier transformation of EXAFS supported that the manganese component in the modified Hopeite crystals has Mn^{2+} state as a structure of $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$.

In this study, it was found that the state analysis relating to metal components in zinc phosphate films by means of XANES and EXAFS was very useful.

4. Conclusions

XANES spectra relating to the zinc components in the Hopeite crystals formed in phosphating solutions with and without Mn^{2+} revealed a crystalline strain by the action of manganese component in the crystals. XANES spectrum of the manganese component in the modified Hopeite crystals support that it exists as Mn^{2+}. XANES spectra corresponding to Mn–K absorption edges showed a difference of photon energy by 5–6eV between Mn^{2+} and Mn^{4+}. Fourier transformation of EXAFS for the zinc·

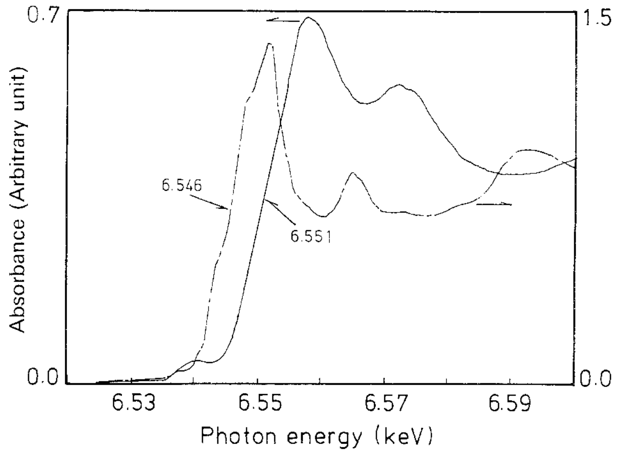


Figure 5 XANES spectra showing Mn–K absorption edge of MnO and MnO_2 as reference samples of manganese. ––– : MnO, —— : MnO_2.

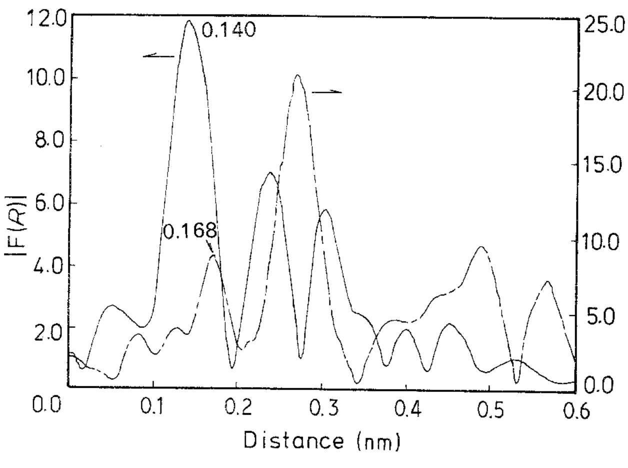


Figure 7 Fourier transformation of EXAFS showing Mn–K absorption edge of MnO and MnO_2 as reference samples of manganese. ––– : MnO, —— : MnO_2.

component in the Hopeite crystals provided information about the local structure of the components. The results correlated well to those of XANES, XANES spectra and Fourier transformations of EXAFS support that the modified Hopeite crystals have a structure of $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$. Analysis methods by XANES and EXAFS for zinc phosphate films were very effective.

References

1. N. SATO, *Surface and Coatings Technology*, **30** (1987) 171.
2. *Idem*, *Boshoku Gijyutsu*, **32** (1983) 379.
3. *Idem*, *Kinzoku Hyomen Gijyutsu*, **37** (1986) 758.
4. *Idem*, *ibid.* **38** (1987) 30.
5. N. SATO and T. MINAMI, *ibid.* **38** (1987) 149.
6. *Idem*, *ibid.* **38** (1987) 108.
7. *Idem*, *Nippon Kagaku Kaishi*, **1987** (1987) 1741.
8. N. SATO, T. MINAMI and H. KONO, *Surface and Coatings Technology* **37** (1989) 23.
9. *Idem*, *Kinzoku Hyomen Gijyutsu*, **38** (1987) 571.
10. A. WHITAKER, *Acta. Cryst.*, **1975** (1975) 2026.
11. R. J. HILL and J. B. JONES, *Am. Mineral.*, **61** (1976) 986.
12. NIHON KAGAKU KAI, in "Kagaku Binran" (Maruzen, Tokyo, 1975) p. 1407.

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