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 原 著 論 文 (5)

Hopeite 皮膜中の常磁性遷移金属成分に 関する ESR スペクトル解析

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Analysis of Paramagnetic Transition Metal Components in Hopeite Films by ESR

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The conversion-coated hopeite $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ films on galvanized steel sheets, containing Mn^{2+} or Ni^{2+} from the bath, have been investigated using electron spin resonance for the purpose of determining the chemical structure of the films.

$\text{Zn}(\text{II})$ in the hopeite crystals, the electron state of which is $3d^{10}$ did not respond to ESR, but manganese and nickel ions in the films did. Six peaks in the spectrum for manganese indicate that the component is $\text{Zn}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, and from the spectrum of nickel the component was thought to be $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$. However, since the g value of the hopeite film containing nickel ions was different from that of $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$, the most probable structure would be $\text{Zn}_{3-x}\text{Ni}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

In this research, it was confirmed that ESR analysis to determine the chemical structure of zinc phosphate films containing metal components were very effective and useful.

1. Introduction

Zinc phosphating of automobile bodies is an important process to provide anti-corrosive property, and adhesion of paint films on the conversion coatings has been greatly improved by modification of the zinc phosphate films. This has been done by incorporating manganese or nickel component into the films, and, therefore, chemical characterization of the zinc phosphate films is of importance. On the other hand, both steel sheet surfaces and zinc phosphating bath constituents influence the properties of the zinc phosphate films¹⁻⁸⁾.

This study has been done in order to establish

the chemical structure of zinc phosphate by using electron spin resonance (ESR).

2. Experimental

2.1 Steel Sheet

Galvanized steel sheets with zinc coatings of 60 gm^{-2} , which consists mainly of δ_1 phase of FeZn_7 , was used as the substrate for zinc phosphating, because they have been widely used for automobile bodies.

2.2 Degreasing Process

Before zinc phosphating, alkaline degreasing was carried out at 55°C for 120 s using degreasing agent CS 310 of Nippon Paint Co., Ltd.

2.3 Zinc Phosphating

After surface conditioning of steel sheets in a titanium phosphate bath, zinc phosphate films were formed in three different kinds of zinc phosphate baths given in **Table 1**.

The chemical structure of hopeite films formed on galvanized steel sheets is usually $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. If metal ions other than Zn^{2+} exists in the bath, they will be contained in hopeite films, although the extent depends on the concentration⁴⁾ of the ions. The baths for zinc phosphating are shown in **Table 1**. The metal contents of the films were determined by atomic absorption using Hitachi 180-60 as shown in **Table 2**.

2.4 ESR Analysis

1) Preparation of Specimens

Hopeite films formed by the methods as described in § 2.3 were scraped out from the steel substrate with a knife and were collected as powdered samples, carefully to avoid that the substrate was cut and metal particles are included in the powdered sample for ESR.

The reference sample was $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ of 97.0 wt% purity, manufactured by KISHIDA Chemical Co., Ltd. The weight of sample used for each ESR measurement was 50 mg.

2) Conditions for ESR measurement

Table 1 Specific values for zinc phosphating baths.

Item		Bath A	Bath B	Bath C
Chemical composition (ppm)	Zn^{2+}	1000	1000	1000
	Ni^{2+}	0	0	800
	Mn^{2+}	0	1800	0
	PO_4^{3-}	20000	20000	20000
	F^-	0	500	500
	ClO_3^-	500	0	0
Temp. (°C)		53	43	43
Time (s)		120	120	120

Table 2 Metal components compositions in zinc phosphate films formed in various baths.

Metal components		Bath A	Bath B	Bath C
Composition (wt%)	Zn	42.6	35.5	41.0
	Mn	0	6.1	0
	Ni	0	0	1.7

ESR instruments used were NIHON DENSHI FE1X and Varian EPR E-109 E. The measuring conditions were selected arbitrarily according to the metal components in hopeite films; the details are shown in **Figures**. The experiments were carried out at room temperature.

3. Results and Discussion

The powdered samples of hopeite films from bath A were measured, but no ESR signal was observed as shown in **Fig. 1**. Since electron magnetic resonance takes place with a paramagnetic transition ions having unpaired electrons, so it is no wonder that hopeite films containing only Zn(II) metal ion, the electron state which is $3d^{10}$, did not show any signal in the ESR spectrum. The ten electron spins in d orbital are oriented with pair.

ESR was then measured for the hopeite films formed in bath B. The spectrum shown in **Fig. 2** indicates that ESR responds to manganese component in the films. The broad spectrum is supposed to be caused by an interaction of manganese compo-

Fig. 1 ESR spectrum for hopeite crystal powder formed in bath A without Mn^{2+} and Ni^{2+} .

Fig. 2 ESR spectrum for hopeite crystal powder formed in bath B with Mn^{2+} .

Fig. 3 ESR spectrum for hopeite from bath B dispersed in H_2O .

nent because of high ion concentration.

Then, the same powdered samples were dispersed in pure water at a concentration $3 \text{ mg}/10 \text{ mL}-\text{H}_2\text{O}$ to eliminate the interaction between powders and were measured. For these samples spectra with six separated peaks were observed clearly as Fig. 3 shows. These peaks imply the typical Mn(II) transition ions⁹⁾. Assuming the manganese component exists in the hopeite films as Mn(II), the electron state of it equals to $3d^5$, the electron spin model of d orbital is as follows.

That is, ESR responded to the five unpaired electrons. These six peaks are due to a hyperfine interaction between the electron spins and the nuclear spins of Mn(II). The nuclear spin I is described as $I=5/2(\pm 1/2, \pm 3/2, \pm 5/2)$; the spectrum with six peaks appeared accordingly.

Here, describing h as Planck constant, ν as frequency, g as a dimensionless constant that means an electron state, β as Bohr constant, and H as a magnetic field, equation (1) holds.

$$h\nu = g\beta H \quad (1)$$

Further, expressing H_1 as a value of resonated magnetic field of third one from low magnetic field and A as a constant of hyperfine coupling that means a magnetic field gap between third and fourth one, equation (1) will be converted to equation (2).

$$g = h\nu / \beta H = h\nu / \beta (H_1 + 1/2 \cdot A) \quad (2)$$

Applying $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$, $\nu = 9.228 \times 10^9 \text{ Hz}$ and $\beta = 9.274 \times 10^{-28} \text{ J}\cdot\text{G}^{-1}$, then $H_1 = 3237.5 \text{ G}$ and $A = 95 \text{ G}$ on the basis of Fig. 3 data, 2.007 of g

Fig. 4 ESR spectra for $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ standard sample.

(a) Powder, (b) Solution in $1 \text{ mol}\cdot\text{dm}^{-3}\text{-HCl}$ at a concentration $2 \mu\text{g}/\text{ml}$

value was gotten.

From these results, it was thought that the manganese component exists in the hopeite films as Mn(II) and the chemical structure corresponds to $\text{Zn}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ which is modified by the action of Mn(II).

In the same way, nickel component in the hopeite films was analysed. ESR spectrum for the hopeite films formed in bath C was compared to that of $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ as reference sample. The results were shown in Fig. 4. The powdered samples (a) responded to ESR, but the samples (b) in HCl solution did not. It was confirmed that the relaxation time of Ni(II) in HCl solution will be reduced.

There were three peaks in the ESR spectrum. As the responded magnetic fields were 3300 G, 3188 G and 2350 G, the g values were calculated by equation (1). Here, ν was $9.520 \times 10^9 \text{ Hz}$. Expressing the g values as g_1 , g_2 and g_3 from high magnetic field, $g_1 = 2.061$, $g_2 = 2.134$ and $g_3 = 2.894$ were obtained.

In case of $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$, nickel component exists as Ni(II) and the electron state is $3d^8$, and, therefore, the electron spin model of d orbital is as follows.

This indicate that ESR responded to the two unpaired electrons.

ESR spectrum for the hopeite powder formed in bath C containing Ni^{2+} was shown in Fig. 5. The measurement conditions were same as those in Fig.

Fig. 5 ESR spectrum for hopeite crystal powder formed in bath C with Ni^{2+} .

Fig. 6 ESR spectrum for (hopeite crystal powder formed in bath C) + KCl.

4. There were also three peaks of ESR spectrum. The responded magnetic fields were 3300 G, 3050 G and 1850 G, and from those $g_1=2.061$, $g_2=2.230$ and $g_3=3.677$ were obtained. The pattern of ESR spectrum was similar to that of $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$, but the g values were different from those of the reference sample.

To ensure the ESR response for the hopeite films formed in bath C, the samples were diluted by KCl powder at a ratio of (1:30), and then ESR was measured. As shown in **Fig. 6**, the pattern of this spectrum was consistent with that of **Fig. 5**, but three peaks of the spectrum appeared sharply. The responded magnetic fields were 3313 G, 3050 G and 2025 G, then $g_1=2.053$, $g_2=2.230$ and $g_3=3.359$ were obtained.

In both **Fig. 5** and **Fig. 6**, the main transition of nickel component corresponds to g_1 and g_2 . The data of **Fig. 5** and **Fig. 6** show the almost same values of g_1 and g_2 .

Through the results of **Figs. 4, 5** and **6**, nickel

component in the hopeite films constitutes Ni(II) in phosphate chemicals. But the chemical structure of nickel component is different from $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ inherently. It was thought that the chemical structure of modified hopeite films was $\text{Zn}_{3-x}\text{Ni}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ by the action of nickel component.

4. Conclusion

1) Hopeite films, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ did not show any ESR signal. This fact means that the purity of the films is adequate to compare with the hopeite films containing manganese or nickel component.

2) Manganese component in the hopeite films showed the ESR spectrum with typical six peaks of Mn(II) .

3) Nickel component in the hopeite films showed the ESR spectrum similar to that of $\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$, but the g values of the former were different from those of the latter.

4) It was concluded that manganese component in the hopeite films constitutes the chemical structure of $\text{Zn}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and nickel component in the hopeite films also constitutes $\text{Zn}_{3-x}\text{Ni}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

5) It was found that the ESR analysis for the metal components in the zinc phosphate films was very effective.

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