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Studies on the formation and thermal properties of manganese phosphate coatings and hureaulite by means of conversion electron and transmission Mössbauer spectrometry

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The chemical states of iron species, produced in manganese phosphate coatings by the immersion of steel in a manganese phosphate bath, were analysed with the help of conversion electron and conventional transmission Mössbauer spectrometry (CEMS and TMS). The modifications of hureaulite by the variation of iron to manganese ratio are discussed with regard to the growth of manganese phosphate coatings. The thermal properties of manganese phosphate coatings and synthetic hureaulite were also investigated by means of differential thermal analysis and the composition analysis of thermal products.

1. Introduction

The phosphating of metals and alloys is now widely used as a means to obtain a corrosion-resistant surface, which also serves as an appropriate surface finishing for lubrication and painting. Various types of phosphating – zinc, manganese, iron and calcium phosphatings, and their modified phosphatings – are in current use [1]. Coatings, which are deposited on a steel surface by the zinc, manganese, calcium, and calcium–zinc phosphatings, consist mainly of hopeite and phosphophyllite, hureaulite, brushite and monetite, and scholzite, respectively [2], whereas the main constituent produced by iron phosphating is amorphous paramagnetic iron (III) compound [3]. Hitherto, the chemical state and epitaxial growth of iron compounds produced at the steel surface by the zinc and calcium–zinc phosphatings, the interfacial state of the substrate [4, 5], the effect of modest heating of phosphate coatings [6], and the thermal deterioration of zinc phosphate coatings [7] have been investigated by the authors and Berry by means of conversion electron Mössbauer spectrometry (CEMS). The thermal transformation and the decomposition of synthetic phosphophyllite [8], and the chemical state of iron in synthetic iron (II) substituted hureaulite [9] were also studied using conventional transmission Mössbauer spectrometry (TMS).

In this paper, we describe the results of the characterization of phosphate coatings obtained by the manganese phosphating. The thermal properties of the coatings and the pyrolysis products of hureaulite are also investigated.

The range of low-energy electrons is estimated by the application of Feldman's equation [10] to hureaulite, $Mn_5H_2(PO_4)_4 \cdot 4H_2O$.

$$R(\text{Å}) = 0.077 \times E(\text{keV})^{4.6}.$$

Therefore, the ranges of 7.3 keV K-, 13.6 keV L-conversion and 5.5 keV Auger electrons re-emitted by the internal conversion process of an ^{57}Fe nucleus after the resonant absorption of 14.4 keV γ-rays are 720, 12 600 and 200 Å (72,

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TABLE I Comparison of Mössbauer parameters for a scraped sample (78 K) from a manganese phosphate coating, calculated by a computer program with and without the restriction of lorentzian parameters. The spectrum was assumed to consist of three kinds of doublet peaks

Line no.	Position (ch.)		Area intensity (%)		FWHM (mm sec^{-1})	
	Restr.	Non-restr.	Restr.	Non-restr.	Restr.	Non-restr.
1	125.3 ± 0.2	124.8 ± 1.1	17.3 ± 0.5	12.8 ± 18.6	0.390 ± 0.008	0.31 ± 0.12
2	128.6 ± 0.6	128.3 ± 3.4	5.9 ± 0.4	7.7 ± 27.7		0.39 ± 0.54
3	134.8 ± 0.1	134.7 ± 0.4	26.7 ± 0.5	29.3 ± 11.4		0.42 ± 0.82
4	143.0 ± 0.4	142.9 ± 0.6	5.9 ± 0.4	5.3 ± 2.5		0.33 ± 0.08
5	174.2 ± 0.1	174.3 ± 0.1	26.7 ± 0.5	28.9 ± 1.0		0.42 ± 0.16
6	184.9 ± 0.1	185.1 ± 0.1	17.3 ± 0.5	15.9 ± 1.0		0.34 ± 0.22
	I.S. (mm sec^{-1})		Q.S. (mm sec^{-1})		χ^2 (ch./para.)	
	Restr.	Non-restr.	Restr.	Non-restr.	Restr.	Non-restr.
	1.384 ± 0.007	1.38 ± 0.02	2.79 ± 0.01	2.81 ± 0.05	1.45	1.35
	1.356 ± 0.006	1.35 ± 0.01	1.85 ± 0.01	1.86 ± 0.02		
	0.48 ± 0.02	0.47 ± 0.08	0.68 ± 0.03	0.68 ± 0.16	(256/11)	(256/19)

1260 and 20 nm), respectively. Because electrons are also emitted from surface materials through the photo-electric and the Compton effects by the irradiation of the resonant scattered X- and γ-rays, the analytical information on surface layers of micron thickness can be obtained by CEMS. The variation of the composition of manganese phosphating layers is also discussed in relation to the phosphating period.

2. Experimental details

2.1. Manganese phosphating procedure and preparation of hureaulite

Rimmed steel sheets (SPCC-D) were degreased, washed, activated in the bath of Parcolene Z (Nihon Parkerizing Co Ltd), and immersed in a manganese phosphate solution at 95° C for several minutes. After the phosphating, the sheets were washed with water and dried by air-blowing at about 110° C for 2 min.

The average thickness of the coatings was estimated from the weight difference of the phosphated steels before and after stripping off the coated layers by immersing them in a solution of 5% chromium (VI) oxide at 70° C for 30 min. The contents of manganese and iron in the phosphate coatings were determined by atomic absorption spectrometry.

Synthetic hureaulite compounds were prepared by adding 100 ml of 1 mol/litre manganese sulphate and iron (II) sulphate solutions in 400 ml of 0.3 mol/litre sodium mono-hydrogen phosphate solution at a temperature higher than 95° C in a stream of nitrogen to prevent oxidation of iron (II) [9].

2.2. Heat treatment of hureaulite

Thermal dehydration properties of the synthetic hureaulite and the phosphate compounds deposited at the manganese phosphated steel were studied using Rigaku simultaneous DTA/TGA thermoanalyser, analytical reagent grade alumina being used as a weight standard. The thermal behaviour of each sample was measured from room temperature to about 1000° C, raising the temperature at a rate of 10° C min^{-1}. The temperatures quoted were determined by the maximum values from in the DTA curve.

2.3. Measurement of Mössbauer spectra

Conversion electron Mössbauer (CEM) spectra of manganese phosphated steel surfaces were observed by detecting resonantly re-emitted electrons with a back-scatter-type gas-flow counter, coupled to a Mössbauer spectrometer. A 30 mCi ^{57}Co (Rh) source was used.

Transmission Mössbauer (TM) spectra of the powder sample, prepared by scraping off the phosphate coating from the steel, and the heated hureaulite samples were measured by detecting transmitted γ-rays by an NaI(Tl) scintilation counter. A 10 mCi ^{57}Co (Rh) was used. The velocity was calibrated by measuring a ^{57}Fe enriched α-iron foil.

TM spectra were analysed by a computer program [11] with the restriction that all peaks have uniform FWHM and that the doublet peaks have equal intensity. The results of the calculation with and without the restriction are given in Table I for comparison. The former gives the more reliable Mössbauer parameters.

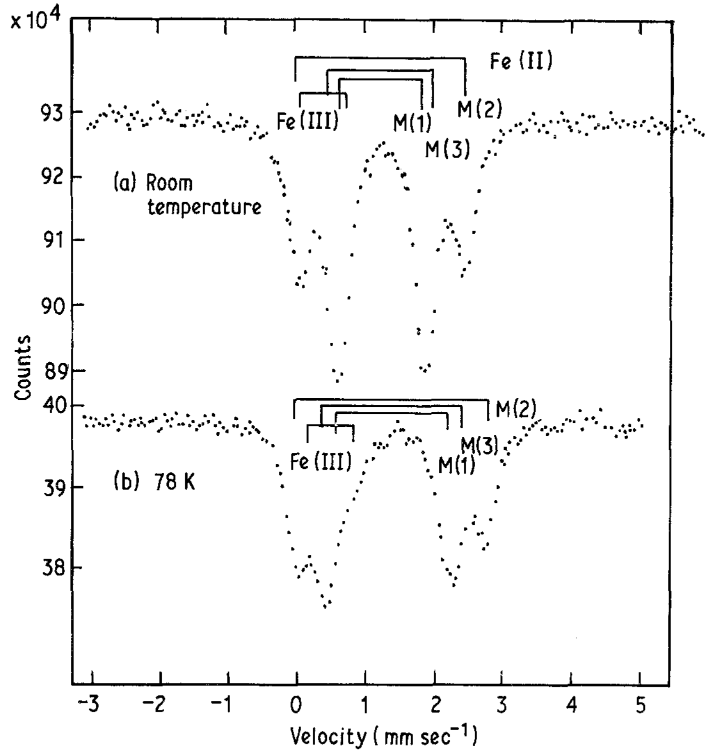

Figure 1 Mössbauer spectra of a powder sample scraped from a manganese phosphated steel surface. Measuring temperature: (a) Room temperature; (b) liquid N_2 temperature.

3. Results and discussion

3.1. Chemical state of iron in manganese phosphate coatings

The TM spectra of the scraped sample from manganese phosphate coatings, measured at room and liquid nitrogen temperatures, are shown in Fig. 1.

The Mössbauer spectra are composed of three doublets showing the presence of three kinds of paramagnetic iron (II) species, the Mössbauer parameters of which agree well with those of iron (II)-substituted hureaulite [9] at three sites of octahedral crystal structure [12, 13], and a doublet of paramagnetic iron (III) species, which is considered to be trapped in the coatings during the formation of manganese phosphate layers. The iron (III) species is assumed to result from the iron (II) ion which has been released from the steel and further oxidized by the nitrate ion present in the phosphate bath. The Mössbauer parameters of iron species in manganese phosphate coating are calculated and summarized in Table II.

3.2. Change of composition of manganese phosphates coatings with immersion time in the phosphating bath

The variation of weight and the contents of manganese and iron in the manganese phosphate coatings with immersion time (0.5 to 20 min) are shown in Figs 2 and 3, respectively.

TABLE II Mössbauer parameters of powder samples scraped from manganese phosphate coatings

Temperature	I.S. (mm sec^{-1})	Q.S. (mm sec^{-1})	FWHM	State of iron
Room temp.	1.244 ± 0.005	2.487 ± 0.007		M(2)
	1.23 ± 0.03	1.49 ± 0.05	0.323 + 0.005	Fe (II)* M(1)
	1.24 ± 0.05	1.24 ± 0.09		M(3)
	0.3 ± 0.3	0.5 ± 0.6		Fe (III)
78 K	1.382 ± 0.005	2.81 ± 0.008		M(2)
	1.36 ± 0.01	1.98 ± 0.02	0.332 ± 0.008	Fe (II)* M(1)
	1.35 ± 0.01	1.64 ± 0.02		M(3)
	0.49 ± 0.01	0.71 ± 0.02		Fe (III)

*Iron (II) states correspond to iron (II) ions substituted at three manganese sites [M(1), M(2) and M(3)] of octahedrons in hureaulite structure [9].

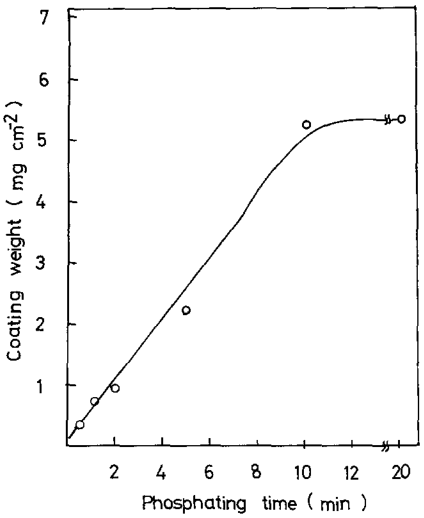

Figure 2 Relationship between phosphating time and weight of manganese phosphate coatings.

At the initial stage of formation of manganese phosphate layers, the weight of the coatings and the iron content in the coatings increase linearly with the duration of phosphating. After 10 min immersion, the greater part of the coatings are deposited. The coating thickness is about 5 mg cm^{-2}, which corresponds to 15.4 μm hureaulite $\rho = 3.24$). The weight of coating remains almost constant with the progress of manganese phosphating. However the manganese content in the coating increases, whereas the iron content decreases. The sum of manganese and iron contents in the coatings is almost 34% irrespective of the duration of the phosphating. The figure is less than the stoichiometric value of manganese and iron contents in hureaulite (36%).

All X-ray diffraction patterns of the manganese phosphate coatings indicate the presence of hureaulite as a major constituent. The coatings are considered to be composed of a large amount of hureaulite with various fractions of iron and manganese in addition to a small amount of the other phosphate compounds.

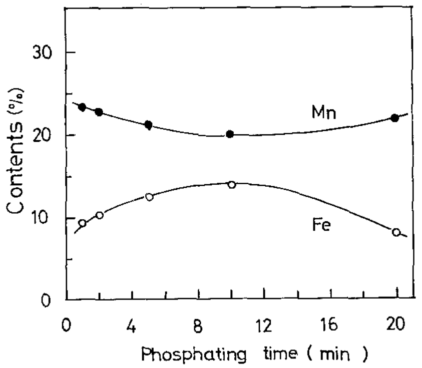

Figure 3 Relationship between phosphating time and contents of manganese and iron in manganese phosphate coatings.

The CEM spectra of the manganese phosphate coatings are shown in Fig. 4. In the CEM spectra of the samples phosphated for 2.5 and 5 min, the sextet peaks of the substrate steel and the doublet peaks of paramagnetic iron (III) compound are seen. The doublet peaks of paramagnetic iron (II) species appear in addition to the peaks of the iron (III) species and substrate for the samples phosphated for 10 and 20 min. Three doublet peaks of paramagnetic iron (II) species are assigned to the iron ions substituted hureaulite reported previously [9].

As shown in Fig. 4c and d, the relative peak intensity of the two inner doublets [M(1) + M(3)] of hureaulite formed on the steel by 20 min phosphating is higher than that of hureaulite formed by 10 min phosphating. A previous study revealed that the highness of the relative peak intensity of inner doublets of hureaulite is attributed to the fact that iron (II) ions preferentially occupy the M(1) and M(3) sites of the octahedrons of the hureaulite crystal lattice [9]. The results of CEMS study indicate that the main composition of manganese phosphate coating changed from hureaulite with high iron (II) content to hureaulite with low iron (II) content after the saturation of coating. This conclusion is also confirmed by the determination of manganese and iron contents in the manganese phosphate coating.

In the course of formation of the phosphate layer, iron-enriched hureaulite begins to grow, and after the steel surface is almost perfectly covered with a leading phosphate compound such as hureaulite, iron ions in hureaulite begin to be substituted by manganese ions in the phosphate solution. The hureaulite with low iron (II) content is formed last as a manganese phosphate coating.

3.3. Estimation of coating thickness detected by CEMS

The spectrum of iron located beneath a manganese phosphate coating of about 16 μm thickness, which is thicker than the range of L internal conversion electrons in hureaulite, is observed. The phenomenon is due to polycrystallinity, porousness and non-uniformity of the manganese phosphate

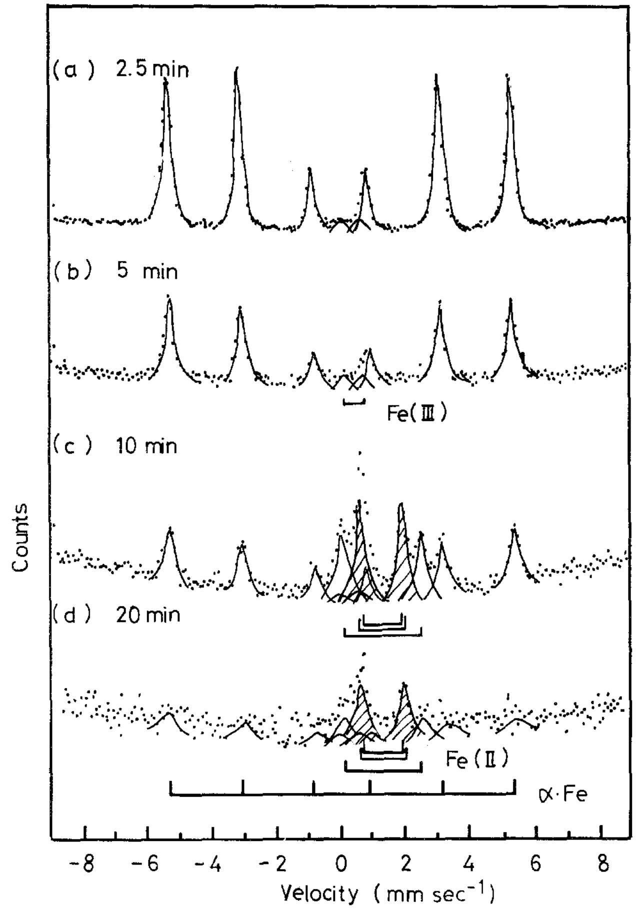

Figure 4 Variation of conversion electron Mössbauer spectra of manganese phosphate coatings with duration of phosphating. (a) 2.5 min, (b) 5 min, (c) 10 min, (d) 20 min.

coating (Fig. 5). Conversion and Auger electrons re-emitted at the interface of steel and coating can pass through the vacant space and come out into the counter, in addition to the contribution of secondary electrons emitted by the irradiation of scattered γ- and X-rays to the surrounding materials.

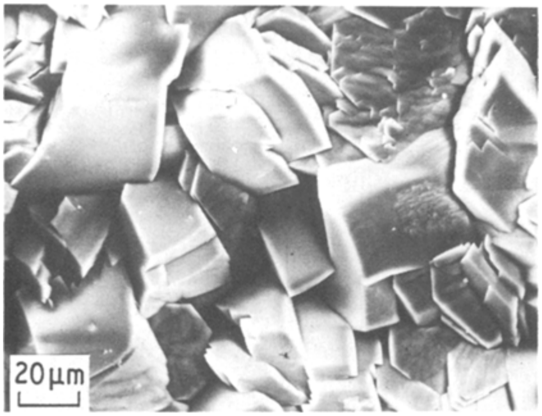

Figure 5 Scanning electron microscopic image of manganese phosphate coating.

The degree of fixation of the coated substances to the steel surface is estimated through the intensity ratio among the magnetically split peaks of substrate iron. Since the ratio of six peaks of iron was 3 : 2.5 : 1 : 2.5 : 3 when the steel was phosphated for 10 min, whereas the theoretical ratios is 3 : 4 : 1 : 1 : 4 : 3 when the magnetic orientation of surface iron is perpendicular to incident γ-ray [14]. The phosphate compounds deposited at the steel surface was considered to be tightly fixed to the steel surface.

3.4. Thermal transformation of hureaulite

The manganese phosphate coating, which contained 7% iron and 27% manganese, was mechanically scraped off from the phosphated steel surface and subjected to the thermal analysis by DTA. The result is shown in Fig. 6a. The thermogram of the scraped-off powders is similar to that of the synthetic manganese hureaulite (Fig. 6b).

The dehydration of hureaulite with higher iron (II) contents is apt to proceed via three steps. In the case of hureaulite, $(\mathrm{Mn}_{0.53}, \mathrm{Fe}_{0.47})_5\mathrm{H}_2(\mathrm{PO}_4)_4\cdot$

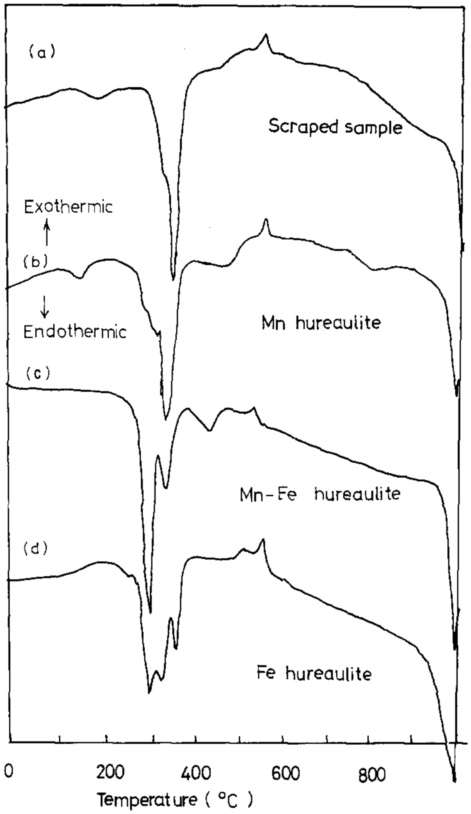

Figure 6 DTA curves of hureaulite. (a) Manganese phosphate coating. (b) Synthetic Mn hureaulite. (c) Synthetic Mn–Fe hureaulite. (d) Synthetic Fe hureaulite.

$4H_2O$, endothermic peaks appear at 286, 328, 431, and 980° C, and the weight loss of the corresponding peaks is 6.6, 3.9, 1.5, and 0%, respectively. The exothermic peak is observed around 538° C. As hureaulite loses 9.8% of its weight due to the dehydration of four water molecules, the dehydration is found to be accomplished under 350° C. The endothermic energy at 980° C causes the fusion of manganese phosphate compounds.

On the basis of the foregoing results, samples of synthetic hureaulite were heated at a rate of 10° C min^{-1} in nitrogen gas and held for 30 min at 280, 380, 580, 850, or 980° C. The diffraction lines of samples heated at 280 and 380° C are not recognized clearly. X-ray diffraction patterns of samples heated at 580, 850 and 980° C prove the presence of anhydrous manganese–iron phosphate compounds, which are presumed to be composed of wolfeite, $(Fe, Mn)_2(PO_4)(OH)$, hetrosite, $(Fe, Mn)PO_4$, and other unidentified compounds.

Mössbauer spectra and parameters of these pyrolysis products are shown in Fig. 7 and Table III, respectively. The peaks due to the paramagnetic iron (III) species (isomer shift (I.S.) = 0.48 mm sec^{-1}, quadrupole splitting (Q.S.) = 0.65 mm sec^{-1}) are found in all spectra. It is considered that the iron (III) compound is the oxidation product of iron (II) in hureaulite because the samples were heated in an atmosphere of nitrogen and residual air. The Mössbauer parameters of phosphate compounds produced by the thermal transformation of hureaulite vary slightly. Characteristic doublet peaks of iron (II) species (I.S. = 1.18 mm sec^{-1}, Q.S. = 3.46 mm sec^{-1}) are seen in the Mössbauer spectrum of the sample heated at 580° C through an exothermic process, besides the paramagnetic iron (II) (I.S. = 1.2 mm sec^{-1}, Q.S. = 2.4 mm sec^{-1}; I.S. = 1.1 mm sec^{-1}, Q.S. = 1.9 mm sec^{-1}) and iron (III) (I.S. = 0.5 mm sec^{-1}, Q.S. = 0.6 mm sec^{-1}) species.

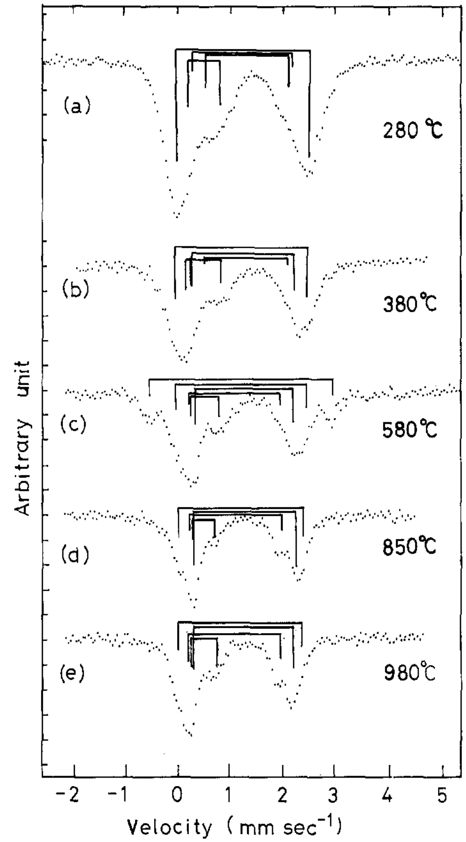

Figure 7 Mössbauer spectra of pyrolysis products of hureaulite. Heating temperature (30 min) – (a) 280° C, (b) 380° C, (c) 580° C, (d) 850° C, (e) 980° C.

Hureaulite is concluded to have a good resistance to thermal deterioration against the dehydration as compared with hopeite [15] and phosphophyllite [8], deposited by phosphating in a zinc phosphate bath.

TABLE III Mössbauer parameters of pyrolysis products of hureaulite, $(Mn_{0.53}, Fe_{0.47})_5H_2(PO_4)_4 \cdot 4H_2O$

Heating temp. (°C)	I.S. (mm sec^{-1})	Q.S. (mm sec^{-1})	FWHM (mm sec^{-1})
280	1.20 ± 0.01	2.55 ± 0.02	0.50 ± 0.01
	1.1 ± 0.9	1.9 ± 1.8	
	1.3 ± 0.8	1.5 ± 1.7	
	0.47 ± 0.02	0.65 ± 0.03	
380	1.18 ± 0.02	2.53 ± 0.03	0.43 ± 0.01
	1.20 ± 0.02	1.99 ± 0.03	
	1.3 ± 0.08	1.5 ± 1.6	
	0.48 ± 0.04	0.65 ± 0.07	
580	1.18 ± 0.02	3.46 ± 0.03	0.336 ± 0.008
	1.18 ± 0.03	2.46 ± 0.04	
	1.25 ± 0.03	1.88 ± 0.04	
	1.06 ± 0.06	1.7 ± 0.1	
	0.48 ± 0.03	0.67 ± 0.04	
850	1.18 ± 0.04	2.38 ± 0.08	0.35 ± 0.01
	1.26 ± 0.1	1.9 ± 0.2	
	1.1 ± 0.2	1.7 ± 0.4	
	0.5 ± 0.5	0.5 ± 0.9	
980	1.18 ± 0.02	2.38 ± 0.04	0.284 ± 0.008
	1.27 ± 0.03	1.92 ± 0.05	
	1.05 ± 0.03	1.81 ± 0.06	
	0.51 ± 0.02	0.47 ± 0.05	

4. Conclusions

The variations of the chemical composition of phosphated coatings and the physical state of the interface between substrate and coating in the course of formation of manganese phosphate coating are revealed by means of CEMS and TMS.

Three different iron (II) species and one iron (III) species are found in the manganese phosphate coating. Three iron (II) species were identified to be the iron (II)-ion substituted hureaulites of the three manganese sites of the octahedral crystal lattice of manganese hureaulite to the order of one, two and three sites.

The degree of iron substitution for manganese sites in hureaulite deposited at the steel surface by manganese phosphating depends on the phosphating time, as well as the concentration of iron (II) and manganese (II) ions in the phosphating bath.

The dehydration and thermal transformation processes of manganese phosphate coatings and synthetic hureaulite were clarified. The DTA curve of the scraped-off sample from manganese phosphate coating is similar to that of manganese-enriched hureaulite.

A characteristic iron (II) species is found to be produced in the pyrolysis products of hureaulite heated to temperatures higher than the exothermic point.

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