Analysis of black layers on steel using conversion electron Mössbauer spectrometry

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Iron and steel were treated in alkaline solutions at boiling point, and the black layers produced on their surfaces were analysed using conversion electron Mössbauer spectrometry (CEMS). The CEM spectra, measured at room temperature, consisted of distorted magnetically split peaks or broad doublet peaks due to ferrimagnetic and superparamagnetic magnetite, respectively. The refined and black surface of steel consisted of fine particles of magnetite with many cations' vacancies at the octahedral structure (B site).

1. Introduction

Alkaline treatment of steel yields a refined and black surface, which sensitively affects the scale of steel goods and contributes in preventing the corrosion of steel. The black coating also has a stronger resistance to mechanical working, such as friction and impact, compared with other coatings deposited by chemical treatment of the steel surface. The black coating produced by alkaline solution has been presumed to be magnetite layers. The coating product, however, could not be confirmed easily because the X-ray diffraction peaks did not appear clearly, as the coating thickness was less than 1 μm.

We have investigated the iron states in various types of phosphate coating — zinc, zinc—calcium, manganese and iron phosphate coatings [1–6] — in oxalate coating of iron and stainless steel [7], and on steel corroded by inorganic solutions [8, 9] using conversion electron Mössbauer spectrometry (CEMS). ^{57}Fe CEMS can be effectively applied to the chemically treated surface of steel and gives information on the chemical state and epitaxial growth of iron compounds produced at the surface or at the interface between the coating and the substrate, and on the thermal deterioration of coatings [10].

The application of Feldman's equation [11] to

magnetite ($\rho = 5.2$) gives the range of re-emitted electrons in the layer, by the internal conversion process after the Mössbauer effect:

$$R(\text{nm}) = 1.11 \, E(\text{keV})^{2.94}$$

The average range of electrons is calculated to be about 400 nm in magnetite, considering an emission probability of 7.3 keV K-(79%), 13.6 keV L-conversion (8%) and 5.5 keV Auger (63%) electrons [12]. In this paper, we describe the results of the characterization of the black coatings obtained by alkaline treatment of steel.

2. Experimental details
2.1. Sample preparation

The sheets of cold rolled steel (SPCC-B) were degreased with an alkaline cleaner at 70° C, washed with deionized water and diluted HCl, and then were immersed in several kinds of sodium

TABLE I Constituents (wt %) of alkaline solutions used for black coating

Number	NaOH	NaNO$_3$	NaNO$_2$	NaCl	H$_2$O
1	25	25	–	–	50
2	25	–	25	–	50
3	28	15	7.0	–	50
4	27	15	7.0	1.0	50
5	46	2.0	1.0	5.0	46

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hydroxide solution containing the oxidizing reagents such as $NaNO_3$ and $NaNO_2$, maintained at boiling temperature (130 to 150°C) for several minutes. The constituents of several of the alkaline solutions are shown in Table I. After alkaline treatment, the sheets of steel were washed in hot water (70°C) and dried in a stream of air.

2.2. Measurement of Mössbauer spectra

CEM spectra of the black coatings were observed by detecting resonantly re-emitted electrons by a gas-flow (95% He + 5% CH_4) counter or a ceramic electron multiplier [12, 13], coupled to a Mössbauer spectrometer. The former electron detector was designed so that incident γ-rays could irradiate the sample at the incident angles of 45° and 90°. The working characteristics of the gas-flow counter designed are described in detail elsewhere [14]. The latter ceramic electron counter was used for measuring CEM spectra at liquid nitrogen temperature. A 25 mCi ^{57}Co(Rh) source was used as the 14.4 keV γ-ray source. A part of the CEM spectra was computer-fitted, assuming a Lorentzian line shape using a Mössbauer fitting programme [15].

3. Results and discussion
3.1. Surface products on iron foil

The CEM spectrum of the iron foil (12.7 μm thick), immersed in alkaline solution for 20 min at boiling point, is shown in Fig. 1a. The peaks of surface iron products were observed in super-position to the sextet peaks of the substrate. The spectrum in Fig. 1b was obtained by the subtraction of the substrate peaks. This facilitated analysis of the CEM spectrum of surface products. These peaks consist of asymmetric peaks of magnetically split sextets. Each peak has the characteristics of tailing to zero velocity, and the intensity ratio $P_{3,4}/P_{1,6}$ deviates from the theoretical ratio (1/3). The magnetically split peaks may be composed of several components. These peaks were resolved into two sextets of broad peaks (6 × 2 = 12). The internal magnetic field of the product was undoubtedly weaker than that of magnetic iron oxide, although some uncertainty remained in the calculation of asymmetric peaks assuming a Lorentzian line shape. The internal magnetic fields of the two components were 47 ± 2 and 43 ± 2 T, which were 2.0 to ∼ 3.0 T smaller than those of magnetite. The spectrum of magnetite consists of two super-imposed sextets due to the Fe^{3+} in the tetra-hedral (A) site and to Fe^{2+} and Fe^{3+} in the octa-hedral (B) site with a relaxation time of 1.1 ± 0.2 nsec at room temperature [16].

The area ratio of B to A sites was smaller than that in stoichiometric magnetite, the actual intensity ratio of which was reported to be 1.88:1 owing to the different recoilless fraction of iron at the two different sites [17]. The magnetite produced on the steel surface was found to be non-stoichiometric, $Fe_{3-x}O_4$, with cation vacancies at the B site [18].
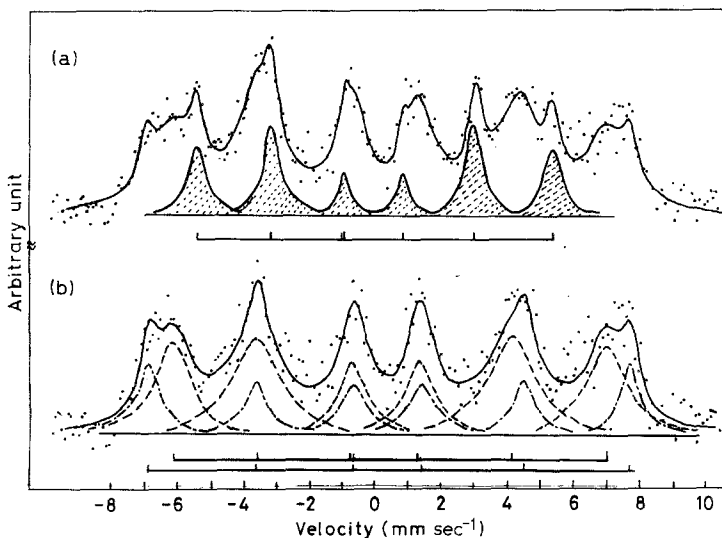

Figure 1 CEM spectra of iron foil treated in alkaline solution 3 at boiling point. (a) Surface products and iron substrate. (b) Surface products (iron substrate peaks were subtracted).

3.2. Effect of oxidizing agent in alkaline solution on the formation of surface products

The surface of iron sheets did not become black by the immersion in sodium hydroxide (50 wt%), or $NaOH$ (6%) + $NaNO_3$ (26%) + $NaNO_2$ (16%) solutions at boiling point for 10 min. In CEM spectra of these samples, no peaks except substrate iron, appeared. Less than 5 nm oxide layer is thought to be deposited on the surface by the treatment, because a detectable depth layer of CEMS is estimated to be more than ~ 5 nm for the sample of natural iron [19].

As shown in Fig. 2, the oxidizing reagents (NO_3^-, NO_2^-) did accelerate the deposition rate of the surface product. The peak intensity of magnetite produced on steel by treatment in alkaline solutions containing nitrite was greater than that of the product deposited by the treatment in alkaline solutions containing nitrate. This phenomenon is explained by the faster decomposition of nitrite than nitrate. The nitrite ion in alkaline solution was considered to facilitate the oxidation of steel to Fe^{2+} and Fe^{3+} and to deposit the black layer effectively compared with the nitrate ion. Using the experimental relationship between the magnetite film thickness (d, nm) and the area intensity ratio (P) of magnetite films to the intensity of all peaks [20],

$$d\,(nm) = -1.95 \times 10^2 \ln(1 - 0.01\,P),$$

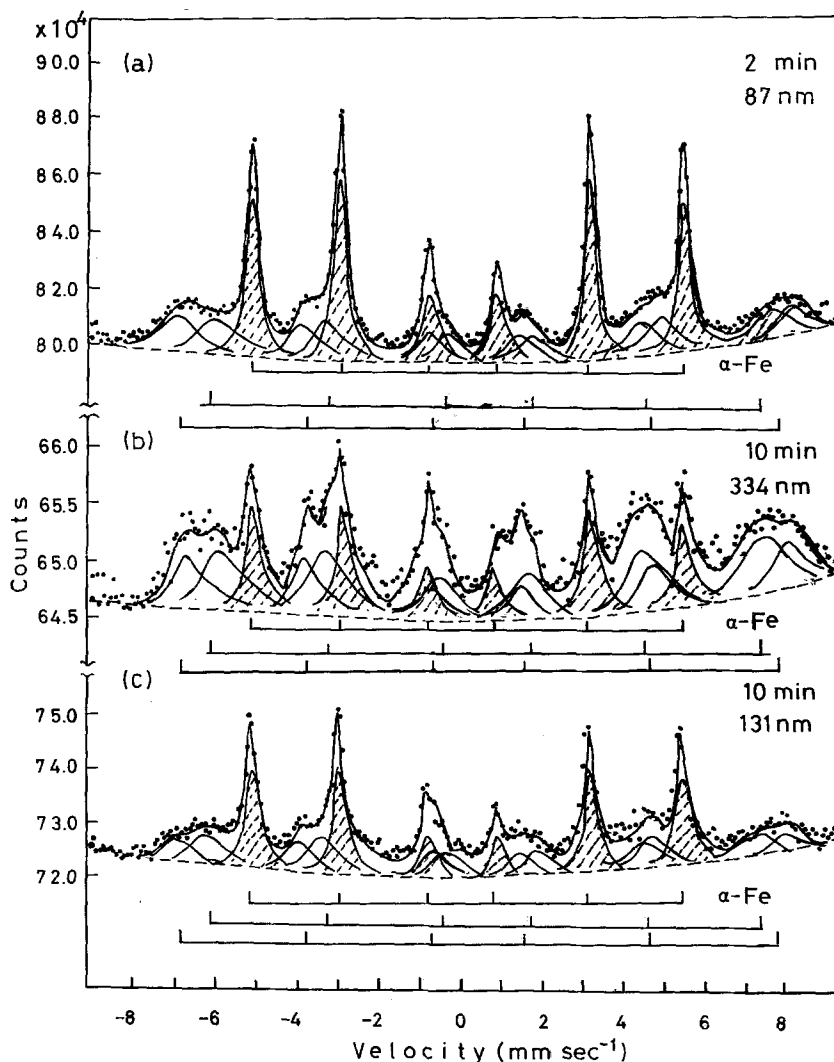the thicknesses of magnetite layers produced by

Figure 2 CEM spectra of steel surface treated in alkaline solutions. (a) Solution 2, immersion time 2 min. (b) Solution 2, immersion time 10 min. (c) Solution 1, immersion time 10 min.
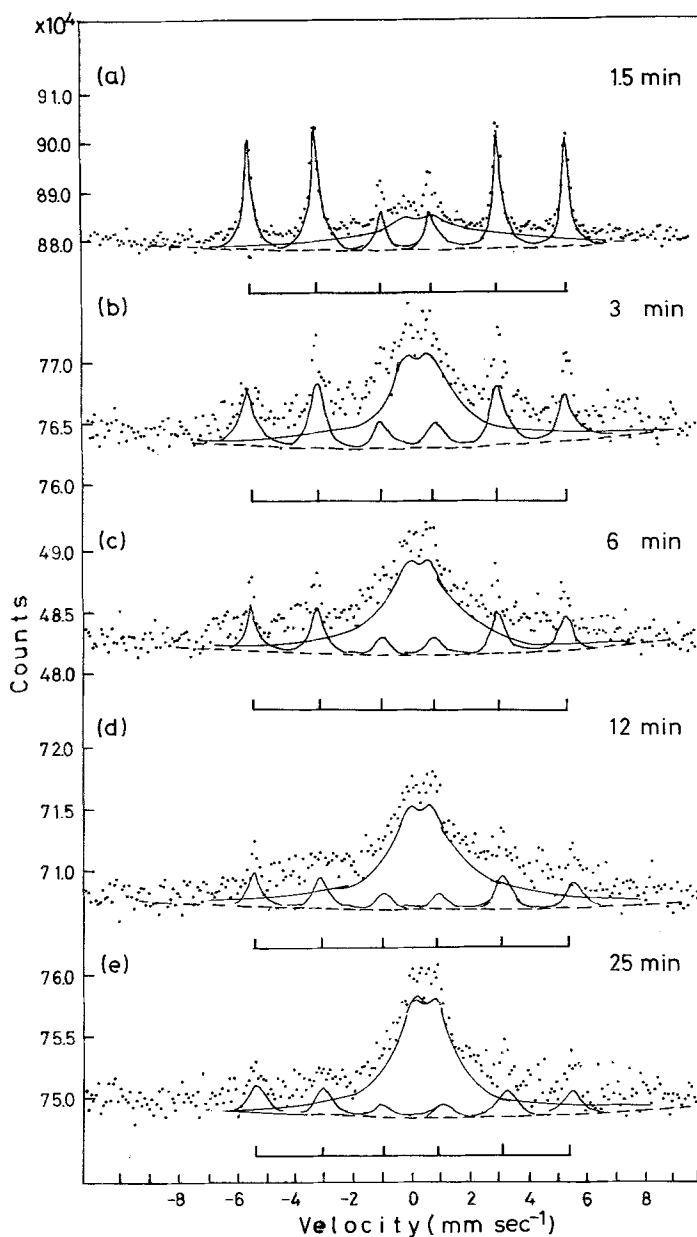
the treatment of steel in an alkaline solution containing nitrite ions were found to be 87 and 334 nm for the immersion times of 2 and 10 min, respectively. On the other hand, the thickness of the magnetite layers produced in an alkaline solution containing nitrate ions was 131 nm after an immersion for 10 min.

3.3. Effect of immersion time on coating

The CEM spectra of the black coating deposited on the steel sheets, dipped in an alkaline solution (NaOH (28%) + NaNO$_3$ (15%) + NaNO$_2$ (7%) + H$_2$O (50%)) at boiling point for 1.5, 3, 6, 12, and 25 min, are shown in Fig. 3. All spectra have doublet peaks (I.S. = 0.40 ± 0.13, Q.S. = 0.74 ± 0.08, Γ = 1.2 ± 0.6 mm sec^{-1}) of the products in addition to the sextet peaks of the substrate. With the increasing immersion time, the broad doublet peaks grew. CEMS for the sample treated for 12 min were measured at liquid nitrogen temperature using a CEM spectrometer equipped with a ceramic electron multiplier detector. As shown in Fig. 4, magnetically split peaks appeared at liquid nitrogen temperature. The form of the sextet peaks was quite similar to that of magnetite below the Verwey transition temperature (119 K)
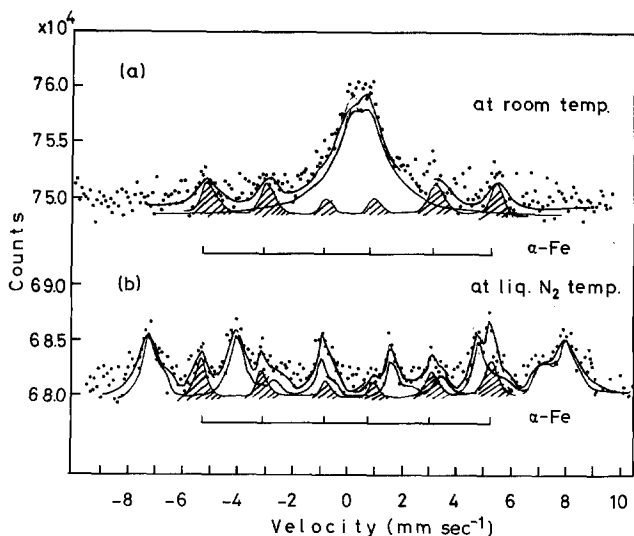
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Figure 4 CEM spectra of black coating measured at (a) room temperature and (b) liquid nitrogen temperature.

[12, 21]. The doublet peaks observed at room temperature were considered to be due to magnetic relaxation, the relaxation time of which was estimated to be shorter than those shown in Figs. 1 and 2.

From the fact that the doublet peaks grew with the increasing immersion time, the particle size of magnetite formed in the nascent stage did not grow, but the number of magnetite particles increased on the steel surface with immersion time. When the oxide film increased to a certain thickness, the substrate was prevented from oxidizing. The relationship between thickness of magnetite film and immersion time is shown in Fig. 5.

The change of reflectance of the surface coatings of various thicknesses to the light incident on the sample surface at 60° is shown in Fig. 6. Although the thickness of the black coatings was saturated by the several minutes immersion, the surface roughness increased with increasing immersion time up to 25 min.
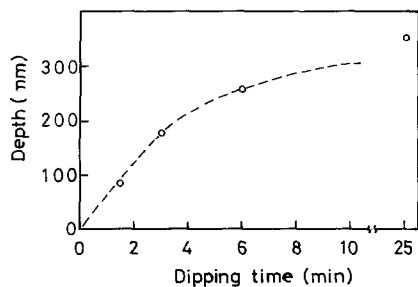

Figure 5 Relationship between the thickness of black coatings and immersion time.

According to the report of Mørups *et al.* [22] on the magnetic relaxation of magnetite due to the particle size effect, these black coatings were estimated to consist of magnetite 7 to 9 nm in size, which could produce a sensitive change in the Mössbauer spectra at room temperature. Even if an alkaline solution of the same constituents was used, magnetically split peaks, different from the broad doublet peaks, sometimes appeared in the CEM spectra at room temperature, depending on many factors such as pre-treatment. It is difficult to control the particle size of magnetite in the coating within several nm by the present technological level.

Berry *et al.* [23] reported that immersion of a peeled iron plate in sodium hydroxide solution (16.6 wt%) containing sodium nitrate and nitrite and drying in a desiccator, gave a dark grey surface on the metal. Since the superimposed peaks of a doublet (I.S. = 0.19, Q.S. = 0.88, $\Gamma = 1.2$ mm sec^{-1}) on a sextet of iron were observed and no peaks characteristic of ferromagnetic haematite or ferri-magnetic magnetite were seen at all in their CEM spectra, Berry *et al.* deduced that amorphous iron (III) hydroxides or oxyhydroxides were contained in the surface films. A CEM spectrum of a steel sheet immersed in an identical solution as that of Berry *et al.* was composed of weak magnetically split peaks characteristic of ferro- or ferri-magnetic iron oxides such as in Fig. 1. The broad doublet peaks reported by Berry *et al.* are considered to be due to the superparamagnetic magnetite or amorphous iron oxyhydroxides formed as by-products.
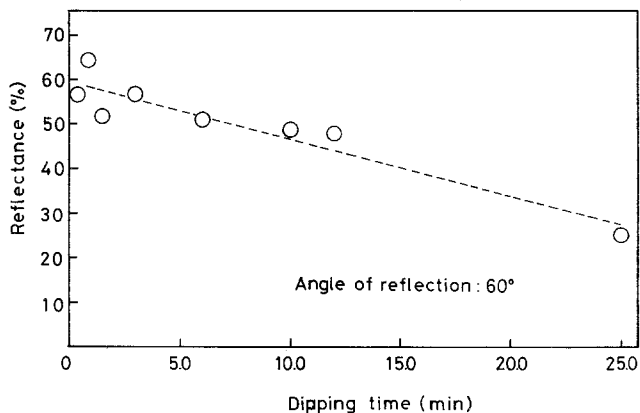
3.4. Effect of chloride ion in alkaline solution on the formation of coating

CEM spectra of coatings produced on steel by immersion in alkaline solutions containing 1 and 5% NaCl are shown in Fig. 7. These coatings were formed in a shorter time than on immersion in alkaline solutions free of chloride ions. The surface of the coating (Fig. 7b) was reddish-brown and gave sharp doublet peaks (I.S. = 0.33 + 0.02, Q.S. = 0.77 + 0.03, $\Gamma = 0.46 + 0.07$ mm sec^{-1}) in the CEM spectra. The shape of the doublet peaks was different from the broad doublet peaks caused by the superparamagnetic phenomenon of magnetite. These doublet peaks were considered to be attributable to β- and γ-forms of FeOOH [24, 25].

A small amount of chloride ion included in the alkaline solution promotes the formation of the black coating but the presence of a large amount of chloride ions changes the properties of the coating to oxidized iron (III) oxyhydroxide.
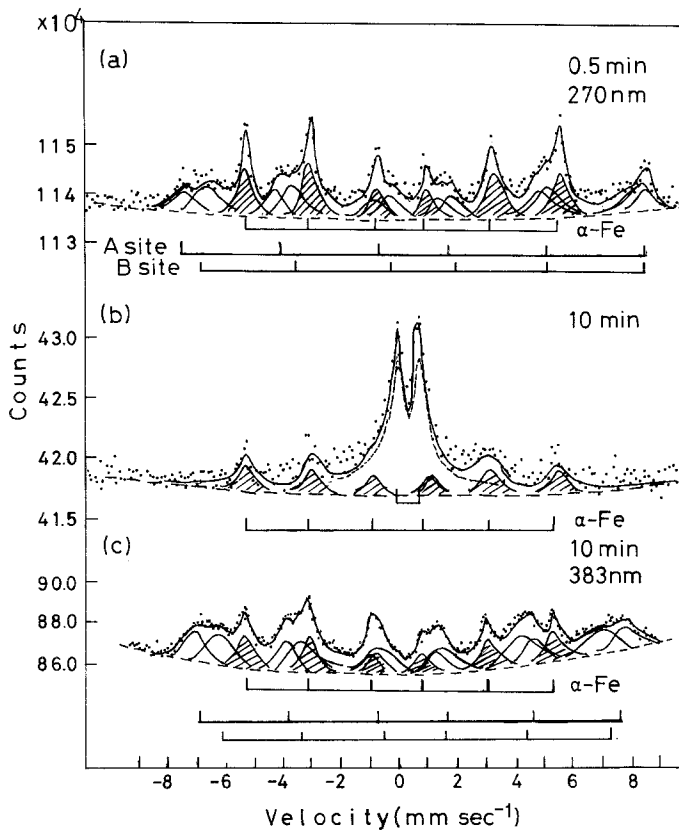

Figure 7 CEM spectra of steel surface treated by alkaline solutions containing Cl$^-$ ion. (a) Solution 5, immersion time 0.5 min. (b) Solution 5, immersion time 10 min. (c) Solution 4, immersion time 10 min.

4. Conclusions

The chemical state of black coatings, produced on steel by treatment in several kinds of alkaline solution at boiling point, were effectively analysed by CEMS.

The broad doublet and magnetically split peaks in the CEM spectra observed at room temperature were attributed to the magnetically relaxed magnetite caused by a particle size effect. The black coating on steel formed by alkaline treatment was found to consist of nonstoichiometric magnetite, the thickness of which was less than about 400 nm and the particle size of which lay between about 7 and 10 nm.

Acknowledgement

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