Investigation of the oxide layer structure of iron pigments by high-resolution TEM

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Abstract

Fine acicular iron pigments have been investigated by transmission electron microscopy in order to elucidate the nature of the oxide shell covering the metal. Different commercial-grade MP pigments were found to exhibit uniform oxide layers of magnetite about 4 nm thick, forming an oriented overgrowth on the metallic core. By means of selected area electron diffraction as well as high-resolution transmission electron microscopy, we have detected an epitaxial relationship between the oxide shell and α-iron core of the Nishida–Wassermann type, i.e. (110)Fe||(211)mag, [001]Fe ||[011]mag; and (100)Fe||(100)mag, [001]Fe ||[011]mag.

Keywords: Iron particles; Magnetic storage pigments; Oxide layer structure

1. Introduction

Needle-shaped iron pigments for magnetic recording are usually covered by natural or artificial oxide layers. Because of this, for example, a particle 0.15 μm long with an aspect ratio of 6 and an oxide layer thickness of 4 nm loses about 40% of its metallic iron. This is more than half of the oxidized particle volume. Consequently, the average magnetization is reduced to about half of the bulk value. The iron pigment production is aimed to optimize the oxide layer formation in order to prevent them from uncontrolled increase and to avoid further losses of metallic iron during the lifetime of the recording medium.

Knowledge of the thickness, structure and chemical composition of the oxide shell as well as its crystallographic relationship to the iron core is required for a better understanding of the durability of MP pigments. Information on the nature of the oxide shell is also important for the selection of suitable organics to enhance the dispersibility, as well as the adhesion between individual pigments and polymer matrix in the tape, and consequently, for the effective protection of the iron particles [1,2].

2. Experimental

Three commercial-grade MP pigments with different aspect ratios (5–10) were prepared for trans-
mission electron microscopy (TEM) examination by dispersing the pigments in acetone solvent and spraying onto microscope grids. Thus the pigments are located on electron transparent carbon films in the form of aggregates (see Fig. 1) and of individual needles (see Figs. 2–6). Selected area electron diffraction (SAED), bright-field and dark-field imaging, as well as high-resolution transmission electron microscopy (HRTEM) was done using JEM 100C and JEM 4000EX electron microscopes operated at 100 and 400 kV, respectively. It was assumed that no changes in the oxide shell structure take place during preparation. There was no evidence of structural degradation of the oxide during the electron microscopy examination.

3. Oxide shell identification

As may be seen in Fig. 2(a), in a bright-field image at medium magnification the appearance of the particles is characterized by a dark core surrounded by a lighter thin shell. The corresponding SAED pattern shown in Fig. 2(b) exhibits typical features: (i) strong diffraction spots according to a single-crystalline α-iron core (lattice constant 0.2866 nm) having a needle axis orientation of [011], as can be concluded from the orientation relationship between the bright-field image and the diffraction pattern; and (ii) weak diffraction spots, situated predominantly perpendicular to the needle axis in the reciprocal space, which are well oriented with respect to the bcc iron spots without showing the characteristics of the α-iron lattice (i.e. spacings and angles). Instead, as indexed in the schematic representation of the diffraction pattern Fig. 2(c), these diffraction spots could be attributed to the cubic lattice of magnetite (\(\text{Fe}_3\text{O}_4\)) which occurs in an epitaxial relationship to the iron core (see below).

The oxide nature of the shell was identified by dark-field imaging using the strong reflections (002), (\(\overline{1}12\)) and (\(\overline{1}10\)) of α-iron, as indexed in Fig. 2(b), and alternatively the weak reflections of magnetite (131), (022) and (113) (see Fig. 2b). The corresponding images are shown in Fig. 3. In Fig. 3(a) the bright contrast results mainly from the metallic core, and in Fig. 3(b) the oxide shell is imaged bright. Slight changes in the brightness of the image in Fig. 3(a) hint at the presence of mechanical strains in the iron core.

The mean characteristics as needle thickness, aspect ratio of the particles and oxide layer thickness, respectively, of the MP samples were determined from bright-field images and presented in Table 1. Despite the different lengths and aspect ratios of the

Fig. 1. Aggregate of rod-like particles of a MP type with high aspect ratio (marker 100 nm).
samples under investigation, in all cases the oxide thicknesses were found to be similar.

Assuming that the aspect ratio remains constant upon oxidation, from the density of iron 7.86 g/cm$^3$ and that of magnetite 5.1 g/cm$^3$, together with the values of Table 1, we can calculate the number ratio of iron atoms in the oxide shell to the overall number of iron atoms in the particles. Accordingly, samples I, II and III have lost 44%, 53% and 39%, respectively, of their initial metallic iron due to oxidation.

4. High-resolution transmission electron microscopy

Due to its ability to image structural details down to an atomic scale of resolution, HRTEM is well suited for the characterization of particulate shell-core materials of nanometer size. As demonstrated schematically in Fig. 4, which shows in cross-section the electron beam transmitting through an individual MP particle, the structure of both shell and core may be elucidated. The image contrast in the central part results from a superposition of the bcc lattice of the α-iron core and the oxide lattice situated at the top and bottom of it. In both side regions the image contrast results from the oxide layer only. The transmitted oxide thickness is larger here than in the centre.

Fig. 5(a) and Fig. 6(a) show HRTEM images of the tip and the body of the needle-shaped particles where the metallic core in (100) orientation is identified by the crossed (011) and (011) lattice plane.
fringes of α-iron running perpendicular to each other. The needle axis orientation here is \(\langle 001\rangle\). The lattice plane distance of α-iron \(d(011)_{Fe} = 0.2027\) nm is used as an internal standard for determining the oxide lattice plane spacings. Most of them are identified as \(022\) lattice plane fringes of magnetite \(d(022)_{mag} = 0.297\) nm running parallel to the needle axis. Obviously, the \(\langle 011\rangle\) direction of magnetite is parallel to \(\langle 010\rangle\) of α-iron. In the tip region of the needle Moiré fringes are weakly visible in the oxide shell; these are due to the superposition of oxide growing in different orientations at the faceted needle tip.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Needle thickness (nm)</th>
<th>Aspect ratio</th>
<th>Oxide thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>21</td>
<td>4.9</td>
<td>3.8</td>
</tr>
<tr>
<td>II</td>
<td>19</td>
<td>7.4</td>
<td>4.2</td>
</tr>
<tr>
<td>III</td>
<td>22</td>
<td>9.5</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Fig. 4. Schematic drawing of the transmitted needle cross-section.

Fig. 5. HRTEM image of a needle tip region: (a) original lattice fringe image; (b) Fourier transform; reconstruction of the core (c) and the shell (d) by Fourier-filtered back-transformation.
In order to visualize the different lattices separated and more clearly, the images were digitized and subjected to Fourier-filtered back-transformation. This means that in the Fourier transforms shown in Figs. 5(b) and 6(b), which are calculated from the corresponding images in Figs. 5(a) and 6(a), alternatively the intensities resulting from the iron core or from the oxide shell, respectively, are used for back-transformation, whereas the remaining intensities are largely suppressed. Thus, the metallic core lattice, as shown in Figs. 5(c) and 6(c), as well as of the oxide shell lattice as shown in Figs. 5(d) and 6(d), can be distinctly recognized.

The observation of oxide layers exhibiting oriented overgrowth with respect to the metal by HRTEM agrees well with that by SAED (see Fig. 2), although different needle axis orientations are concerned.

4.1. Oriented overgrowth models for magnetite on iron

Uchikoshi et al [3] pointed out that magnetite or maghemite layers grown on clean iron surfaces are particularly effective for the passivation of ultrafine particles. Only by atmospheric corrosion is a further iron oxyhydroxide layer added to that oxide. After natural oxidation of iron particles the oxide is found to be amorphous [4] or poorly crystallized [5]. Annealing in a diluted atmosphere improves the oxidation resistance of the pigment by converting the amorphous oxide into the crystalline state [6].
By high-temperature oxidation of iron foils at high oxygen partial pressures, Kuroda et al. [7] found the development of highly strained fine-grained magnetite. This magnetite was converted to hematite only at a later stage of oxidation. Under high vacuum conditions strained FeOx is grown, which decomposes to an oriented magnetite during cooling to room temperature. The known epitaxial relationships between α-iron and magnetite are summarized in Ref. [8] as follows:

1. (100)Fe || (100)magn [001]Fe || [011]magn
2. (001)Fe || (001)magn [100]Fe || [100]magn
3. (110)Fe || (110)magn [001]Fe || [110]magn
4. (110)Fe || (111)magn [001]Fe || [110]magn
5. (111)Fe || (110)magn [110]Fe || [110]magn
6. (111)Fe || (111)magn [110]Fe || [110]magn

Describing the electron microscope examination of alloy steel, Edington [9] refers to the Nishiyama–Wassermann orientation relationship reported for magnetite and α-iron by Keown and Dyson [10]. These are:

7. (110)Fe || (111)magn [001]Fe || [011]magn
8. (110)Fe || (211)magn [001]Fe || [011]magn

Two of the results presented in the literature (1 and 8) obtained on thinned and oxidized iron foils agree with the results obtained here on small passivated MP pigments:

9. (110)Fe || (211)magn [001]Fe || [011]magn
10. (100)Fe || (100)magn [020]Fe || [022]magn

The pigments investigated here show a smooth iron surface with a large area epitaxial magnetite thin film. The oxide film is continuous, uniform in thickness, and shows good adherence, resulting in reasonably good corrosion resistance.

5. Conclusions

The MP pigments studied consist of single-crystalline α-iron cores which are covered by a continuous and adherent oxide shell about 4 nm thick, identified as cubic magnetite. The needle axis orientations observed are [011] and [001], respectively, in terms of the iron lattice.

The oxide shell is uniformly grown with an epitaxial orientation of the Nishiyama–Wassermann type to the underlying iron.

Depending on aspect ratio and size, the particles lose up to 50% of their initial metallic iron by oxidation.

References