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Mechanism of Biological Fe_3O_4 Synthesis, in Relation to Ferrite Plating

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Abstract: The mechanism of the magnetosome (Fe_3O_4) formations is elucidated from the basic findings on chemical reactions of iron oxides, especially those occurring in ferrite plating—a chemical process synthesizing spinel ferrite films from an aqueous solution. It is suggested that in both the biomineralization and the ferrite plating, (1) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation by NaNO_2 plays an essential role, (2) γ -FeOOH is formed as a precursor, and (3) Fe^{2+} ions are adsorbed on γ -FeOOH which is followed by spinel formation. It is also discussed how to synthesize ferrite films at room temperature by mimicking the biological Fe_3O_4 formation.

1. INTRODUCTION

Magnetite (Fe_3O_4) is the only known biogenic materials exhibiting ferromagnetism, which is found in fossil records and living organisms of various creatures [1]. Among the Fe_3O_4 biomineralizations, magnetosomes (which magnetotactic bacteria synthesize to use as a compass) has been attracting most intensive interest. The magnetosomes are Fe_3O_4 single crystals encapsulated by a membrane of lipid bilayer. Mann et al. [2] proposed that the Fe_3O_4 crystals are synthesized in the vesicles of the lipid bilayer, which involves the following steps: (1) uptake of Fe^{3+} ions from the environment into within the magnetosome vesicles by reduction step transforming Fe^{3+} to Fe^{2+} , (2) precipitation of hydrated ferric oxide within the vesicles, and (3) transformation of the hydrated ferric oxides to Fe_3O_4 .

In order to further elucidate the mechanism of the biological Fe_3O_4 formation, we will examine in this paper the basic findings on chemical reactions of iron oxides, especially those occurring in ferrite plating — a chemical process synthesizing spinel ferrite films from an aqueous solution [3, 4]. We will also discuss how to synthesize ferrite films at room temperature by mimicking the biological Fe_3O_4 formation.

2. BIOMINERALIZATION AND FERRITE PLATING

A close reaction has been found between the biomineralization and the ferrite plating as follows.

[1] In vitro experiments using an enzyme, cytochrome cd₁, extracted from magnetotactic bacteria suggested that the magnetite is synthesized from an aqueous solution of Fe^{2+} via oxidation of Fe^{2+} to Fe^{3+} by NaNO_2 activated by the enzyme [5]. The $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation plays an essential role also in the ferrite plating, for which NaNO_2 has been found to be the most expedient oxidizing reagent [3, 4].

[2] In the biological formation of Fe_3O_4 found in the denticles of the radular teeth of chiton, a shellfish, the Fe_3O_4 coating is formed, as shown in Fig.1, on apatite intermediated by γ -FeOOH, a ferric hydroxy oxide [6, 7]. This suggests that γ -FeOOH is found as a precursor on which Fe_3O_4 is produced. In the ferrite plating similar event is thought to occur, as inferred from the following experimental results.

When an aqueous solution (pH=8.5) of Fe^{2+} ions, or $\text{Fe}(\text{OH})_2$, was added continually to the aqueous solution (pH=8.5) suspending fine particles of γ -FeOOH, the amount of γ -FeOOH reduced, while that of Fe_3O_4 increased, as analyzed by X-ray and chemical analyses (Fig.2)[8]. When Fe^{2+} ions were added to an aqueous solution (pH=8.5) in which a stainless steel plate with a γ -FeOOH coat on the surface was immersed, Fe_3O_4 was formed on the γ -FeOOH layer as directly shown by an electrochemical method (Fig. 3) [9].

Fig. 1 (a): dorsal of chiton [7], (b): cross sections of chiton and its radula having denticles. (c): cross section of denticle [6].

Fig. 2 Amount of $\gamma\text{-FeOOH}$ (open circles) and Fe_3O_4 (closed circles), plotted as a function of time [8].

Fig. 3 Cathodic reduction curves obtained for oxide layers, A: Fe^{2+} ions were adsorbed on substrate surface which were then oxidized by air; B: Fe^{2+} ions were adsorbed again on the layer A; α : $\gamma\text{-FeOOH}$ layer; and β : Fe_3O_4 layer. A has an inflection point around -660mV, which coincides with that observed for α , showing that the layer A is $\gamma\text{-FeOOH}$; while B has no inflection point similar as β , thus revealing that the layer B is Fe_3O_4 [9].

3. ROOM TEMPERATURE Fe_3O_4 SYNTHESIS MIMICKING BIOMINERALIZATION

The ferrite plating is enabled only at high temperature, above $\sim 60^\circ\text{C}$, while the biological Fe_3O_4 formation is realized at room temperature. How to realize ferrite plating with reasonable speed of film deposition at room temperature?

As shown in the previous section, the formation of Fe_3O_4 from the Fe^{2+} aqueous solution have two major steps, (1) oxidation of Fe^{2+} to Fe^{3+} , forming the precursor, or $\gamma\text{-FeOOH}$; and (2) adsorption of Fe^{2+} on $\gamma\text{-FeOOH}$ which accompanies the spinel formation. When temperature is decreased from $\sim 60\sim 100^\circ\text{C}$ to room temperature, the rate of the spinel formation decreases much, while the rate of the Fe^{2+} oxidation decreases moderately. Therefore, the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation overwhelms the Fe^{2+} adsorption accompanying the spinel formation, so that not Fe_3O_4 but ferrous compounds such as $\gamma\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$ are formed at room temperature from the aqueous Fe^{2+} solution, as long as the conditions other than the temperature are unchanged in the ferrite plating. When the speed of the oxidation is reduced by some way, e.g. using very dilute air/ N_2 mixed gas as the oxidizing reagent, Fe_3O_4 has been actually synthesized at room temperature, though the growth rate is very low [10]. Therefore, we must stimulate the spinel formation in order to realize room temperature ferrite plating of reasonable speed. This may be attained by using substrates with functionalized surface [11], as of lipid bilayer of vesicles [12] or cast films [13], and of Langmuir-Blodgett films, which mimic the magnetosome membrane. It may be also attained by utilizing enzymes which the magnetotactic bacteria use to stimulate the spinel formation.

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