Metamorphosis of Single Crystalline Hematite to Iron Sulfides Influenced by Sulfate-reducing Bacteria

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ABSTRACT

In the presence of sulfate-reducing bacteria (SRB), hematite(α-Fe₂O₃) dissolution is affected potentially by a combination of enzymatic (hydrogenase) reduction with hydrogen sulfide oxidation. As a consequence, ferrous ions are free to react with excess H₂S to form insoluble iron sulfides. Morphology of single crystalline hematite cubes, prepared by a hydrothermal synthesis at 130°C from a solution of urotropine ((CH₄N₄)₂) and ferric chloride, and its metamorphosis to iron sulfides in SRB-containing medium are observed by transmission electron microscopy in the present study. Iron oxide hydrate (Fe₂O₃·H₂O) and the γ-FeOOH form of hydrated ferric oxide are the primary forms of corrosion product. Two typical morphologies of the iron sulfides, globule and plate, are observed after immersion of about a month. The morphological changes of the corrosion product are interpreted from analyses made using energy dispersive spectroscopy (EDS) and the spectra confirm that the plates and the globules are different morphologies of the same chemical species, iron sulphide product. Electron diffraction identifies the presence of a hexagonal structure associated with observed crystallites, indicating the identification of the iron sulfide phase as pyrrhotite.

KEY WORDS: Sulfate-reducing bacteria (SRB); Corrosion; Hematite; Single crystalline.

INTRODUCTION

Sulfate-reducing bacteria, belonging to anaerobe, exist widely in the polluted seawater and sea mud. SO₄²⁻ can be reduced to S²⁻ by their metabolic activities, and H₂S formed in aqueous solution results in the corrosion damage of metal pipelines and constructions, as well as pollution of environment. Comprehensive research has been carried out in terms of microbiologically influenced corrosion (MIC) of carbon steel and low alloy steel in environment containing SRB(Tiller,1983).

Iron oxide occurs with the formation of ferrous sulfide or before it in the primary stage of the corrosion process. Iron oxide should be responsible for the emergence and development of MIC, which haven’t been well investigated yet. In the environment abundant in sulfide, metal oxide may react with sulfide as the resource of metal ions.

Influenced by SRB, transformation occurs from oxide to sulfide, which has an important role in the MIC process (Melchers, 2003).

In this paper, with the aim of investigating iron sulfide chemistry resulting from SRB activity we present transmission electron microscopic evidence using single crystalline hematite(α-Fe₂O₃) particles prepared by hydrothermal synthesis method.

Experimental Materials

Single crystalline hematite (α-Fe₂O₃) cubic particles were used for this study, a gift of School of Material Science and Engineering, Shandong University(Hou and Wu, 2006). The cubes were prepared by a hydrothermal synthesis at 130°C from a solution of urotropine ((CH₄N₄)₂) and ferric chloride.

Organisms and culture

Sulfate-reducing bacteria were enriched and cultivated from the marine sediment in the Huanghai Sea, China. A modified Postgate’s C medium was used for enrichment culture, which contained 0.5g KH₂PO₄, 1g NH₄Cl, 0.06g CaCl₂, 6H₂O, 0.06g MgSO₄·7H₂O, 6ml 70% sodium lactate, 1g yeast extract, 0.3g sodium citrate in 1 L aged seawater from Qingdao offshore area. The medium was deaerated by purging with high-purity nitrogen and autoclaved at 121°C, then was added sterile 0.004g/L FeSO₄·7H₂O. 30 ml of the medium were poured into a 50 ml clean serum bottle, prior to inoculation with 5%(v/v) enriched sulfate-reducing bacteria. Then the medium was given anaerobic treatment mentioned above and ready for experiment.

Instrumentation and experimentation

Samples were exposed to modified medium mentioned above inoculated rich SRB in serum bottles and sealed with cover and paraffin for a month at a constant temperature of 37°C. Following incubation, samples with associated precipitates were dispersed in an ultrasonic cleaner, removed from the culture medium and observed using Hitachi H-800 TEM and FEI Sirion200 SEM. The morphological changes of the corrosion product were interpreted from analyses made using EDS and electron diffraction.