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Note

Evidence of direct crystal growth and presence of hollow microspheres in magnetite particles prepared by oxidation of $Fe(OH)_2$

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Abstract

We provide new information relevant to the crystallinity and growth mechanism of magnetite particles that were fabricated following the method of Sugimoto and Matijević [J. Colloid Interface Sci. 74 (1980) 227]. These authors observed that in a small excess of Fe^{2+}, particles grew by aggregation and recrystallization of smaller units, so that until now the resulting particles were thought to be polycrystalline. With the help of transmission electron microscopy (TEM) and selected area electron diffraction (SAED), we also detected the presence of monocrystalline particles, which are strong evidence of the occurrence of direct crystal growth. This growth mechanism seems to coexist with that of the aggregation of primary units proposed by Sugimoto and Matijević. Careful examination of electron microscopy micrographs also revealed the presence of many hollow polycrystalline microspheres.

Keywords: Magnetite; Colloidal magnetite particles; Magnetite single crystals; Hollow particles; Crystal growth

1. Introduction

Sugimoto and Matijević [1] reported in 1980 the fabrication of magnetite particles by means of a method that consisted in the precipitation of a $Fe(OH)_2$ gel upon the mixing of $FeSO_4{\cdot}7H_2O$ and KOH, and in the slow oxidation of the gel in the presence of KNO_3 at 90 °C for 4 h. Explicit expressions of the redox reactions can be seen in Ref. [1]. This process is a clear example of particle growth by phase transformation from a solid precursor. Depending on the composition of the starting mixture, the authors observed two very different types of magnetite particles. On the one hand, as long as the pH of the medium is close to the isoelectric point (IEP) of magnetite (pH ∼6.7), which happens when there is a small excess of Fe^{2+} in the starting reactant mixture, spherical micron-sized particles grow by aggregation and contact recrystallization [2] of minuscule primary particles. These primary particles are formed first by oxidation within the $Fe(OH)_2$ platelets and are held by the $Fe(OH)_2$ gel until dissolution of this network allows the coagulation of the primary particles. The network serves then the double purpose of being a source of iron and a deterrent of the aggregation of the growing secondary particles. In contrast, when particle growth occurs in excess of OH^-, the pH is far from the IEP of magnetite, and resulting particles are smaller and have well-developed facets (they were initially described as cubic). This morphology suggested that they were single crystals and Sugimoto and Matijević concluded that in this case electrostatic forces between growing particles prevented their aggregation and growth occurred by 'direct crystal growth.' 'Direct crystal growth,' also referred to as 'classical crystal growth' by some authors, would be a process in which particles grow by ion-to-ion attachment and unit cell replication [3], in contrast to particle-mediated growth. In the case of the phase transformation of $Fe(OH)_2$ to Fe_3O_4, direct crystal growth would be a dissolution/reprecipitation process in which the $Fe(OH)_2$ gel dissolves, a portion of the Fe^{2+} ions oxidize to Fe^{3+} and both ions combine with oxygen and reprecipitate to form Fe_3O_4. Growth by aggregation of primary subunits has also been proposed [4] for the formation of particles of Ni [5]

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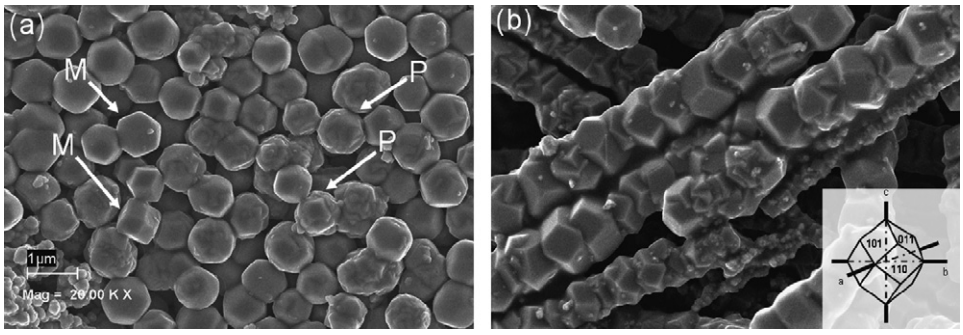

Fig. 1. Scanning electron micrographs of magnetite particles fabricated following the recipe of Sugimoto and Matijević with an excess of Fe^{2+} of 0.005 M in the starting solution. (a) Particles not exposed to any magnetic field during the synthesis process. Arrows indicate particles that turned out to be monocrystalline (M), and particles that were found to be polycrystalline (P). (b) Particles cured in the presence of a magnetic field of 0.405 T. Note the presence of polygonal units in both cases. Insert in (b) shows a rhombic dodecahedron, which is the polygon that seems to predominate.

and Co [6] ferrites, and models that explain the narrow size distribution of particles grown by aggregation of primary units have been developed [7,8].

In summary, precipitation in the presence of a small excess of Fe^{2+} yields micron-sized particles which are thought to be composed of a subarray of primary particles. These particles were therefore expected to be polycrystalline [4,9], in other words, they were expected to be an ensemble of randomly oriented grains or crystallites. These grains or crystallites are volumes within the particle in which a homogeneous crystal ordering is maintained.

In our past experience [10] with Sugimoto and Matijević's method, we observed, to our surprise, that some particles were polygons and exhibited well-developed facets even when they grew in an excess of Fe^{2+}. This suggested that they were monocrystalline. When the synthesis process was carried out in the presence of a magnetic field [10], the polygons appeared as rod-segments instead of isolated particles (see Fig. 1). Rhombic dodecahedra (see insert in Fig. 1) was the predominant shape among the observed polygons. It should be mentioned that particles with straight edges, which imply the presence of facets, are discernible upon careful inspection of some of the micrographs—see for instance micrographs 3b, 3c, and 5b—presented by Sugimoto and Matijević in their article [1].

In light of those observations, and because the fact that a particle has a well-defined geometry does not necessarily mean that it is a single crystal [11], we decided to use transmission electron microscopy (TEM) and carry out selected area electron diffraction (SAED) of single particles to ultimately determine whether the particles were single crystals or were polycrystalline. This information seemed important since the presence of monocrystalline particles could have implications regarding the growth mechanism. Also the microstructure, including grain size, porosity, and crystallite orientation, has a major influence on the magnetic properties of a given material [12,13]. Furthermore, to the best of our knowledge, there are no detailed studies on the crystallinity of individual micron-sized magnetite particles fabricated by oxidation of $Fe(OH)_2$ in KNO_3. In the past, the crystalline structure of these particles has been only studied by means of X-ray powder diffraction [1]. This latter method provides only information averaged over a large ensemble of particles.

2. Experimental

Magnetite particles were grown following the method first proposed by Sugimoto and Matijević [1], with concentrations of reactants that lead to a concentration of $Fe(OH)_2$ of 0.025 M and an excess of Fe^{2+} of 0.005 M. Experimental details can be found elsewhere [10].

The samples observed in the scanning electron microscope (SEM) were prepared by drying on top of a glass substrate a droplet of a suspension of the magnetite particles dispersed in ethanol. A thin (ca. 20 nm) coating of carbon was then applied. Samples were examined in a LEO Gemini 1530 field-emission scanning electron microscope in a secondary electron (SE) mode.

For the transmission electron microscopy (TEM) analysis, a droplet of suspension containing the magnetite particles was deposited on a carbon-coated copper grid. After drying in air, the particles were examined in a JEOL JEM 2010F field emission gun microscope operating at an acceleration voltage of 200 kV. Images of polycrystalline particles were also obtained by means of scanning TEM (STEM) using a high angle annular dark field detector (HAADFD) to enhance the internal contrast of these particles. Selected area electron diffraction (SAED) was employed to study the crystalline structure of individual particles.

3. Results and discussion

Fig. 2 shows TEM and STEM micrographs of magnetite particles synthesized in the absence of a magnetic field. The lower particle in Fig. 2a exhibits smoother edges and a more homogeneous look, without marked contrast differences in its interior. It also has fairly straight edges, which are a sign of well-defined facets. The other two particles in this image have rougher edges, seem to be more spherical, and show different contrast areas. Some of these contrast differences could be attributed to the fact that these particles were actually an ensemble of smaller grains, which led to a nonhomogeneous density caused by the presence of defects and internal interfaces between subunits. It is interesting to note that upon TEM observation the former type of particles also exhibits a low contrast (lower density and/or lower thickness to the electron beam) area in the center, which