

Copper (II) oxide as a morphology directing agent in the hydrothermal crystallization of magnetite

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Magnetite crystals with unique morphological characteristics have been grown from hematite under hydrothermal conditions at 150 and 175 °C in the presence of hydrazine and copper (II) oxide. In the absence of CuO, octahedral crystals of magnetite with a distribution of particle sizes were grown in accordance with literature procedures. In the presence of CuO, magnetite crystals with distorted morphology were prepared in which the [1 1 1] crystal faces were absent, leaving a framework structure of corners and edges. Examples of crystal intergrowths were observed, as well as the partial collapse of the framework structure of the magnetite. The results are discussed with reference to the possible effect of copper redox couples on the hematite reduction reaction.

1. Introduction

Magnetite [Fe_3O_4 , or $\text{Fe}^{3+}(\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4)$] is a technologically important iron oxide which has found applications as a heterogeneous catalyst [1, 2], a pigments material [3] and as a precursor for magnetic fluids [4]. In corrosion science, magnetite films can function as a protective layer on carbon steel [5]; and yet, magnetite is also the principal corrosion product that is found in secondary water circuits of nuclear reactors and in deposits on steam generator tubes [6–8]. Magnetite deposits have been implicated in the loss of heat transfer efficiency, which has subsequently led to reactor derating. Many of its properties, such as high electrical conductivity and magnetism, result from the fact that Fe^{2+} and Fe^{3+} coexist within the same lattice. Magnetite is classified as an inverse spinel because the more abundant Fe^{3+} is evenly distributed between octahedral and tetrahedral lattice sites.

Magnetite can be prepared by the high temperature reduction of hematite in CO–CO₂ mixtures [9], hydrothermal syntheses in the presence [10, 11] or absence [12] of organic chelating agents, oxidation of ferrous solutions using KNO₃ [13], and solvothermal methods [14]. Each of the methods mentioned above, and other modifications of the synthetic procedures [13], can be used to produce magnetite with different particle size distributions and morphologies.

The ability to direct the morphology of magnetite particles may be a key feature in the development of new applications, particularly if other physical, chemical and electronic properties are retained. To date, magnetite with spherical [15] and octahedral [11] particle morphologies has been prepared using hydrothermal synthesis conditions. The preparation of

crystals with severely defected or “hopper-faced” octahedra has been reported for ferrites that were synthesized using the vapour phase reaction of metal halides with water at high temperature [16]. The morphology of these crystals is peculiar in that the [1 1 1] faces are missing and therefore is based solely on the structure of the crystal edges and apices. The authors are not aware of any reports of similar morphologies for magnetite or other ferrites prepared using hydrothermal methods. High temperature hydrothermal synthesis of Fe_3O_4 at 500–550 °C has shown that the morphology of the crystals was dependent on the hydrogen concentration in the solution [17]. As the quantity of H₂ was raised from 2.6 to 8.0 mmol in the reaction vessel, the predominance of the [1 1 1] faces was replaced by the growth of the [1 1 0] faces, to the extent that the magnetite grown in the solution with the highest hydrogen concentration possessed only [1 1 0] faces. Identical lattice parameters were obtained for all of the magnetite samples, indicating that the morphology and stoichiometry were not necessarily related.

The formation or transformation of iron oxide phases is often influenced by the addition of secondary additives to aqueous systems containing either soluble or insoluble precursors of the iron oxides. Silicate [18, 19] and orthophosphate [20] anions, and certain organic molecules, i.e. triethanolamine [10], have been shown to be particularly influential in directing iron oxide phase formation.

There have been relatively few reports of studies that considered the influence of transition metals on the dissolution–precipitation reactions in which iron oxides can participate under hydrothermal conditions. Inouye has studied the effect of Cu (II) on the

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oxidation of colloidal ferrous hydroxide $[\text{Fe}(\text{OH})_2]$ to magnetite [21, 22]. Copper (II) was proposed to influence the reaction through two distinct mechanisms: the promotion of the growth of crystalline $\text{Fe}(\text{OH})_2$, and the facilitation of the decomposition of a coordinated $\text{Fe}(\text{OH})_2$ complex with water, as a result of the Jahn–Teller distortion, leading to the subsequent growth of magnetite. Inouye and coworkers also observed that Cu (II) additions hindered the low temperature growth of $\gamma\text{-FeOOH}$ particles, and in particular altered the length of the particles [23]. The authors also implied from their work that the presence of Cu (II) may promote the formation of magnetite, although no justification was given for this statement. A more recent study of the influence of copper on the transformation of ferrihydrite to more crystalline products showed that goethite, hematite and magnetite were formed depending on the Cu^{2+} concentration [24]. When copper concentrations of greater than 15 mol % Cu were employed, copper-substituted magnetite was formed.

In this paper, the authors describe the morphology-directing effect of copper (II) oxide on magnetite precipitation following the dissolution of hematite in aqueous hydrazine under hydrothermal conditions.

2. Experimental procedure

Experiments were performed using a series of 23 ml stainless steel Parr autoclaves equipped with polytetrafluoroethylene liners. Hematite (0.5 g) (Johnson–Matthey, 99.999%) was placed in the autoclave either with, or without, 0.09 g of CuO (Aldrich, 99.99%). The solution phase that was added to the reaction vessel (10 ml) was either pure, double distilled water, 10 vol. % hydrazine–double distilled water or 5/5/90 vol. % hydrazine–morpholine–double distilled water. The autoclaves were heated at 150 or 175 °C for a period of 3–14 days. Reaction products were characterized by powder X-ray diffraction (XRD, using $\text{CuK}\alpha$ radiation and a Rigaku Rotaflex diffractometer) and scanning electron microscopy (ISI DS-130 microscope). Single experiments were performed in which CuO was replaced by NiO, ZnO or Ag_2O and the mixture with hematite was reacted in 10% hydrazine for seven days at 150 °C.

3. Results and discussion

When hematite was placed in pure water at 175 °C for seven days, not surprisingly, there were no alteration or transformation reactions detectable by powder XRD. Addition of 10% hydrazine under otherwise identical conditions led to extensive, but not complete, transformation of the hematite to magnetite. Analysis of the powder XRD patterns revealed that the principal diffraction peak of hematite ($d = 0.270$ nm) had been reduced to 19% of the intensity of the principal magnetite peak ($d = 0.253$ nm). The scanning electron micrographs in Fig. 1 show the octahedral morphology of the magnetite that was produced along with fine particles of residual hematite. The magnetite morphology obtained in this study is similar to that which

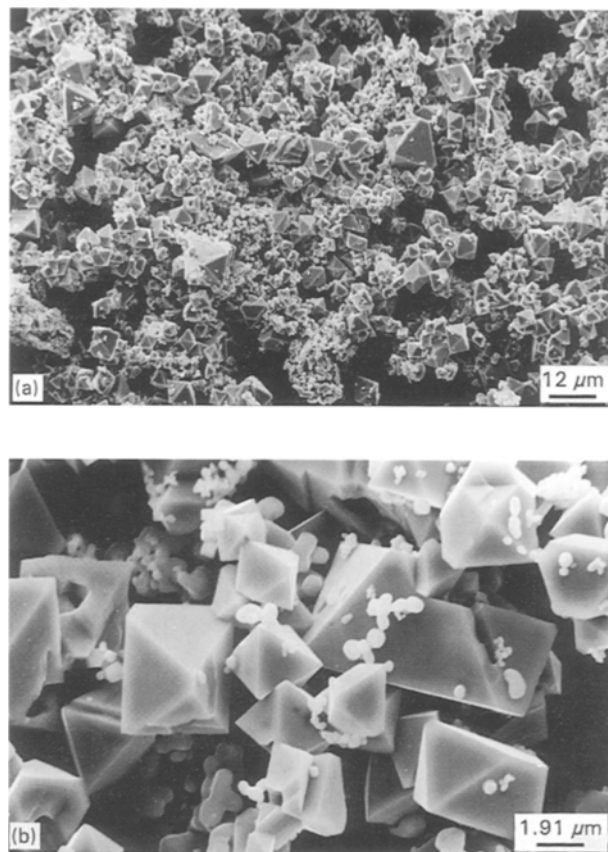


Figure 1 (a) Low magnification scanning electron micrograph of octahedral magnetite prepared by dissolution–precipitation of hematite in 10% aqueous hydrazine at 175 °C. (b) Higher magnification scanning electron micrograph showing the presence of residual hematite particles.

was precipitated in other reducing hydrothermal syntheses [10, 25]. Fig. 1a provides a good representation of the magnetite particle size distribution that was obtained, with most particle diameters around 2–4 μm and some crystals up to 15 μm in diameter. An odour of ammonia was detected when the autoclave was opened following cooling to room temperature and the pH of the filtrate was 10.7 as compared to 8.2 for the experiment in which hydrazine was not added.

Copper (II) oxide addition with hematite in pure water did not alter the hematite stability, and powder XRD investigations showed that there were no transformation products of either hematite or CuO. The transformation of hematite in 10% hydrazine was, however, influenced by the presence of CuO. Whereas in the absence of CuO there was residual hematite following a reaction time of seven days at 175 °C, powder XRD indicated that complete transformation to magnetite was achieved when CuO was present, along with complete reduction of the CuO to copper metal. The metallic copper grew in a weakly agglomerated mass that collapsed upon filtering. There was no indication from the XRD patterns for the formation of copper–iron oxides, such as delafossite (CuFeO_2) or cuprospinel (CuFe_2O_4), i.e. no additional peaks, and no measurable changes to the widths of the magnetite diffraction peaks were observed in the XRD patterns. Once again, the odour of ammonia was detected and the solution had the blue colour of a copper

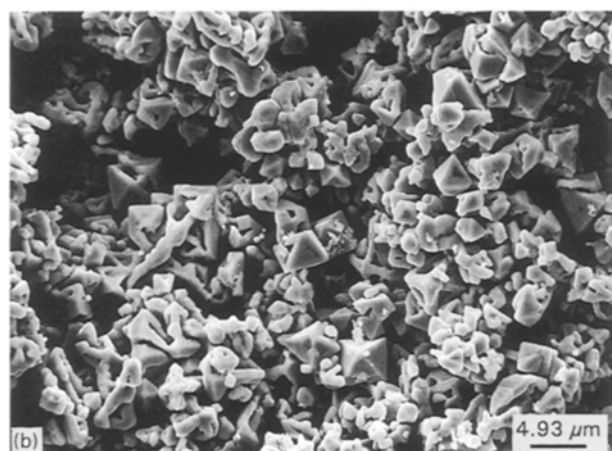
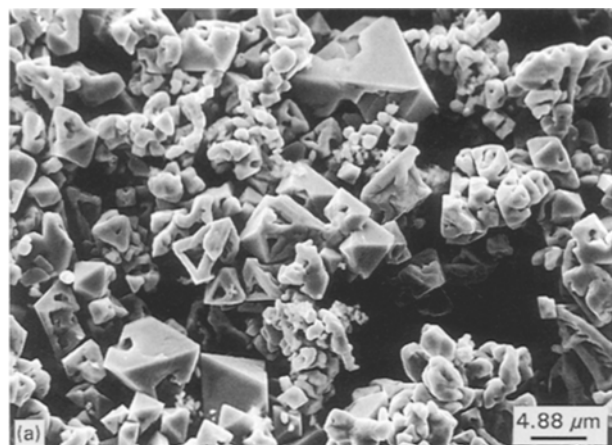


Figure 2 (a, b) Magnetite particles formed from the transformation of hematite in 10% aqueous hydrazine in the presence of CuO at 175 °C. Note the variation in the degree of morphological degradation from perfect octahedral structure.

(II)-ammine complex. The pH of the solution was 11.1, an increase of 0.4 pH units from the experiment with N_2H_4 in which CuO was not added. The presence of the soluble copper complex and metallic copper provide indirect evidence that the experimental conditions do not permit appreciable incorporation of Cu into the magnetite lattice.

Although the XRD patterns suggested that the magnetite formed in the absence and presence of copper was identical ($a_0 = 0.894$ nm), scanning electron microscopy of the magnetically separated black powder revealed significant morphological differences between the two samples, illustrated in Fig. 2. Virtually all of the magnetite crystals that were grown in the presence of CuO had varying degrees of imperfection. Many of the crystals possessed well defined octahedral edges and corners, but lacked the $[111]$ faces, leaving what can best be described as a crystal frame of edges and corners. These observations remain consistent with the powder XRD results which did not show significant differences in the intensities of the $[111]$ reflections for the two samples. It does indicate that macroscopic morphology of the magnetite does not necessarily reflect the arrangement of atoms in sub-lattice [17].

Other crystals, in addition to possessing this framework appearance, had rounded edges and corners,

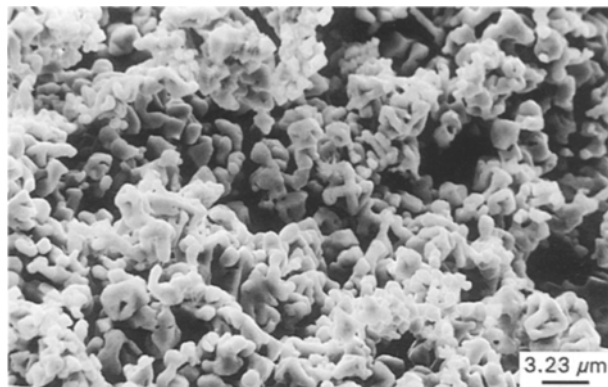


Figure 3 Magnetite crystals that were grown in aqueous hydrazine at 175 °C displaying a morphology with rounded edges and corners in addition to the distorted $[111]$ faces.

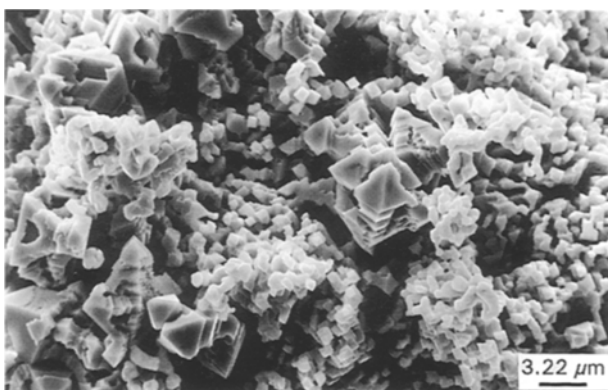


Figure 4 Intergrowth of magnetite crystals observed when CuO was present during the reduction of hematite to magnetite in aqueous hydrazine at 175 °C.

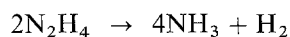
and in some cases the framework has collapsed (Fig. 3). Finally, there were examples of crystal intergrowths in which the crystal growth demonstrated some directional preferences (Fig. 4). This type of growth pattern has been observed in high temperature vapour phase transport systems [16], but apparently not in hydrothermal syntheses.

The defects in the magnetite produced in this study are unlike those that have been shown to develop when octahedral magnetite crystals are partially dissolved in solutions containing complexing anions [20]. This indicates that the role of the CuO is to influence the nucleation and crystallization of the magnetite following the dissolution of the hematite, as well as to promote complete transformation to magnetite.

Lowering the reaction temperature to 150 °C and varying the reaction time from three to 14 days did not alter the reaction significantly, as magnetite with similar morphology was obtained in each case. A trace of hematite remained after three days, but not after longer reaction times. Substitution of NiO, ZnO or Ag_2O for CuO produced somewhat different results. When hydrazine was present, no magnetite was formed in the presence of ZnO, and a mixture of magnetite and hematite resulted when Ag_2O was in the mixture. There was significant reduction of the Ag_2O immediately following the addition of hydrazine at room temperature. Magnetite was

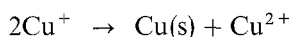
formed when NiO was present, but only minor defects were observed on the magnetite crystals. The results suggest that it is not sufficient to have a transition metal oxide present to produce the magnetite with defective morphology; but, instead, the effect appears to be strongest for CuO. The observed behaviour is consistent with the trend in reduction potentials for the divalent metal oxides. Both Cu^+ and Cu^{2+} are reduced to metallic copper at positive potentials (relative to the standard hydrogen electrode), while Ni^{2+} and Zn^{2+} are reduced to the respective metals at progressively negative potentials (-0.23 and -0.76 V, respectively).

Although one cannot derive a detailed mechanism for this complex reaction, it is clear that the presence of CuO accelerates the magnetite formation, as well as modifying its morphology. The complete transformation of the hematite in the presence of the CuO may be governed by catalytic decomposition of hydrazine through a route that is not possible in the absence of copper ions. Copper (II) oxide has been shown to be an effective catalyst for hydrazine oxidation at low temperature [26, 27] and there is evidence to suggest that its decomposition to ammonia (possibly with hydrogen generation) is possible in systems containing copper and iron based materials [28]. If additional hydrogen is generated via the following path



it may serve to drive the hematite reduction reaction to completion, as well as influence the morphology of the magnetite as was described earlier for higher temperature hydrothermal syntheses of magnetite [17].

The presence of metallic copper and a copper (II)-ammine complex in the products is indicative of the complex series of reactions that occurred under the conditions of this study. One explanation for the observed distribution of copper products involves coupled redox cycles for the copper species. The initial step would be the one electron reduction of Cu^{2+} to Cu^+ by hydrazine. The cuprous ion is not expected to be stable under the reducing conditions of the experiment [29]; it appears to undergo disproportionation to metallic copper and Cu^{2+} in solution(s) as a copper (II)-ammine complex, rather than complete reduction



An interesting feature of the present study is that under the reaction conditions, hydrazine has undergone both oxidation (with coupled reduction of Cu^{2+} and Fe_2O_3), and reduction to form ammonia. This parallel reactivity has been reported previously, and is particularly evident in secondary feedwater systems of nuclear power reactors where ammonia is generated from hydrazine that is added to the system to serve as an oxygen scavenger [28].

This study indicates that copper, as a result of having three accessible oxidation states [Cu (0), Cu (I) and Cu (II)] and rapid electron transfer between the species, is able to participate in a redox catalytic mechanism involving hydrazine to facilitate the

reduction of hematite to magnetite as well as direct its morphology. The present study has also considered the influence of oxides of nickel, zinc and silver, none of which exhibited the same propensity to influence the magnetite morphology as did CuO. Further studies are required to determine the role of other transition metal oxides with multiple oxidation states, i.e. vanadium, chromium, in the hydrothermal reduction of hematite to magnetite in the presence of hydrazine.

Magnetite particles with these unique morphologies may have applications in some or all of the technologies mentioned previously. They may also be more representative of corrosion products found in secondary feedwater systems than perfect octahedral magnetite, as investigations using electron microscopy often reveal that only a fraction of the observable particles possess octahedral symmetry.

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