Effects of Transition Zone on Magnetic Properties of Low Temperature Oxidation of Magnetite Particle: Comparison of Experiment and Micromagnetic Modeling

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Abstract. A relationship of hysteresis parameters and oxidation of ultrafine magnetic particles on both experimental measurements and micromagnetic simulations is obtained through a step-by-step oxidation of magnetite. Numerical simulations of hysteresis loop and microstructure of a core-shell geometry with transition zone using a multi-layer structure show two categories of behaviour for magnetic grains during oxidation. First, the SD (Single Domain, <70 nm) and larger SV (Single Vortex, >130 nm) particles remain unchanged ratio of saturation remanence to saturation magnetization ($M_r/M_s$), and slightly decreased coercivity ($B_c$) during oxidation. Second, the fine SV particles (80 nm to 120 nm), the hysteresis parameters respectively increase and dramatic decrease at the early and late stage of oxidation, and the micromagnetic behaviors vary significantly. Finally, the hysteresis parameters of larger SV particles remain nearly unchanged during oxidation. The predicted magnetic properties for the core-shell model exhibit better agreement with experimental data than that of previously used core-shell geometry (a stoichiometric core surrounded by an oxidized shell). It indicates that the magnetic properties of partially oxidized magnetic grains are controlled by the multi-layer coupling effects and can record paleomagnetic signals.

1. Introduction
Wide practical use of magnetic core/shell nanoparticles in biomedicine, electronics, catalysis and composite materials [1–2] has given rise to numerous studies on the effects of various factors on their magnetic properties. In Geosciences, the core-shelled oxidized magnetite or titanomagnetite particles is one of the paramount important effects of weathering under natural atmospheric conditions [3]. The oxidation of magnetite or titanomagnetite starts at its surface, where Fe$^{2+}$ is oxidized to Fe$^{3+}$. It is either partially removed from the crystal or it reacts with oxygen to form a new crystal layer [4]. Further oxidation is a diffusion process driven by the oxidation gradient: Fe$^{3+}$ diffuses from the interior of the grain to the surface, leaving vacancies in the interior. Because of the isolation effect of the oxidized layer and the rapid reduction of the solid state diffusion coefficient at low temperature [5-6], a strong oxidation gradient builds up close to the grain surface: an oxidized shell is formed around an unoxidized core (so called the core-shell structure).

However, based on the diffusion process of iron cations, the actual oxidation of single magnetite crystals occurs continuously and nonlinearly from the interior of the grain to the surface [4-5]. [1] suggested a low temperature method for testifying the oxidation of magnetite and considered that a
transition zone may exist between the surfacial maghemite shell and the magnetite core, where the lattice parameters gradually change. The core-shell structures of oxidized magnetite has attracted interests from researchers both experimentally and numerically [7-10]. Regardless of these attempts, how the core-shell structure, especially the transition zone affects the magnetic behaviors of the partially oxidized magnetitic particles has not been well resolved.

Micromagnetic modeling is a novel approach to explain magnetization reversal, hysteresis effects and research on complex microstructure influence, and typically efficient to present internal images of the microscopic domain structures for further evaluating how magnetic record varies under an applied field [11]. The aim of this study is to correlate the micromagnetic results with experiment measurements using a multi-layer core-shelled model during the whole process of oxidation. The more realistic core-shell model will provide a better understanding of low temperature maghemization.

2. Samples and experiments
The experiment data of synthetic reduced and oxidized magnetite were used as described by [10]. The low temperature oxidized magnetite were obtained by heating reduced magnetite to different temperatures for various periods of time. X-ray cell edges for the stoichiometric and partial oxidized magnetite particles were measured using an X-ray spectra using Cu-Kα radiation. By comparison with the corrected curve [12] of cell size and oxidation parameter z, which is determined by [13] with the following formula:

\[ \text{Fe}^{2+} + (z/4)\text{O}_2 \rightarrow (1 - z)\text{Fe}^{2+} + z\text{Fe}^{3+} + (z/2)\text{O}^2- \]  

(1)

Hysteresis loops of the dispersed powders were measured on MicroMag 3900 Vibrating Sample Magnetometer (VSM; Princeton Measurements Corp., USA) at room temperature with field ranging from -1.0 to 1.0 Tesla.

3. Micromagnetic modeling
The calculation of the core-shell structure was performed using a finite element method (FEM). Micromagnetic models calculate stable magnetic structures by minimizing the total magnetic energy \( E_{\text{total}} \) as the initial guess, which is the sum of the exchange energy \( E_{\text{ex}} \), the magnetostatic energy \( E_{\text{d}} \), the anisotropy \( E_{\text{ani}} \) [14] and the external field energy \( E_{\text{h}} \). \( E_{\text{d}} \) is calculated by using the fast-Fourier transforms (FFT) method to accelerate the computation [15]. That is to say:

\[ E_{\text{total}} = E_{\text{ex}} + E_{\text{ani}} + E_{\text{d}} + E_{\text{h}} \]  

(2)

In the micromagnetic modeling, the normal material parameters appropriate to magnetite at room temperature were used, namely Exchange Constant \( (A_{\text{ex}} = 1.33 \times 10^{-11}\text{Jm}^{-1}) \), Magnetocrystalline Anisotropy \( (K_1 = -1.24 \times 10^4\text{Jm}^{-1}) \) and Saturation Magnetization \( (M_s = 4.8 \times 10^5\text{Am}^{-1}) \) [16-17]. For maghemite, the corresponding principle magnetic parameters applied in this core-shell model are \( 1 \times 10^{-11}\text{Jm}^{-1}, -4.6 \times 10^3\text{Jm}^{-1}, \) and \( 3.8 \times 10^5\text{Am}^{-1} \) respectively [18]. [5] described a kinetics numeric modeled function of depth with iron diffusion (oxidation state) for continuous oxidized magnetite grains (Figure 1). The material parameters of the partially oxidized layer for the core-shell model were hence determined by simply linearly interpolations of the parameters of magnetite and maghemite on the basis of their oxidation parameter. Averaged exchange parameters between bordered layer were employed on the boundaries of layers [10].
Simulations of hysteresis were conducted with applied field varying from 180 mT to -180 mT in steps of 5 mT. Values for the coercive force \(B_c\) and ratio of saturation remanence to saturation magnetization \(M_{rs}/M_s\) are averaged from the modeling results with applied fields aligned along the easy <111>, hard <100> and intermediate <110> directions.

4. Results and discussions

The coercivity and the ratio of saturation remanence to saturation magnetization as a function of oxidation parameter are shown in Figure 2. For grains from 40 nm to 70 nm, the \(B_c\) decrease gradually with the proceeding of oxidation process. While the \(M_{rs}/M_s\) stays stable with the increase of oxidation parameter. The hysteresis behaviors of fine SV grains (80 to 120 nm) show a greater variability as a function of oxidation. It appears that hysteresis parameters of these grains during oxidation are larger than those of two end members, and specifically, dramatic increase and decreases could be seen at the early and late stage of oxidation, respectively. For larger grains (140 to 160 nm), the parameters remain nearly unchanged during oxidation in comparison of finer SV particles. Specifically, the \(B_c\) decrease slightly with the increase of oxidation parameter, however the \(M_{rs}/M_s\) shows slight increase with the oxidation proceeds.

Figure 2. Micromagnetic results of (a) coercive field \((B_c)\) and (b) ratio of saturation remanence to saturation magnetization \((M_{rs}/M_s)\) versus oxidation parameter \(z\) for multi-layer core-shelled models.
As seen from Figure 3, the hysteresis parameters of experiment data as a function of oxidation states exhibit similar behaviors, which is a slight increase increasing up to \( z = \sim 0.9 \), and then decreases dramatically. A dramatic decrease of hysteresis parameters appears both for multi-layer core-shell model and 2-layer core-shell model before magnetite is totally oxidized, which is well consistent with the experimental observations. The micromagnetic data for multi-layer core-shelled model show that both trend and values of \( B_c \) and \( M_{rs}/M_s \) versus oxidation parameters are more similar to the experimental observation than the data of the simple no-transitioned core-shell model. In particular, the \( M_{rs}/M_s \) as a function of oxidation parameter is almost indistinguishable with the experiment results.

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**Figure 3.** Weighted micromagnetic modeling results of (a) coercive field and (b) ratio of saturation remanence to saturation magnetization, versus oxidation parameter \( z \), according to the grain size distribution, in comparison with previous experiments by [10]. Note that the interaction effects have been considered in the weighted multi-layer model.

Note that a slight increase of coercive force shows up in the micromagnetic model at an early oxidation stage (Figure 3a). There are experimental explanations of this increase of remanence stability. For instance, [19] proposed that the increase of coercivity is believed to result from stress in the absence of any other quantitatively plausible mechanism. The followed decrease may be due to a decrease in the magnetostriction constant as a function of oxidation. However, this slight change probably results from the multi-layer coupling effect during oxidation.

5. Conclusions

Based on experimental characters of low temperature oxidized magnetic particles, micromagnetic simulations were performed to investigate the hysteresis parameters versus oxidation state as a comparison. Using the FEM calculation of a multi-layer structure, the averaged results based on grain size distribution are in good agreement with the experimental data, and show two types of variations of magnetite properties from SD to SV particles. The dramatic change of hysteresis parameters before totally oxidized in experiments is mainly because of the variability of magnetic properties for partially oxidized fine SV grains. Magnetic particles of other sizes are magnetically stable during oxidation. Overall, the partially oxidized magnetite prefers an multi-layer coupled core-shell structure, and is capable of record reliable magnetic signals.

6. References

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