Study on magnetite-maghemite-hematite transformation

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Magnetite (Fe_3O_4) widely distributed in the Earth's crust changes into hematite (α-Fe_2O_3) by the oxidization of Fe^{2+} to Fe^{3+}. In the oxidization process, maghemite (γ-Fe_2O_3) with the same spinel structure as magnetite emerges as an intermediate phase. Maghemite differs from magnetite by the presence of cationic vacancies within the octahedral site. It is important to understand the oxidization mechanism of magnetite, however, the local structure change during the oxidization has been still nuclear. In the study, therefore, the phase transition mechanism from magnetite to hematite through maghemite was investigated by using, thermal analysis (TG・DTA), powder X-ray diffraction (XRD) measurement, and high-temperature ex-situ and in-situ X-ray absorption fine structure (XAFS) measurement. The TG・DTA curves of magnetite showed continuous oxidization up to 400 °C. High-temperature ex-situ EXAFS spectrum of magnetite heated up to 250 °C exhibited weaker peaks concerning Fe_{oct}-O, Fe_{oct}-Fe_{oct}, and Fe_{tet}-Fe_{oct} than those of magnetite. In addition, the averaged Fe-O bond distance appears to become shorter. The results suggest that magnetite is continuously transformed to maghemite in the temperature range from room temperature to 400 °C. The high-temperature ex-situ EXAFS spectrum of magnetite heated up to 500 °C finally displayed characteristic peaks corresponding to hematite, suggesting that the phase transition from magnetite to hematite was completed.
High-temperature in-situ XANES spectrum indicated that the average oxidation number of Fe gradually increased for 135 min from the start of heating at 500 °C, and then became almost constant. The radial structure function obtained from the high-temperature in-situ EXAFS revealed that the peaks of Fe-O, Fe_{oct}-Fe_{oct} and Fe_{tet}-Fe_{oct} become weakened continuously until 70 min from the start of heating. After 80 min peaks corresponding to hematite began to increase. It can be concluded from these results that the phase transition from magnetite to hematite through maghemite starts from the diffusion of the Fe^{2+} in the octahedral sites, resulting in the formations of cationic vacancies and amorphous phase concentrating Fe^{2+}. Subsequently, the reconstruction of the octahedral coordination of Fe and additional oxidization of the amorphous phase lead to the crystallization into hematite.

Keywords: magnetite, maghemite, hematite, thermal analysis, X-ray diffraction, X-ray absorpition fine structure

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