

Measurements of the vacant sites in crystal structure of magnetite by Mossbauer spectroscopy

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Magnetite ($[\text{Fe}^{3+}][\text{Fe}^{3+} \text{Fe}^{2+}]\text{O}_4$) is a strongly magnetic oxide iron mineral. When magnetite undergoes low temperature oxidation, vacant sites are formed at octahedral sites, and magnetite changes to maghemite ($[\text{Fe}^{3+}][\text{Fe}^{3+} \text{Fe}^{2+}_{2/3}] X_{1/3} \text{O}_4$ (X shows vacant sites.)). Magnetite changes to maghemite with increasing vacant sites, so a degree of low temperature oxidation can be estimated from the vacant sites. According to Nishitani and Kono (1982), grain size controls the transformation of titanomagnetites. When the grain size of titanomagnetite is less than 1 micrometer, titanomagnetite transforms to titanomaghemite under low temperature heating. However, titanomagnetite larger than 1 micrometer breaks into Fe-rich titanomagnetite and Ti-rich ilmenite under low temperature heating. In this case, titanomagnetite suffers high temperature oxidation. Nishitani and Kono (1982) estimated the degree of low temperature oxidation of titanomaghemite by X-ray diffractometer and Curie temperature. Another method to estimate vacant sites is a Mossbauer spectroscopy. Mossbauer spectroscopy is a sensitive method to estimate degree of low temperature oxidation than X-ray diffraction.

In this study, we measured Mossbauer spectra of natural titanomagnetite of Oarai, Ibaragi Prefecture, and estimated vacant sites in titanomagnetite. Titanomagnetite samples of various grain diameter were heated at fixed time and temperature. After measuring those heated samples by X-ray diffractometer to distinguish low temperature oxidation samples from high temperature oxidation samples, Mossbauer spectra of samples which underwent low temperature oxidation were measured. The vacant sites in titanomagnetite is calculated from the results of Mossbauer spectra.

Natural magnetite has solid solution between Fe_3O_4 , Fe_2TiO_4 and FeAl_2O_4 . Ti^{4+} and Al^{3+} must be considered to estimate vacant site of titanomagnetite by Mossbauer spectra, because Ti^{4+} and Al^{3+} must be vacant for Mossbauer spectra. However, method of correction remains unsolved. Therefore, we considered a new correction method.

Keywords: Mossbauer spectroscopy, Magnetite, Titanomagnetite