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Modeling of iron diffusion in the iron oxides magnetite and hematite with variable stoichiometry

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Abstract

The vacancy model of diffusion is applied to magnetite and hematite, and mathematical expressions for the iron flux in the lattice-fixed frame of reference, as a function of the defect structure, are presented. The defect structures, i.e. the vacancy content on the different type of sites, and the thermodynamic factors are calculated from the available Calphad type of thermodynamic descriptions for the oxides. Expressions for Fe tracer diffusion coefficients are derived and the relations between mobility and tracer diffusivity are given. The mobilities are fitted by a least-squares optimization to experimental data on tracer diffusion from the literature. For magnetite, an excellent representation of the experimental tracer data is achieved together with a satisfactory description of the sparse chemical diffusion data available. For hematite, the experimental scatter is very large and anomalous large frequency factors and activation energies have been reported. In the present report a compromise is suggested.

Keywords: Lattice defects; Thermodynamics; Bulk diffusion; Kinetics; Binary oxides

1. Introduction

Oxidation of a pure metal occurs by formation of an external oxide layer and the subsequent oxidation rate is then controlled by diffusion through that layer. Hillert et al. [1] recently analyzed the diffusion-controlled growth of an external phase with a fixed composition, i.e. a stoichiometric phase. In the present article models for diffusion in the iron oxides Fe_3O_4, and Fe_2O_3, i.e. magnetite and hematite, respectively, are proposed. Magnetite has the spinel structure with a considerable homogeneity range at higher temperatures. The off-stoichiometry at higher oxygen potentials is achieved by vacancies on the iron sites and at lower oxygen potentials by some extra iron atoms on interstitial sites. Hematite has the corundum structure and is quite stoichiometric.

As the predominant mechanism for diffusion in crystalline phases is the jumping of atoms or ions to neighboring vacant sites, the distribution of vacancies plays a key role in the diffusion behavior. The distribution of vacancies as function of temperature and oxygen potential may be calculated from the thermodynamic properties if they are sufficiently well characterized. In the present report we shall develop a model based on the defect structure of the oxides. The model will be tested and compared with experimental data and implemented into the DICTRA code [2] to allow simulation of the oxidation of pure iron.

In subsequent work we shall include oxygen diffusion that results in an inward growing oxide, and develop a similar model for wüstite. This will allow us to extend the treatment to include several alloy elements, e.g. chromium, and hence enable simulation of the oxidation of steels.

2. Diffusion in magnetite

2.1. Defects in magnetite

The defects and thermodynamic properties of the Fe–O system were analyzed in detail by Sundman [3]. His analysis

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and thermodynamic description will be accepted in the present work. The ideal stoichiometry of magnetite is Fe_3O_4 and its spinel structure may be regarded as oxygen ions in a face-centered cubic (fcc) lattice with divalent and trivalent metal ions distributed at the tetrahedral and octahedral interstices. The number of octahedral interstices is the same as the number of oxygen sites, whereas there are twice as many tetrahedral interstices. In spinel with ideal composition only half the octahedral and one-eighth of the tetrahedral interstices are occupied by metal ions. In the so-called normal spinel the trivalent metal ions occupy the octahedral interstices and the divalent ions the tetrahedral interstices. For magnetite, this would correspond to a formula unit $(Fe^{+2})_1(Fe^{+3})_2(O^{-2})_4$, where each pair of parentheses represents a sublattice; the first the tetrahedral, the second the octahedral interstices and the last the oxygen sites. It should be noted that the vacant sites are not included in the formula unit because in the ideal case the vacancies always occur on specific lattice sites, i.e. there is no positional disorder.

At low temperatures magnetite is an inverse spinel with Fe^{+3} mainly at the tetrahedral interstices and both Fe^{+2} and Fe^{+3} at the octahedral interstices. At higher temperatures the distribution of di-and trivalent ions becomes more like a normal spinel. At higher oxygen potentials there is a deviation from ideal stoichiometry, which may be achieved by increasing the number of vacant octahedral interstices. The electroneutrality is then maintained by increasing the number of trivalent ions. At low oxygen potentials there is also some deviation from stoichiometry which may be accommodated by divalent ions on the extra octahedral interstices that are vacant in the ideal case. Allowing for all these possibilities, Sundman wrote the formula unit with four sublattices as:

$$(Fe^{+2}, Fe^{+3})_1(Fe^{+2}, Fe^{+3}, Va)_2(Va, Fe^{+2})_2(O^{-2})_4 \quad (1)$$

where the first and second sublattices denote the tetrahedral and octahedral interstices, respectively, and the third the extra octahedral interstices which are vacant for the stoichiometric composition and the fourth the oxygen sublattice.

From Sundman's thermodynamic parameters the sublattice occupancy may be calculated. In the present work Thermo-Calc [2] was used. Fig. 1 shows the calculated distribution of Fe^{+2} between the tetrahedral and octahedral interstices as a function of temperature for the stoichiometric composition. The calculated occupancy of Fe^{+2} as a function of oxygen partial pressure at 1273 K is shown in Fig. 2.

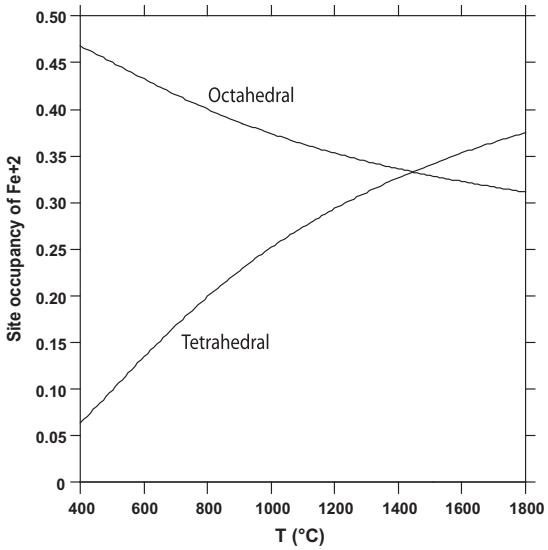

Fig. 1. The site occupancy of Fe^{+2} as a function of temperature for stoichiometric magnetite calculated from Sundman's data [3].

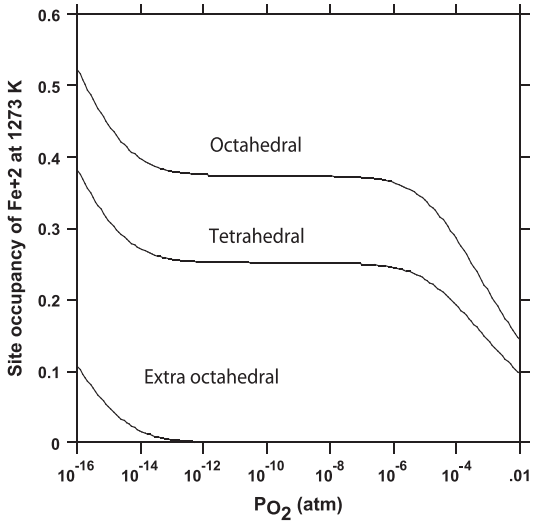

Fig. 2. The site occupancy of Fe^{+2} as a function of oxygen partial pressure at 1273 K calculated from Sundman's data [3].

2.2. Defects and diffusion in magnetite

Peterson et al. [4] analyzed experimental data by Dieckmann and Schmalzried [5] and discussed, in particular, correlation effects. Peterson et al. assumed that the electrons are much more mobile than the Fe-ions and that all Fe-ions are identical at high temperature, i.e. have an average charge. In fact, magnetite exhibits a so-called Verwey transition at around 120 K [9], above which it is half metal with quite mobile electrons. It thus seems reasonable to consider diffusion of one type of Fe without any consideration of its valency. The electron transfer needed to maintain a zero charge flux would then be much faster than the diffusive jumps. When considering diffusion we may then simplify the formula unit given by Eq. (1) to:

$$(Fe)_1(Fe, Va)_2(Va, Fe)_2(O)_4 \quad (2)$$

As iron dissolves interstitially it may diffuse via a vacancy mechanism, and the rate should thus depend strongly on the fraction of vacant sites. Here we consider only diffusive jumps between octahedral sites. Admittedly this conjunction should be tested by more detailed calculations of activation barriers, e.g. by ab initio methods (e.g. [10]). It should be pointed out that the second and third sublattices