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Surface Instability and Nonstoichiometry of α-Fe_2O_3

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The thermodynamic stability region of α-Fe_2O_3 is investigated by thermogravimetric measurements. By means of electron microscopy, the surface of the grains of sintered compacts is shown to be already reduced well within the α-Fe_2O_3 stability region. Based on this information, an electrical conductivity model is presented, in which the inhomogeneous character of the nonstoichiometry of the grains is emphasized.

Introduction

The electrical conductivity of α-Fe_2O_3 can be strongly influenced by atmospheric pretreatment. Both the temperature and the partial oxygen pressure play a decisive role in the departure from stoichiometry, as was already shown by Bosman and van Daal (*1*). At low temperatures the pure material is only slightly oxygen deficient and therefore its conductivity is of n-type character, with a low absolute value of 10^{-8} ohm^{-1} cm^{-1} at room temperature. Cooling down sintered compacts in an atmosphere with the same partial oxygen pressure as experienced during sintering results in high-resistivity samples (*1, 2*). Here the average grain size of sintered compacts is also of importance, as was shown by Gardner *et al.* (*2*).

We have shown before (*3, 4*) that the overall poor conductivity does not result from homogeneous high-resistivity grain boundaries, but from local variations of the stoichiometry at the accessible parts of the grains at open pores. Cooling from 900°C to room temperature in a nitrogen atmosphere having 150 ppm of oxygen results in an increased overall conductivity qualitatively similar to the increased conductivity of quenched samples after an air sintering procedure at 1300°C.

We performed TG experiments in air on quenched samples to determine the average departure from stoichiometry. At the same time we investigated the reduction of hematite to magnetite in a nitrogen atmosphere for our sintered compacts. Although the bulk thermodynamics of the Fe–O system were investigated quite elaborately by Salmon (*5*), these TG experiments were necessary to get information on the reduction at the surface of the grains, because bulk thermodynamics do not apply to these surface layers. Also, the limited porosity (15%) might influence the kinetics of this reduction process.

Based on these TG experiments in combination with data on the electrical conductivity, we present a model for the electrical conductivity of the material that emphasizes the inhomogeneous character of the

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grains after a quench or nitrogen pretreatment.

Experimental

Sintered compacts were prepared from spectrochemically pure α-Fe_2O_3 of JMC (Puratronic, Grade I). The powder was pressed into tablets using a pressure of 3×10^6 N/m^2. These pressed tablets were sintered in air at 1300°C for 24 hr, reaching an ultimate density of 85% of the theoretical value (*6*). For some experiments these tablets were quenched to room temperature by dropping them into liquid nitrogen, for others a slow-cooling procedure in air in 900°C and a further slow-cooling procedure in a nitrogen atmosphere (150 ppm O_2) to room temperature were performed. The sintered compacts were then used for TG analyses or electrical conductivity experiments under various atmospheric conditions. The TG analyses were performed with Dupont equipment in conjunction with a Cahn electrobalance (model RH). This balance has a sensitivity of 1 μg and a precision of 2 μg. The measurements were performed in a gas flow of 25 cm^3 min^{-1}, while the heating or cooling rate normally was 6°C min^{-1}! For a more detailed description of the TG analyses we refer to Ref. (*7*). The electrical conductivity was measured with a four-points technique using a Kelvin bridge arrangement, described before (*8*, *9*). The measurements were performed at 1000 Hz and the voltage used was 5 V (pp). Electrode contacts were provided by platinum paint (Degussa).

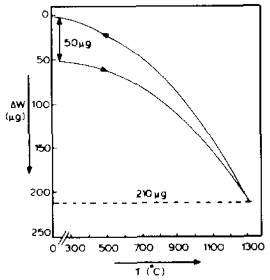

FIG. 1. The weight signal of a 360-mg α-Fe_2O_3 sample as recorded in air as a function of temperature.

Results and Discussion

Figure 1 represents the weight signal, as recorded in air, of a 360-mg quenched tablet as a function of temperature. When warming up, the sample starts loosing weight above 300°C. A total weight loss of 160 μg is reached at 1300°C. When cooling from 1300°C to RT an overall weight gain of 210 μg is observed.

According to Salmon (*5*) and Gardner (*2*) the oxygen vacancy concentration in α-Fe_2O_3 can be given by

$$N_{\mathrm{d}} = 3.27 \times 10^{26} \times p_{O_2}^{-1/4} \times \exp(-2.03/kT)\mathrm{cm}^{-3}. \quad (1)$$

From this equation it follows that

$$N_{\mathrm{d}\,\substack{1300^\circ\mathrm{C} \\ \mathrm{air}}} = 1.5 \times 10^{20}\ \mathrm{cm}^{-3}. \quad (2)$$

This is in good accordance with our overall weight difference of 210 μg for the 360-mg sample (theoretical density: 5.23 g · cm^{-3}). If this weight difference is attributed to the evolution of O_2 we find a value of 1.2×10^{20} cm^{-3}, which is slightly lower than the true thermodynamic value. This difference can be expected because below 300°C no true equilibrium is obtained when cooling, so that at RT some unfilled oxygen vacancies will still remain.

The difference between the two curves in Fig. 1 is then the result of the quenching procedure before the warming curve was taken. The ultimate weight difference amounts to 50 μg, which is equivalent to an overall quenched-in oxygen-vacancy concentration of 3×10^{19} cm^{-3}. This increased concentration of oxygen vacancies, acting as electron donors at higher temperatures, results in an increased electrical conductivity, as is indeed observed (curve 1, Fig. 2). This increased conductivity vanishes again after warming in air and cooling, as can also be observed in Fig. 2. The oxygen-vacancy concentration of 3×10^{19} cm^{-3} as a result of the quenching procedure is equal to the equilibrium concentration of the material, according to Eq. (1), at 1150°C. The conductivity at these temperatures is very good as can be seen from an extrapolation of the curves in Fig. 2 to higher temperatures. Therefore we conclude that the conductivity of these quenched samples is influenced by the following effects.

First, the overall influence of the grain boundaries on the mobility cannot be neglected. This can readily be seen in Fig. 2, where curve 4 represents the conductivity of a sample of Gardner pretreated in a manner similar to that used for our samples, but with bigger grains resulting in a higher conductivity. The second reason for the poor conductivity despite the high donor concentration is the inhomogeneous character of the grains themselves. The evidence for this explanation will be presented in the next section. The observed increased conductivity and also the high-temperature part of Fig. 2 cannot result from intrinsic band–band transitions. The bandgap of α-Fe_2O_3 is not exactly known, but generally one accepts a value of about 2 eV. With this value, and accepting an effective mass of 1 for the charge carriers, we find an intrinsic electron concentration, cf. Eq. (3), at 1150°C of 8.4×10^{16} cm^{-3}, which is very much below the observed $[V_{\dot{O}}]$ concentration.

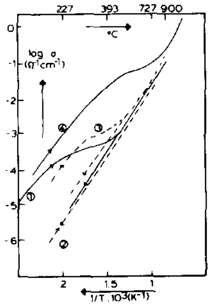

FIG. 2. The electric conductivity of some pure α-Fe_2O_3 samples as a function of reciprocal temperature: (1) quenched sample; (2) slowly air-cooled sample; (3) sample treated in nitrogen at 900°C; (4) sample of Ref. (2) bigger grains.

$$n_i = \frac{2(2\pi m\, kT)^{3/2}}{h^3} \cdot \left(\frac{m_n^* \cdot m_p^*}{m^2}\right)^{3/4} \cdot \exp(-E_g/2kT), \quad (3)$$

where n_i denotes the electron concentration, m the electronic mass, k the Boltzmann constant, h the Planck constant, T the temperature, and E_g the bandgap.

Thermodynamic Stability and Reducing Conditions

The equilibrium partial oxygen pressure for the equilibrium between hematite and magnetite: $6\ Fe_2O_{3(s)} \rightleftarrows 4\ Fe_3O_{4(s)} + O_{2(g)}$ as deduced from thermodynamical data (*10*) can be given by the relation

$$\ln(p_{O_2}) = -59{,}800/T + 33\ .5 \text{ atm}. \quad (4)$$

This equilibrium pressure has been pictured in Fig. 3. From this picture it is immediately clear that all our experiments in air are well within the stability region of hematite. For a nitrogen atmosphere with 150 ppm of oxygen, experiments should be performed below 1125°C to avoid reduction to magnetite. However, since these thermodynamical data are based on the assumption that true equilibrium between two pure solid phases exists (thus implying for both solids an activity of 1), we were

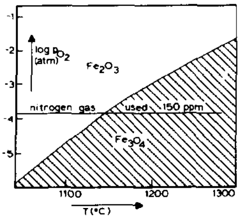

FIG. 3. The equilibrium partial oxygen pressure as a function of the temperature for the equilibrium between magnetite and hematite.

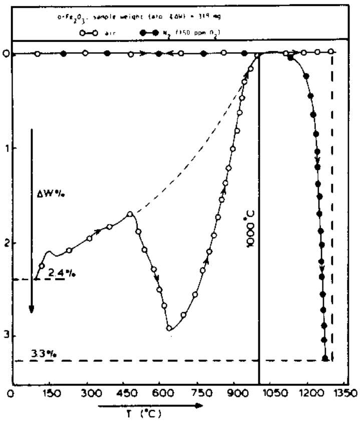

FIG. 4. The weight signal of a partly reduced hematite (see text) sample as a function of the temperature in air (ooo) and nitrogen (●●●).

obliged to investigate the behavior of our sintered tablets under reducing conditions. Here a possible dissolution of magnetite into the hematite phase (e.g., microregions of magnetite in hematite) might influence the equilibrium, and moreover, for these compact samples, the kinetics of the reduction process might be disturbing.

Figure 4 shows the weight change of a sintered tablet under varying atmospheric conditions as a function of temperature. Prior to this TG experiment the tablet was reduced to an overall composition of 70 wt% Fe_3O_4 and 30 wt% Fe_2O_3. This composition was verified with magnetic susceptibility and X-ray diffraction measurements. Warming up in air results in a reoxidation to hematite, which is complete at 1000°C, where 2.4% of weight increase was established. The enormous dip in the warming curve is an apparent weight effect resulting from the change in magnetic behavior of the sample (*11*). The windings of the furnace used, though bifilarly wound, obviously provided a magnetic field. When we cooled a reduced sample in nitrogen (not shown), a similar dip (now upwards) was observed, which did not show up when cooling was performed with a disconnected furnace!

Cooling in air to room temperature shows no further weight change. Warming again, but now in a nitrogen atmosphere, results in an observable weight loss starting at 1000°C, where the reoxidation mentioned above had been completed. This weight loss increases sharply at 1125°C, and results in an ultimate weight loss at 1300°C of 3.3%, which is exactly in accordance with the reduction of hematite to magnetite:

$$Fe_2O_3 \xrightarrow[\text{or } -11 \text{ wt\% oxygen}]{-3.3 \text{ wt\%}} Fe_2O_{2.67} = Fe_3O_4.$$

From these data it can be understood that at 900°C indeed no reduction to magnetite takes place in a nitrogen atmosphere, as was expected from equilibrium thermodynamics. Only at 1000°C does reduction start at an observable rate and this rate increases as a second phase of Fe_3O_4 if formed at 1125°C, also in accordance with the equilibrium picture in Fig. 3. The formation of Fe_3O_4 at these temperatures was also verified with X-ray diffraction on cooled samples. Judging from the data on the thermodynamic stability, we can treat sintered tablets in a nitrogen atmosphere (150 ppm O_2) at 900°C without any chance of reduction to a second phase. The application of

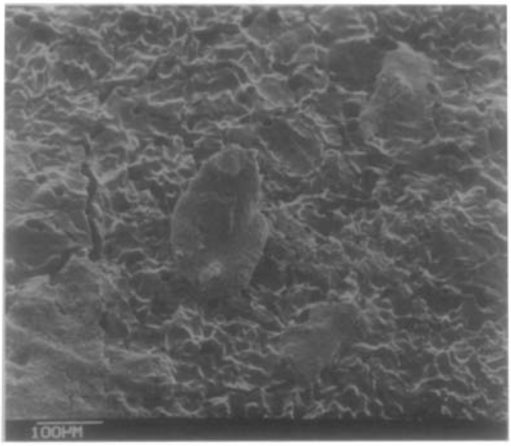

FIG. 5. Partly reduced surface of hematite sample showing smooth surface and adhering magnetite.

Eq. (1) is still allowed and results in an oxygen-vacancy concentration of

$$N_{\mathrm{d}_{900^\circ}}^{\mathrm{N}_2} = 5.4 \times 10^{18}\ \mathrm{cm}^{-3}.$$

This concentration is even smaller than the quenched-in concentration of 3×10^{19} cm^{-3} we observed before. However, the conductivity of these nitrogen-treated samples is better than observed for the quenched samples. (see Fig. 2). The grain structure and the density of both types of material are the same. Therefore we ascribe this contradiction again to the inhomogeneous character of the grains.

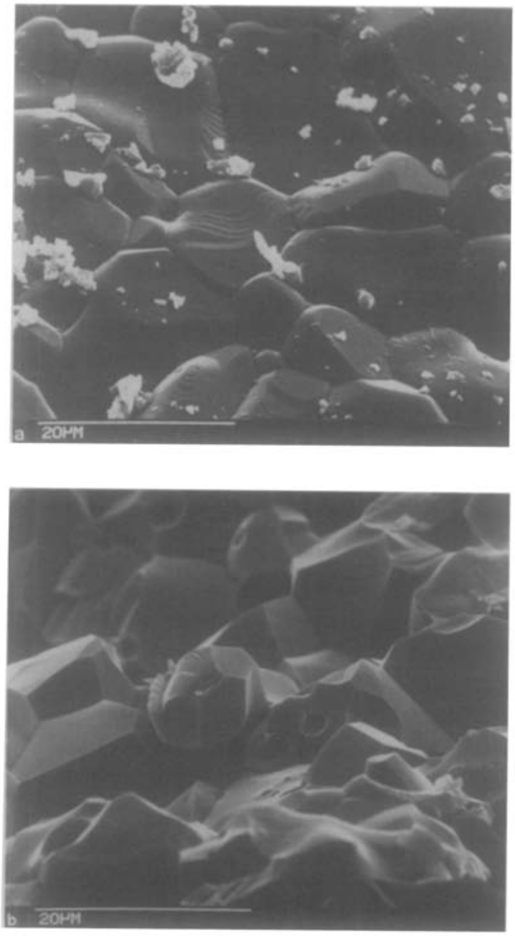

FIG. 6. (a) Normal surface of sintered α-Fe_2O_3 compact. (b) Inside of broken α-Fe_2O_3 compact.

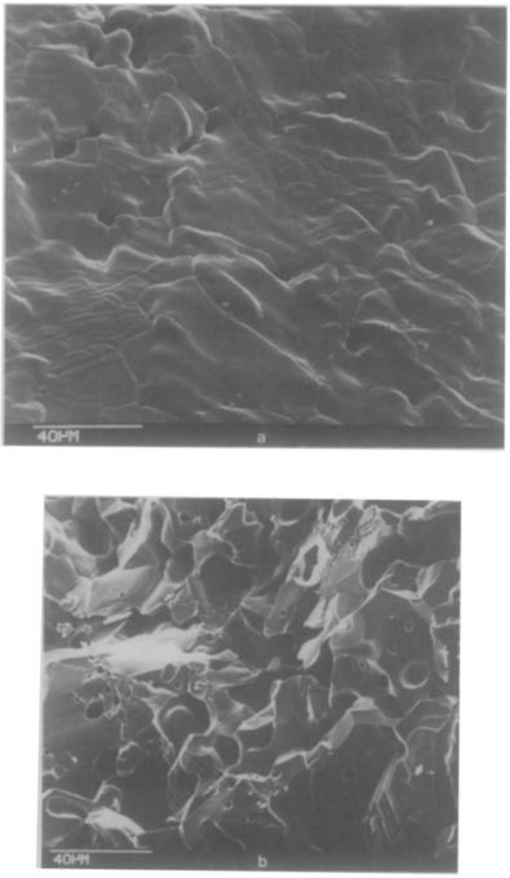

FIG. 7. (a) Surface of nitrogen-treated (see text) α-Fe_2O_3 compact. Compare with more crystalline surface of Fig. 6a. (b) Inside of broken nitrogen-treated α-Fe_2O_3 compact, showing surface reduction at original open pores. Compare with more crystalline surface of Fig. 6b.

The Grain Structure Model

Though equilibrium thermodynamics do exclude the presence of a reduced second phase under the mentioned experimental conditions, this need not necessarily be the case for the surface of the materials. The surface also includes the internal surface as far as it is accessible to the gas atmosphere via open pores.

When a true reduction in a nitrogen atmosphere at high temperature (1300°) has taken place, the surface of the sample

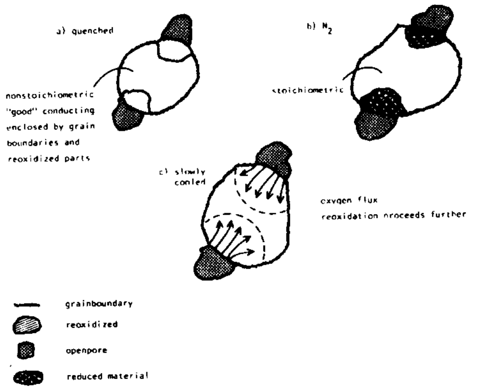

FIG. 8. Grain structures resulting from various pretreatments.

shows small magnetite particles and bigger magnetite lumps adhering to the remaining hematite surface, as can be seen in the electronmicrograph in Fig. 5. However, the remaining hematite surface is smoothed very much as compared with the original surface (Fig. 6). This surface deterioration is ascribed to the formation of a nonstoichiometric suboxide (thermodynamically unstable), which is an intermediate phase during the course of reduction (see also Ref. (*12*)). This surface smoothing is also observed when a hematite sample is treated in nitrogen at 900°C: far from the thermodynamical phase boundary!

Clearly, no magnetite is formed but the smooth grain surface can be seen in Fig. 7. This brings us to the following conclusion. The quenched samples have a lower conductivity despite the higher average oxygen vacancy concentration, because of the inhomogeneous grain structure as pictured in Fig. 8. Figure 8a shows the reoxidation of the material (one grain), where the grain is accessible to the atmosphere at the open pores, when the quenching procedure is not infinitely fast. These reoxidized parts block the current. Figure 8b shows the opposite picture at the open pores, where the nonstoichiometric suboxide has been formed during the 900°C treatment in nitrogen. These samples have an overall better conductivity, because no poor conducting blocking parts at the grain surface exist. A further reoxidation at the open pores from the surface into the bulk of the grains results (cf. Fig. 8c) when a slow cooling procedure in air is performed, which indeed results in very poorly conducting material, as was observed in Fig. 2.

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