Mechanism and kinetics of the reduction of magnetite to iron during heating in a microwave *E*-field maximum

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The time-resolved x-ray diffraction method was applied *in situ* to investigate the carbothermal reduction of magnetite by carbon black in a 2.45 GHz microwave field. The kinetics of the phase transformation sequence is analyzed within the Kolmogorov–Johnson–Mehl–Avrami formalism. The first reduction stage is the solid-state transition of magnetite to wüstite, followed by the partial conversion of nearly stoichiometric wüstite to iron. The kinetics of the initial reduction of Fe_3O_4 to primary wüstite is phase boundary controlled. Behind the reaction front, primary wüstite rapidly evolves toward stoichiometric FeO . Cation vacancies and the dynamic clustering of structural defects influence the kinetics of the reduction of the nearly stoichiometric secondary wüstite to porous iron. © 2009 American Institute of Physics. [DOI: 10.1063/1.3148264]

I. INTRODUCTION

The interest in highly efficient, energy saving, and environmental friendly heating processes is nowadays higher than ever. Microwave heating benefits from several remarkable advantages over its competitors: fast volumetric heating, frequency or chemical phase selectivity, or the proven ability to kinetically avoid the formation of undesirable phases or the coarsening of nanoscale features in bulk solids.^{1,2} The lack of detailed knowledge on the transformation of materials during their complex interaction with the microwave field yet hinders the wider use of this attractive method in the modern industrial heating of materials. In support to this need, the *in situ* time-resolved monitoring of microwave heating by the wide-angle synchrotron radiation powder diffraction technique was implemented and recently used to study the microwave heating behavior of Al-, Fe-, and Co-based alloys.^{3–5}

Magnetite (Fe_3O_4) is a well-known material with an exceptionally broad application base. It is the oldest magnetic material known to man. It was shown to be a performant catalyst for key Fischer–Tropsch reactions.⁶ Magnetite/carbon nanorods are regarded as promising anode materials for Li-ion batteries.⁷ Of outmost interest today is the use of iron oxide particles in contrast-enhanced magnetic resonance imaging (MRI) and also in drug delivery, hyperthermia, and several other *in vivo* biomedical applications^{8,9} which exploit the unique microwave ability to heat remotely and selectively.

In this paper, the microwave-assisted carbothermic reduction of magnetite Fe_3O_4 to iron is studied *in situ* by the time-resolved x-ray powder diffraction (TRXRD). The reduction of magnetite to iron usually using coal, graphite, or carbon black is essential to iron and steel industries. There is a keen interest in the use of microwave heating technology for this application.^{10,11} This interest is driven by the potential for energy saving and significant reduction in CO_2

emission.^{2,11,12} From the point of view of its interaction with microwaves, magnetite is attractive because both *E* and *H* components of the electromagnetic field result in strong heating.¹³ Unusual microwave effects such as the decrystallization of Fe_3O_4 without melting were reported in the past.¹⁴

II. EXPERIMENTAL DETAILS

Microwave heating of pure magnetite/carbon black mixed powders¹⁵ was carried out *in situ* using a portable monomode microwave furnace operating at 2.45 GHz. The TRXRD experiments were performed in transmission geometry at the MS-X04SA wiggler beamline at the Swiss Light Source (monochromatic radiation, $\lambda=0.062$ nm). The Mythen II detector enables the collection of high-resolution wide-angle diffraction patterns at data acquisition rates of up to 10 Hz. The mixed powders were mounted in sapphire capillaries and placed in the calculated *E*-field maximum of the resonant cavity. Temperature was measured with a Luxtron PhotriX optical pyrometer placed next to the sample. More details on the experimental setup are given in Refs. 3–5.

The input microwave power was kept equal to 0.5 kW throughout the *in situ* x-ray experiment (Fig. 1). In order to initiate microwave absorption, the resonating cavity is remotely tuned by adjusting a three-stub tuner and/or a sliding plunger. After the onset of heating, no further tuning is exercised. The specimen temperature normally rises up to a saturation value at which a dynamic equilibrium between the amount of heat generated in the sample and the radiative heat losses to the specimen environment is established. The maximum temperature attained can be regulated within certain limits by varying the microwave input power.

As shown in Fig. 1, the onset of strong microwave absorption (at which the absorbed microwave power stabilizes to about 100 W) occurs once the specimen temperature rises irreversibly above the Curie temperature of Fe_3O_4 ($T_C \approx 580$ °C).^{16,17} It was recently shown¹⁷ that intense local magnetization fields are induced by the *E*-field component of

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FIG. 1. Power and temperature evolution during the *in situ* microwave heating experiment.

the external microwave field. These dynamic magnetization processes significantly contribute to heating by raising the internal energy of the sample. Dissipative spin dynamics simulations¹⁷ for magnetite indicate that this contribution to specimen heating is maximum at the Curie temperature and nonzero above T_C . The significant enhancement of the heating efficiency and of the coupling to the microwave field once the sample passes through the Curie point (Fig. 1) is related to the above heating mechanism.

At $t=100$ s, the temperature rises from 783.5 to 1142.6 °C in 2.8 s, which corresponds to a high heating rate of 128 °C/s. The temperature varies between 1052 (at $t=103$ s) and 1100 °C (at $t=600$ s) following the changes in the microwave absorption of the specimen. The microwave generator is turned off at $t=600$ s and the sample cools down at a cooling rate of 30 °C/s.

III. RESULTS AND DISCUSSION

The reduction of Fe_3O_4 to Fe is completed within the first 3 min following the onset of the reaction at $t=120$ s. Figure 2 shows a two-dimensional map of the diffracted x-ray intensity as a function of time for this region of inter-

FIG. 2. (Color online) Two-dimensional map of the x-ray diffracted intensity against time.

FIG. 3. Enlarged view of the x-ray diffraction patterns showing the splitting of the wüstite (200) Bragg peak.

est. Magnetite Fe_3O_4 is a ferrimagnetic material with an inverse spinel structure AB_2O_4 .¹⁸ The Fe^{3+} cations occupy tetrahedral (A) and octahedral (B) sites, while Fe^{2+} ions are found in octahedral positions only. The initial Bragg peaks were all assigned to pure Fe_3O_4 , which is the only iron oxide phase detected before the reaction start-up.

The solid-state reduction of magnetite to iron occurs in two steps. In the first reaction step, Fe_3O_4 is reduced to wüstite Fe_xO (with x as the Fe:O ratio, $x=1-z$, and z as the metal deficit). A closer look at the x-ray diffraction patterns reveals the splitting of the wüstite Bragg peaks starting from $t=150$ s. We hereafter distinguish between *primary* wüstite (W1) detected at the reaction onset and *secondary* wüstite (W2), which is observed for the first time at $t=150$ s (Fig. 3).

Magnetite and the primary wüstite disappear simultaneously at $t=180$ s. Between $t=180$ and 200 s the specimen consists of a single-phase secondary wüstite. The second reaction step is the partial reduction of W2 to iron. Iron is first detected at $t=200$ s (Fig. 3).

The evolution of the lattice parameters of W1 and W2 wüstite phases is shown in Fig. 4. The lattice expansion is less pronounced for the primary wüstite (rate of 1.72×10^{-5} nm/s) compared to W2 (rate of 8.08×10^{-5} nm/s). Starting with $t=180$ s secondary wüstite is the only phase detected and its lattice parameter stabilizes to $a=0.4364$ nm. The change in the slope of the lattice parameter of secondary wüstite may signal an order-disorder transition between wüstite subphases, i.e., the crossing over a boundary line in the Fe–O phase diagram.^{19,20} The lattice expansion is mainly due to the evolution of W2 toward stoichiometry. The linear correlation established in Ref. 20 between the lattice parameter of wüstite and its composition x at 1050 °C is used to quantify the gradual change in the composition of secondary wüstite (Fig. 4). The W2 phase evolves from an initial nonstoichiometric $\text{Fe}_{0.88}\text{O}$ state to a

FIG. 4. Evolution of lattice parameters of the primary (W1) and secondary (W2) wüstite phases during the magnetite to wüstite reduction stage.

nearly stoichiometric $\text{Fe}_{0.94}\text{O}$ phase in excellent agreement with the recent results of Pineau *et al.*²¹ The conversion to Fe proceeds only after the transformation to nearly stoichiometric $\text{Fe}_{0.94}\text{O}$ wüstite is completed.

The amount of each constituent phase during the transformation sequence was determined from the integrated intensities of the x-ray diffraction lines (Fig. 5). Briefly, the whole-pattern fitting method was used to numerically deconvolute the elastically scattered intensity contribution of each phase within a fixed interval of the 2θ scattering angle (here between 8° and $25^\circ 2\theta$). The ratio of the integrated intensity separately contributed by each constituent phase to the total intensity scattered within the fixed 2θ interval is a measure of the weight fraction α of each particular phase. In this way the kinetics of the individual reduction reactions could be quantified (Fig. 5). The initial reduction in magnetite to wüstite is described by the change in the cumulated (W1+W2) amount of wüstite (open circles, Fig. 5). The individual contributions of W1 (triangles) and W2 (filled circles) phases are also shown.

The transformation kinetics is described using the Kolmogorov–Johnson–Mehl–Avrami equation^{22–24}

$$\frac{\alpha}{\alpha_{\max}} = 1 - \exp[-(kt)^n] = 1 - \exp\left[-\left(\frac{t}{\tau}\right)^n\right], \quad (1)$$

where $k = \tau^{-1}$ is the reaction rate and n is the Avrami number. In logarithmic form, Eq. (1) becomes

FIG. 5. Relative weight fractions of magnetite, wüstite, and iron as a function of time.

FIG. 6. Schematic representation of the magnetite to wüstite transformation mechanism.

$$\ln\left[-\ln\left(1 - \frac{\alpha}{\alpha_{\max}}\right)\right] = n \ln k + n \ln t. \quad (2)$$

For the first reduction step (magnetite to wüstite), the Avrami plots evidence two distinct dynamic regimes. For the interval between 125 and 155 s we obtain the rate constant $k = 17.545 \times 10^{-3} \text{ s}^{-1}$ and the Avrami number $n = 1.62$. For the subsequent time interval between 155 and 180 s the rate constant equals $k = 22.956 \times 10^{-3} \text{ s}^{-1}$ and the Avrami number $n = 3.14$. Finally, for the conversion of the nearly stoichiometric $\text{Fe}_{0.94}\text{O}$ wüstite to Fe we obtain the maximum conversion rate $\alpha_{\max} = 58.8\%$, the rate constant $k = 20.4 \times 10^{-3} \text{ s}^{-1}$, and $n = 1.15$. At $t = 300 \text{ s}$ the wüstite conversion to iron stops presumably due to the consumption of solid carbon and/or gaseous CO reduction agents. The final reaction product consisting of 58.8% Fe and 41.2% wüstite is preserved upon rapid cooling, i.e., no disproportionation reaction takes place.

The reduction of pure magnetite to iron upon microwave heating at 2.45 GHz in an electric field maximum therefore also proceeds stepwise. The first reaction step is the reduction of Fe_3O_4 to wüstite Fe_xO . This reduction reaction is initiated at the surface of magnetite particles (Fig. 6) at first in contact either with carbon black powder or other magnetite particles. Both carbon black²⁵ and magnetite^{13,14} are rapidly heated by the microwave E -field. The temperature and/or the chemical gradient across this interface initiates the reaction. The nonstoichiometric primary wüstite W1 forms at the surface of the unreacted Fe_3O_4 core and propagates toward the center of the magnetite particles (Fig. 6).

The unreacted Fe_3O_4 core rapidly shrinks until all magnetite is consumed in the reaction. The W1 boundary layer represents an inward propagating reaction front, repeatedly generated at each instance of time, therefore experiencing negligible compositional changes. It also naturally disappears simultaneously with magnetite in agreement with the present observations. Behind the primary wüstite reaction front, the remaining secondary wüstite W2 phase gradually evolves toward the FeO stoichiometric state. This is mainly achieved by the oxygen diffusion to the initial boundaries of the magnetite particles, where carbon gasification takes place. The partial conversion of the nearly stoichiometric wüstite to Fe follows at a rate comparable with those of the first reduction step. In fact, the observed kinetics of phase transformations is nearly the same throughout the reduction process. This consequently suggests that oxygen depletion of the iron oxide structure is the dominant diffusion mechanism that controls the reaction rate.

IV. CONCLUSIONS

The reduction in magnetite Fe_3O_4 to iron in a microwave electric field maximum at 2.45 GHz is completed within 3 min. Neither melting nor decrystallization events were observed. Stable heating above 1000 °C is readily achieved due to microwave absorption by both Fe_3O_4 and carbon black. Heating to high temperatures appears to be triggered by magnetite powder being irreversibly heated above its Curie temperature, in agreement with the recent results of Tanaka *et al.*¹⁷ The magnetite reduction to Fe is mediated by wüstite. Wüstite is formed as a nonstoichiometric reaction layer at the surface of unreacted Fe_3O_4 cores. The primary wüstite reaction front propagates toward the inner volume of the magnetite particles. The transformation kinetics at this initial stage of the magnetite-to-wüstite transition (from $t = 120$ to 155 s) is controlled by the formation and propagation of this reaction layer. The Avrami exponent $n = 1.62$ indicates a diffusion-controlled process in which particles of arbitrary shape grow from small dimensions at zero nucleation rate.²⁶ Behind the reaction front, wüstite approaches a nearly stoichiometric $\text{Fe}_{0.94}\text{O}$ state. This process determines the rate of the magnetite-to-wüstite transition between $t = 155$ and 180 s. The Avrami exponent $n = 3.14$ indicates a transformation mechanism with nearly zero nucleation rate and three-dimensional growth. Finally, the $\text{Fe}_{0.94}\text{O}$ phase is partially converted to iron (up to 58.8 wt %). The Avrami number for the wüstite reduction to iron $n = 1.15$ describes the diffusion-controlled axial growth of cylinders or rods.²⁶ This result also complies with the porous coral-like iron structures commonly observed.²¹

The TRXRD method used in conjunction with *in situ* microwave heating allows for a detailed description of the mechanism and kinetics of the high-temperature reduction of magnetite to iron in the presence of carbon black. At this time, a direct comparison with the results of conventional heating experiments is difficult due to wide differences in the nature and amount of the starting powders, final treatment high temperature, heating rate, and heating environment. To facilitate this interesting comparison, further work is however underway to investigate the reduction in magnetite using conventional heating and in a microwave H -field on the

same powder specimens and under similar experimental conditions as in the present study.

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