Journal of Alloys and Compounds 724 (2017) 728–734

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Phase transformations of stoichiometric mixtures of hematite and iron under FAST conditions

Kerstin Witte [a], [*], Wiktor Bodnar [a], Norbert Schell [b], Gerhard Fulda [c], Eberhard Burkel [a]

[a] University of Rostock, Institute of Physics, Albert-Einstein - Str. 23, D-18059, Rostock, Germany
[b] Helmholtz-Center Geesthacht, Institute of Materials Research, Max-Planck-Str. 1, D-21502, Geesthacht, Germany
[c] University Medicine Rostock, Medical Biology and Electron Microscopy Centre, Strempelstr. 14, D-18057, Rostock, Germany

ARTICLE INFO

Article history:
Received 13 December 2016
Received in revised form
20 June 2017
Accepted 8 July 2017
Available online 10 July 2017

Keywords:
Iron oxides
Magnetite
Phase transformations
Nanocomposites
Field assisted sintering technique (FAST)

ABSTRACT

Since the mechanism of the synthesis of magnetite from a stoichiometric mixture of hematite and iron is still under debate, systematic studies of the phase transformations in such powder mixture processed under field assisted sintering conditions, are presented. Phase contributions, grain sizes and stoichiometries of the sintered composites were determined using scanning electron microscopy, high energy X-ray diffraction and Mößbauer spectroscopy. It was shown that with an increasing sintering temperature an accelerated growth of magnetite can be observed, while the amount of hematite decreases. Additionally, intermediate wustite phase was observed with a maximum intensity where iron vanished from the samples. Therefore, it was concluded that the transition from hematite - iron mixture to magnetite actually takes place in two steps. In the first step, iron reduces hematite to magnetite and oxidizes itself to wustite. In the second step, wustite enables the nucleation of magnetite and with the help of hematite it transforms into nearly pure stoichiometric magnetite at higher sintering temperatures. In composites sintered from pure hematite under the same conditions only a minor transition to highly nonstoichiometric magnetite was observed emphasizing the above mentioned route of transformation.

1. Introduction

Nanostructured materials attracted a lot of attention in the last years due to their unusual chemical and physical properties which are promising for further technological development [1–3]. The properties of these nanostructured materials differ from those of normal bulk materials due to the small particle- or grain sizes which are in the nanometer regime leading to the presence of size and surface effects [1].

The rather novel field assisted sintering technique (FAST), also called spark plasma sintering (SPS), is a promising tool for the consolidation and synthesis of such nanostructured bulk materials. During FAST a pulsed directed current and a mechanical load are applied on precursor powders placed in a graphite die, leading to rapid heating of the powders [4]. Advantages of FAST are short process times and the possibility of maintaining nanostructured grains [4,5].

The preparation as well as the properties of iron oxides still attract considerable interest and attention in materials technology. Particularly, the interest in magnetic nanoparticles based on iron oxides rose drastically because of their wide range of potential applications, especially in biomedicine [2,3,6–8]. For nanoparticles and thin films, a broad range of interesting effects like superparamagnetism [9], giant magnetoresistance [10] or increased energy product [11] has been observed, while the behaviour of nanostructured bulk materials based on iron oxides is widely unknown. First studies on iron oxide systems already showed changes in the coercivity and the saturation magnetisation for different grain sizes [12–16].

In the family of iron oxides magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are the most important ferrimagnetic compounds. The stoichiometry of magnetite, which is often referred to as a solid solution of magnetite and maghemite, strongly influences the physical and chemical properties as the reduction potential, coercivity or crystal structure of the particles [17]. Magnetite has a cubic unit cell which belongs to the space group Fd-3m and a crystal unit edge of a ~8.39 Å [18]. The unit cell of the stoichiometric spinel contains 32 oxygen atoms and has 8 equivalent tetrahedral and 16

---

[*] Corresponding author.
E-mail address: kerstin.witte@uni-rostock.de (K. Witte).

http://dx.doi.org/10.1016/j.jallcom.2017.07.089

equivalent octahedral sites which can be occupied by iron atoms. Magnetite contains not only trivalent but also divalent iron in the octahedral sites. The formula of Fe_3O_4 can also be presented as $(Fe^{3+})_{tetra}[Fe^{3+}+Fe^{2+}]_{octa}O_4^{2-}$ [19]. Magnetite has a wide range of oxidation states depending on the structural Fe^{2+} states, which can be discussed as the stoichiometry of magnetite ($x = Fe^{2+}/Fe^{3+}$). $x = 0.5$ refers to the stoichiometric magnetite Fe_3O_4 and $x = 0$ to its completely oxidised form, maghemite γ-Fe_2O_3. Maghemite is characteristic of a crystal unit edge a ~8.33 Å [18]. For non-stoichiometric magnetite, the structure formula can be presented as $Fe_{3-\delta}O_4$ with δ ranging from 0 to 1/3. Assuming that the vacancies $\square$ are only present on the octahedral sites, the formula can be written as $(Fe^{3+})_{tetra}\ [Fe^{3+}{}_{1+2\delta}+Fe^{2+}{}_{1-3\delta}\square_{\delta}]\ {}_{octa}O_4^{2-}$ [17].

Furthermore, the family of iron oxides stands out due to the great variety of possible interconversions between different phases [18]. This means that nearly every iron oxide can be transformed into another. For example, magnetite can be obtained from hematite by reduction in a reducing gas, as well as by reduction-dissolution reprecipitation in an alkaline solution [18]. Likewise, maghemite can be obtained from hematite by thermal conversion [18]. Bulk ferrimagnetic nanostructured iron oxides were mainly synthezised from maghemite. Field assisted sintering of commercially available γ-Fe_2O_3 powders with particle sizes of 8 nm and 40 nm in the temperature regime 300 °C - 900 °C resulted in a partial conversion of maghemtite into hematite [12–14]. It was also shown that the obtained materials were composites of multiple iron oxide phases, and that with an increasing sintering temperature the fraction of hematite phase decreased [13]. It enabled the observation of exchange bias in the large three dimensional components [14]. Moreover, pure bulk nanostructured maghemite was obtained by field assisted sintering of precipitated γ-Fe_2O_3 powder at relatively low temperatures of only 300 °C - 350 °C and an applied pressure of 120 MPa [15]. Other approaches of top- down methods showed that using a stoichiometric mixture of hematite and iron in high energy ball milling can lead to pure magnetite with enhanced coercivity values [20]. Nervertheless, the obtained powder was not stable upon heating in air [20].

Considering this, it was interesting to process with FAST a stoichiometric mixture of hematite and iron in a wide temperature range. The grain sizes, the composition and the stoichiometry of magnetite all influence the overall physical properties of the resulting bulk composites. Therefore, the transformation and the evolution of particular phases in the sintered materials were investigated ex-situ. In particular, the phase contributions, the grain sizes as well as the stoichiometry were studied in dependence of the sintering temperature using scanning electron microscopy, high energy X-ray diffraction and Mößbauer spectroscopy. These results were compared with their counterparts obtained for composites sintered only from pure hematite powder.

2. Field assisted sintering

Hematite and iron powders with mean particles size of 190(10) nm and 220(60) nm, respectively, were mixed assuming the following reaction

$$4\,Fe_2O_3 + Fe \rightarrow 3\,Fe_3O_4. \tag{1}$$

Further details on the precursor powders are summarized in the supplementary. All samples were designed to have a thickness of approximately 4 mm after consolidation. The appropriate amounts of powders were weighted using a precise laboratory balance and blended in grinding jars for 20 min in order to ensure homogeneity. The obtained precursor was placed in a graphite die with an inner diameter of 40 mm. The powder was separated from the inner walls of the die and the punches by a graphite foil in order to prevent reactions with the graphite dies and to ensure an electric contact. In order to reduce radiation heat losses from the outer surface of the die, the graphite die was covered with a porous carbon felt. The application of a carbon felt also reduces possible gradients of temperature in the sample [21,22] and ensures maximal possible in-plane homogeneity of the obtained sample. The sintering procedure was performed in Tycho Sinterlab Rostock using a HP D125 unit from FCT Systeme GmbH Rauenstein, Germany. A series of samples was sintered at different temperatures ranging from 600 °C to 950 °C with a step of 50 K.

Fig. 1 presents exemplary real-time data of the temperature (solid line) and the plunger displacement (dashed line), corresponding to the densification of material [4], during the sintering procedure. In the case of the hematite and iron precursor, the plunger displacement cannot lead to further conclusions due to occurring phase transition into magnetite. The process was divided into four characteristic phases marked in Fig. 1 with vertical dashed lines.

In the first phase, the sintering chamber was evacuated to approximately 1 mbar. Next, the pressure and the temperature were increased to 28 MPa and 400 °C, respectively. Here, it is worth to mention that due to technical limitations the heating process below 400 °C was controlled by a thermocouple mounted in the graphite die and above 400 °C by an optical pyrometer focused on a surface approximately 4 mm away from the sample, in a hole drilled in the upper graphite punch. In the second phase, the temperature was raised to 900 °C and the pressure to 50 MPa. In all cases, this segment time was kept constant (5 min) in order to exclude its influence on the phase transformations and the grain growth. Next, the temperature and the pressure were held constant for another 5 min. Finally, the pressure was released and the pulsed directed current was turned off.

The post-sintered discs were cleaned from the protective graphite foil and broken. Pieces from the middle of each disc were used to prepare samples for further investigations with scanning electron microscopy, high energy X-ray diffraction and Mößbauer spectroscopy.

3. Experimental details

3.1. Scanning electron microscopy

The microstructure of the sintered iron oxide composites was

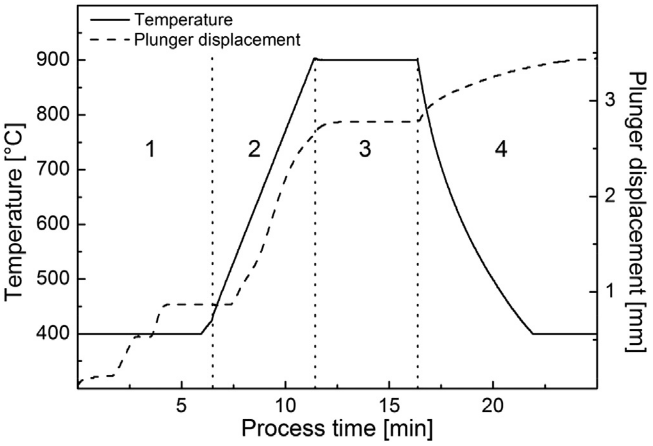

Fig. 1. Temperature and plunger displacement versus sintering time of hematite and iron precursor. Four characteristic phases of the sintering process, described in detail in text, are marked with vertical dotted lines.