

ZINC FERRITE NANOPARTICLES AS PERSPECTIVE FUNCTIONAL MATERIALS FOR APPLICATIONS IN CASTING TECHNOLOGIES

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In this article it discusses on possible application of magnetic oxide nanoparticles, namely non-stoichiometric zinc ferrite nanoparticles as a functionalizing agent in foundry processes. Thermal analysis showed a weight loss of the sample at 1 273 K in an amount of 7,7 %, which is a result of the following processes taking place in different temperature ranges. Upon its thermal treatment $Zn_{0,4}Fe_{2,6}O_4$ decomposes to zinc oxide and iron (III) oxide (first stage) and next to iron (II,III) oxide and oxygen (second stage). The degree of decomposition was expressed as Fe^{2+} / Fe_{total} . Mössbauer spectroscopy showed that the over 30 % of Fe^{3+} present in starting material was reduced to Fe^{2+} .

Key words: casting, zinc ferrite nanoparticles, Mössbauer Spectroscopy, magnetic nanoparticles, thermal decomposition

INTRODUCTION

Nanotechnology is a rapidly growing field of science and chemical engineering that allows obtaining new materials of nanometric size and unique properties. Many materials properties (physical, optical, physico-chemical, electrical, technological) are significantly changed upon reduction of dimension down to nm scale. The particular properties of the nanostructures with respect to the micro-structures are characterized also by specific behavior in the magnetic field. These changes result from increasing impact of the surface ions as well as single domain particles. Reduced size is often associated with increase of density of vacancies and defects as well as reduced stress in the crystal lattice. Therefore, among others, lower heat energy might be used for decomposition of complex compounds and simultaneous formation of new products in the nanoscale. An example of such behavior may be observed in ferrite materials, which essentially consists of Me^{2+} oxide and αFe_2O_3 . Among them non-stoichiometric Zn ferrite, $Zn_xFe_{3-x}O_4$, focus lots of attention due to good control of nanoparticle shape by synthesis conditions and ability to tune magnetic properties by fine tuning of Zn-Fe stoichiometry. However, magnetic properties of nanoscale metal oxides, e.g. coercivity and susceptibility depends not only on the size of the nanoparticles, but also on their shape and morphology [2]. Super-paramagnetism or ferrimagnetism at room temperature is generally reported for nanosized zinc ferrite ($ZnFe_2O_4$) due to unusual occupancy of the magnetic ferric ions in the tetrahedral sites and divalent zinc ions in the octahedral

sites, i.e. spinel inversion. There have been several attempts to synthesize $ZnFe_2O_4$ with different distributions of Zn^{2+} and Fe^{3+} ions in the tetrahedral and octahedral sites [3]. Zinc ferrite is a component of dust extraction furnaces for melting iron alloys, which is the result of the use as feedstock galvanized sheets, mainly from scrap vehicles. Due to the content of zinc compounds, and often cadmium and lead waste, it is classified as hazardous, which is associated with high costs of its storage. Nanocrystalline zinc ferrite $ZnFe_2O_4$ is important material in several technological applications such as gas sensor, magnetic materials, catalysis, and foundry [1]. Yet another important feature of nano zinc ferrite, inter alia, is their high surface area, thus they are used as catalysts in many chemical processes [3].

CASTING TECHNOLOGIES

In the manufacturing process of castings, as in the case of any product, it is important to obtain irreplaceable product, by optimizing conditions of preparation. One of the basic criteria for the evaluation of the casting is the quality of the surface and the nature of the microstructure of the surface layer. They decide primarily on the physico-chemical phenomena determining the metal/sand mold interface that also affects the properties of the entire casting (mechanical properties, corrosion resistance, wear resistance, etc.) [4]. The growing demand for metal alloy castings and aiming at optimizing their shape, size, weight, quality and care for the environment forces the castings manufacturers and suppliers of foundry to undertake research work in developing new materials and alloys, more environmentally friendly. In terms of environmental protection [5, 6] molding sands with water glass are considered harmless. However, molding sands with water glass are characterized by

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low strength in the first phase of hardening, because the process does not proceed “to the end” and is retrying activated after pouring a liquid alloy into casting mold. To eliminate or reduce these disadvantages of the molding sands with sodium silicate used to modify the binder. Among the modification methods of binder one can distinguish: chemical modification with nanoparticles ZnO or/and MgO [7]. Red iron oxide prevents the formation of defects in castings (e.g. vinings, metal penetration) [13]. The aim of the experiment presented was to determine (i) the feasibility and (ii) the degree of thermal decomposition of nonstoichiometric zinc ferrite nanoparticles to obtain specific nanosized products, namely: ZnO and Fe₂O₃ (first stage) and Fe₃O₄ and oxygen (second stage). Assessment of the potential use of the resulting products in foundry processes is discussed.

MATERIALS FOR INVESTIGATIONS AND METHODOLOGY

The starting material for this study was nonstoichiometric zinc ferrite (Zn_{0,4}Fe_{2,6}O₄) particles having an average grain size of 4 - 10 nm, obtained by co-precipitation from water solution. In order to optimize thermal decomposition processes we determined the transition temperature and heat capacity of phase transformation, changes in weight of the sample (substrate/product), the effect of temperature, and the nature of the atmosphere of the processes using Differential Scanning Calorimetry (DSC). The analysis was performed by means of NETZSCH DSC/TGA type 204 F1. The experiment was conducted in N₂ atmosphere, carrier gas flow of 50 ml/min, heating rate 10 K/min. Annealing was at a temperature range from 373 to 1 273 K. They allow to track the energetics and temperature of phase transformations. Phase composition of the starting material and decomposed one was probed using Mössbauer spectroscopy. Measurements were performed using a MS-4 Renon spectrometer in the temperature range of 80 ÷ 300 K, with the thermal stability of the order of 0,05 deg. Spectra collected at room temperatures provides a qualitative indication of grain size [8], while the spectra collected at low temperature allowed us to determine the degree of decomposition following the atomic ratio between Fe²⁺ and all Fe ions in the starting material and after thermal decomposition [9].

RESULTS AND DISCUSSION

TG/DTG ANALYSIS

Thermogravimetric analysis of nanoparticles of a nonstoichiometric zinc ferrite revealed the existence of characteristic temperature ranges, in which there are a significant losses in the mass of the sample (Figure 1).

The first characteristic temperature range of 351,5 ÷ 473 K corresponds to the sample weight loss of 2,35 % that is attributed to release of water physically or chemically bound to the particles' surface;

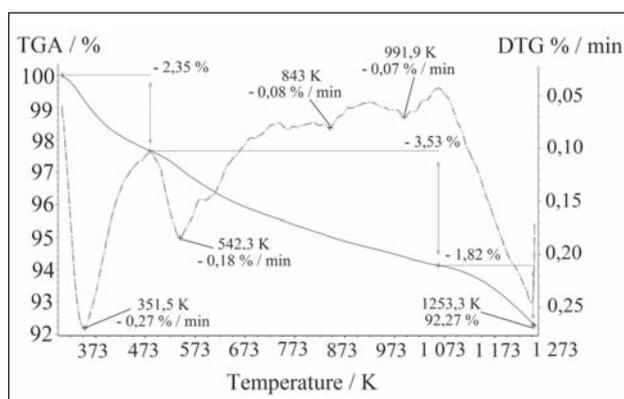
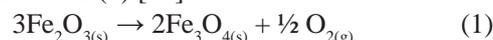


Figure 1 Thermogram obtained for the zinc ferrite nanoparticles synthesized by precipitation method

- second temperature range of 473 ÷ 1 073 K is accompanied by weight loss of 3,53 %, which is tentatively associated to release of oxygen according to the reaction (1) [10]:



Above 473 K the process of thermal decomposition of zinc ferrite begins.

- third temperature range above 1 073 K, which corresponds to the weight loss of 1,82 % which is probably associated with evolution of oxygen from stoichiometric zinc oxide (ZnO) to form a ZnO_{1-x} which indicate the high temperature of the reaction [11]. The total weight loss of the sample within temperature range of 298 ÷ 1 273 K equals to 7,70 %.

MÖSSBAUER SPECTROSCOPY

Mössbauer spectra were collected for nanoparticles of a nonstoichiometric zinc ferrite and the final products of decomposition reaction both at room temperature (Figure 2) and 80K (Figure 3). They show a considerable differences that demonstrate the significant changes taking place in the structure and size of the final product with respect to starting material.

Typical relaxation spectrum measured at room temperature for ‘as prepared’ Zn ferrite (Figure 2 a) confirms that the studied material is composed predominantly of the small-sized (<10 nm) nanoparticles. Lowering the temperature of measurement allows to reduce the influence of thermal relaxation and better adjust the hyperfine interaction parameters.

Table 1 compares the characteristic parameters of the Mössbauer spectroscopy, i.e. isomer shift, mean magnetic hyperfine field and quadrupole splitting. Isomer shift values (IS) for all the three sites of iron ions are close to 0,3 mm/sec indicating that the starting material consists of Fe³⁺ mainly. Mean magnetic hyperfine field (H) values is consistent with the spinel structure of zinc ferrite.

Upon decomposition (‘heated’ sample) a clear increase of the mean grain size is demonstrated by two well-developed magnetic components (Figure 2 b). One

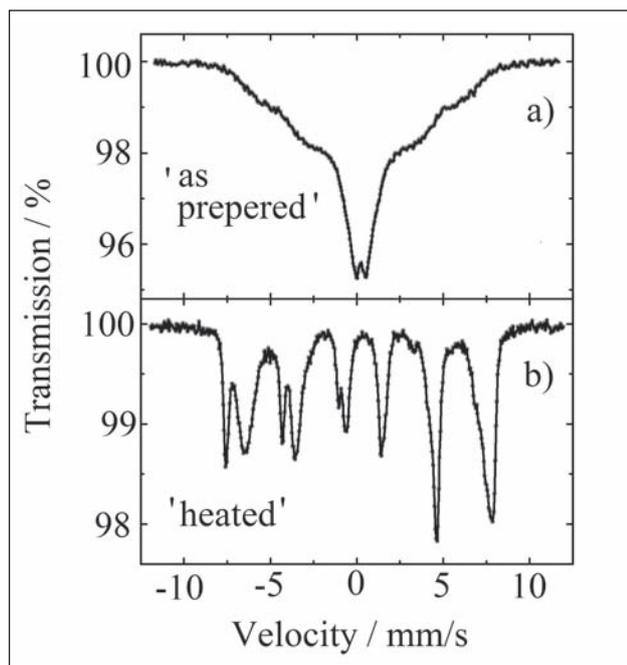


Figure 2 ^{57}Fe Mössbauer spectra measured at 300 K for 'as prepared' nanoparticles $\text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_4$ (a) and product of their thermal decomposition (b)

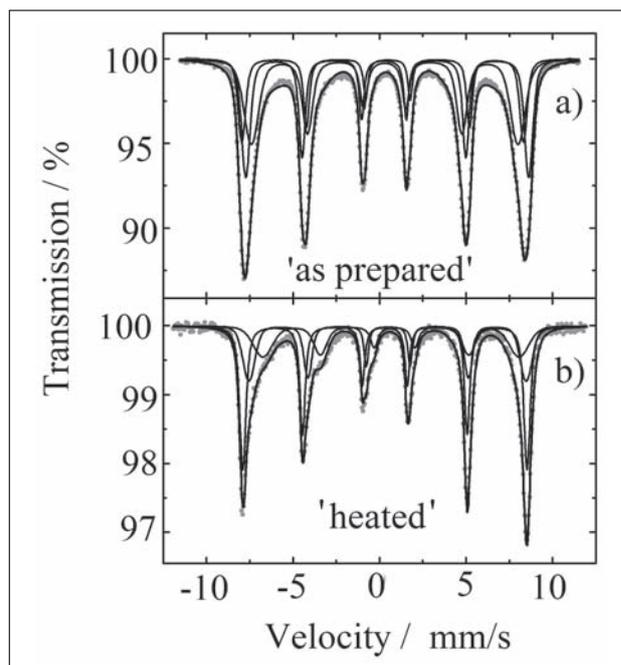


Figure 3 ^{57}Fe Mössbauer spectra measured at 80 K for 'as prepared' nanoparticles $\text{Zn}_{0.4}\text{Fe}_{2.6}\text{O}_4$ (a) and product of their thermal decomposition (b)

of them has a very sharp absorption lines – a typical static spectrum expected for a system with mean particle size above 100 nm. Hyperfine parameters fitted to the spectrum measured at 80 K (Table 1) show that the sharp component can be assigned to hematite phase with hyperfine field (H) exceeding 500 kG. It is in line with the assumption that the reaction (4) is slower than reaction (3).

Table 1 Mössbauer parameters: component contribution (Contrib.), magnetic hyperfine field (H), isomer shift (IS) relative to ^{57}Co (Rh), quadrupole splitting (QS)

| Sample as "prepared" | | | | |
|---|--------------|---------|-----------|-----------|
| No | Contrib. / % | H / kGs | IS / mm/s | QS / mm/s |
| 1 | 39,0 | 493 | 0,338 | 0,100 |
| 2 | 24,2 | 492 | 0,328 | -0,155 |
| 3 | 36,8 | 456 | 0,355 | -0,015 |
| $\langle H \rangle = 479$ (3) KGs $\langle IS \rangle = 0,342$ (6) mm/s | | | | |
| Sample as "heated" | | | | |
| 1 | 43,0 | 509 | 0,308 | 0,001 |
| 2 | 27,0 | 496 | 0,479 | -0,016 |
| 3 | 29,6 | 450 | 0,746 | -0,039 |
| $\langle H \rangle = 488$ (2) KGs $\langle IS \rangle = 0,489$ (5) mm/s | | | | |

Another constituent of the spectra is attributed to Fe^{3+} -rich phase, that is likely composed of other iron oxide and/or not fully decomposed zinc ferrite. In addition, the third magnetic component is observed for which a large isomer shift value ($IS > 0,7$) indicates the presence of Fe^{2+} ions.

They are likely constituents of spinel iron oxide, which is the final product of decomposition of zinc ferrite. The degree of decomposition was expressed as $\text{Fe}^{2+} / \text{Fe}_{\text{total}}$. As indicated in Table 1, over 30 % of Fe^{3+} present in starting material was reduced to Fe^{2+} .

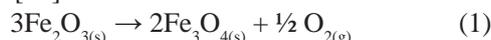
SUMMARY AND CONCLUSIONS

The thermal decomposition of nonstoichiometric zinc ferrite nanoparticles carried out to obtain specific nano-sized products, namely zinc oxide and iron (III) oxide (first stage) and next to iron (II,III) oxide and oxygen (second stage). As a result of thermal decomposition:

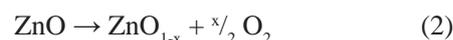
- Products obtained with particle size at the nano and mesoscale level of the order of 200 - 400 nm,
- TG / DTG analysis showed a weight loss of the sample at 1 273 K in an amount of 7,7 %, which is a result of the following processes taking place in different temperature ranges, respectively:

351,5 - 473 K - loss of water physically or chemically bound.

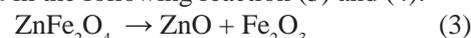
473 - 1 073 K - release of oxygen according to the reaction (1) [10]:



Above 1 073 K an evolution of oxygen from the zinc oxide (ZnO) to form a ZnO_{1-x} according to the reaction (2) [11]:



Research with Mössbauer spectroscopy have shown that the decomposition products were rich in Fe^{2+} (not present in the starting zinc ferrite) and Fe^{3+} . Fe^{2+} ions originate from magnetite or maghemite, which is the product of decomposition of zinc ferrite (kept under the condition of the experiment). It contains both Fe^{2+} and Fe^{3+} ions and is sometimes formulated as $(\text{FeO} \cdot \text{Fe}_2\text{O}_3)$. It was formed in the following reaction (3) and (4):



The effective temperature for reaction (4) is likely above 900 K (Figure 1).

Fe³⁺ ions observed in the decomposition products are attributed to stoichiometric zinc ferrite, which has not been fully decomposed. It is also possible that the Fe³⁺ ions are present in Fe₂O₃ phase assuming that the reaction (4) is slower than reaction (3). The resulting products are rich in zinc oxide that can be used to modify the water glass, which is used as a binder for molding sand [7]. While iron oxide (III) added to molding sand prevents the formation of defects in castings e.g. veining [12]. The oxygen formed in the reaction (4) can oxidize nitrogen released in the case of sands with resins containing nitrogen compounds [13]. A number of problems that have arisen in the course of this work requires further investigation.

Acknowledgements

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REFERENCES

- [1] S. Stopić, B. Friedrich, *Proceedings of EMC* (2009) 4 - 10.
- [2] D. L. Leslie-Pelecky, R. D. Rieke, *Magnetic properties of nanostructured Materials*, *Chem. Mater.* 8 (1996) 1770-1783.
- [3] D. Sasanka, *Superparamagnetic nanocrystalline ZnFe₂O₄ with a very high curie temperature*, *Journal of Nanoscience and Nanotechnology* 8 (2008) 3955 - 3958.
- [4] M. Holtzer, M. Górny, R. Dańko, *Microstructure and properties of ductile iron and compacted graphite iron castings*. Ed. Springer, London, 2015.
- [5] <http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:268:0014:0019:PL:PDF> (document online; access:11.04.2016).
- [6] M. Holtzer, A. Bobrowski, R. Dańko, A. Kmita, S. Żymankowska-Kumon, M. Kubecki, M. Górny, *Emission of PAHs and BTEX from the furan moulding sands with addition of the reclaim*. *Metalurgija* 53 (2014) 4, 451-454.
- [7] A. Kmita, *Modification of water glass, the moulding sands binder, by nanoparticles of metal oxides in organic solvents*. (Ph.D. Thesis, Krakow, (2014) (in Polish).
- [8] L. Rebbouh, R. P. Hermann, F. Grandjean, *57Fe Mössbauer spectral and muon spin relaxation study of the magnetodynamics of monodispersed γ -Fe₂O₃ nanoparticles* *Physical Review B*, 76 (2007) 174422 - 1 - 174422 - 12.
- [9] M. Atif, S. K. Hasanain, M. Nadeem, *Magnetization of sol-gel prepared zinc ferrite nanoparticles: effects of inversion and particle size*, *Solid State Communications* 138 (2006) 8, 416-421.
- [10] B. Janković, S. Stopić, A. Guven, B. Friedrich, *Kinetic modeling of thermal decomposition of zinc ferrite from neutral leach residues based on stochastic geometric model*. *Journal of Magnetism and Magnetic Materials* 358 - 359 (2014), 105-118.
- [11] E. Wiberg, A. F. Holleman, *Inorganic Chemistry* (2001) Elsevier, London. ISBN 0-12-352651-5.
- [12] R.E. Showman, E.S. Scheller: *Comparing sand additives for steel casting*. *AFS Transactions* 109 (2015) 113 - 124.
- [13] C. Umezurike, W. O. Onche, *Experimental analysis of porosity in gray iron castings*, *Global Journal of Researches in Engineering* 10 (2010) 7, 65-70.

Note: The responsible translator for English language: Piotr Paliwoda Krakow, Poland