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Application of Mechanochemistry in Ferrite Materials Technology

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Abstract. An overview of progress and implications of recent technological advances in mechanochemical processing of ferrites is presented. We discuss the potential for applications of mechanical activation by induced phase transformations and chemical reactions in soft and hard ferrite materials through enhancement of structural and magnetic properties .

1. MECHANOCHEMICAL ACTIVATION

Advances in mechanical alloying [1], and in mechanochemistry [2] provide promising novel techniques for advanced materials synthesis and preparation. The simplest reactions initiated mechanochemically are reactions that involve decomposition or synthesis. These reactions can be envisaged as a particular sequence of stages that include the formation of excited states, the rupture of chemical bonds, and system relaxation (physical and chemical) with final removal of the reaction products [3-4]. Materials produced are often non-equilibrium or metastable structures that include amorphous, quasicrystalline, and crystalline materials with nanometre-sized grains. For example, a broad range of new ceramic and ceramic-metal composites, amorphous and nanocrystalline alloys or high temperature phases of nitrides, carbides and silicides have been made by room temperature high energy ball milling [5]. Mechanical treatment has long played a key role in magnetic powder technology. Standard preparation methods for ceramics which embrace the successful manufacture of sub-micron grain polycrystalline soft and hard ferrites [6] sit in juxtaposition to processes that involve mechanical alloying of amorphous, quasicrystalline or nanocrystalline Fe based magnetically soft and hard intermetallics and composites [7]. So far that advantages , that accrue to mechanical alloying techniques have not been exploited. In these new applications grinding is not used for the sole purpose of reducing the sizes of particles. It provides also a pathway to disordering of solids and induction or activation of phase transformations or chemical reactions. In this paper a short overview of recent advances in mechanochemical processing in ferrite powder technology will be discussed, together with its advantages and limitations.

Some of the first studies of sintering of nano-grained ceramics were performed over 25 years ago on simple metal oxides (eg. MgO, TiO_2). It was found that sintering temperatures could be reduced by several hundred degrees kelvin [8]. The same effect of volume-diffusion enhancement has been extended for preparation of ferrite materials. Two main groups have been investigated in detail: spinel and hexagonal type ferrites. Further, by using prolonged grinding of Fe_2O_3 with ZnO (400 h in a conventional ball mill) a noticeable amount of $ZnFe_2O_4$ (the normal type spinel) was first reported in 1978 [9]. Similar experiments to produce inverse type spinel $NiFe_2O_4$ were unsuccessful, and the overall hypothesis concerning formation of mixed oxide - solid solutions remained unsupported [3, 4]. Again, the influence of mechanical treatment on complex iron oxide based ferrites, Ba- or Sr-ferrites was studied extensively during the 1960's and 1970's. The deficiency in then available experimental techniques and their reproducibility for structure determination, and an understanding of the influence of milling conditions affected the consistency of published results and conclusions drawn therefrom. Recently performed studies show similar controversy in interpretation of results due to fact that mechanochemical phenomena span a wide range of scientific and engineering aspects.

2. FERRITE PROCESSING

2.1. Simple iron oxides

2.1.1. Hematite - magnetite phase transformations

Phase transformations of simple iron oxides during mechanical activation have been extensively studied over the last two decades. Chemical topotactic transformations as a result of thermal oxidation or hydrogen reduction reactions in this system have long been well known. The influence of mechanical pressing was first studied via the γ-Fe_2O_3 - α-Fe_2O_3 isothermal transformation [10], and the first synthesis of Zn spinel via ball milling was suggested a few years later [9]. The structural transformation of maghemite to hematite does not require changes in stoichiometry, and is due only to thermal energy delivered to the material during mechanical treatment [3]. In another study the dehydration process of lepidocrocite (γ-FeOOH), induced by wet grinding was discussed [11]. Fractional conversion to maghemite (< 50 %) and hematite (< 15 %) and an increase in the γ-Fe_2O_3 - α-Fe_2O_3 transformation temperature were found with increasing milling time. By far the most interesting transformation so far found, is room temperature formation of magnetite from hematite. This normally requires hydrogen supported reduction at temperatures above 450 °C. It was established that dry grinding does not induce formation of new phases from hematite. Only by dry milling of a hematite- graphite powder mixture was partial reduction (formation of magnetite) achieved [12]. But that process induces high level of contamination from the mill. Formation of ferrimagnetic

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phases during wet milling of α-Fe_2O_3 was first reported in 1981 [13]. The product obtained was a multiphase powder with estimated composition of 60% Fe_3O_4, 30% α-Fe_2O_3 and 10% γ-Fe_2O_3 (wt). The following reactions were suggested: $Fe + 2H_2O \Rightarrow Fe(OH)_2 + H_2$,or $3Fe + 4H_2O \Rightarrow Fe_3O_4 + 4H_2$; and finally $3\alpha\text{-}Fe_2O_3 + H_2 \Rightarrow 2Fe_3O_4 + H_2O$. The suggested basis for the process was reduction of water, so producing hydrogen on mill or abraded steel particle surfaces. This was unsupported by the observation that with decreasing size of the initial hematite powder particles, the efficiency of the process decreases as well. Our recent study showed that total reduction to Fe_3O_4 is possible only when wet milling is conducted under an oxygen free atmosphere in a liquid with high permittivity [14]. For water acting as a reducing agent at low oxygen pressure the process proceeds through the reaction: $4Fe^{3+}(aq) + H_2O\ (l) \Rightarrow 4Fe^{2+} + O_2\ (g) + 4H^+\ (aq)$.

2.1.2. Cobalt doped magnetite and metal-ceramic nanocomposites

More recently, the above study was extended to allow for the possibility of formation of multi-cation spinel structures by wet milling in a nitrogen atmosphere. The chemical reaction investigated : $Fe_2O_3 + Co(OH)_2 \Rightarrow CoFe_2O_4 + H_2O$ for different Fe-Co ratios and milling conditions showed promising results [15]. It was found that up to ~14 % at. of Co can be incorporated into a $(Co_xFe_{1-x})_3O_4$ structure as a result of Co^{+2} substitution. Additionally, a small fraction of Co hydroxide is totally reduced and forms nanocrystalline Co metal insertions (2-5 nm) [16]. Finally, as a result of annealing at 220 °C, a nanostructural magnetic composite containing Co-spinel, maghemite and metallic cobalt can be formed. In this way structural and magnetic properties can be modified for production of advanced materials. Other possibilities in this field are also currently being investigated. Application of replacement reactions e.g. $3Fe_3O_4 + 8Al$ - $9Fe + 4Al_2O_3$, or $4CuO + 3Fe$ - $4Cu + Fe_3O_4$, can produce interesting soft and semi-hard magnetic metal-ceramic nanocomposites [17-18].

2.2. Complex iron oxides

2.2.1. Dry milling - influence of air pressure

From the first studies of the influence of dry grinding on Ba- or Sr-ferrite properties it is well known that the saturation magnetization [19] and coercivity [20] decrease with milling time. The observed decrease of both parameters was explained by an increase of crystal lattice distortions and formation of additional weak ferrimagnetic (unverified experimentally) [19], or nonmagnetic phases (BaO and α-Fe_2O_3) [20]. The problem of barium ferrite decomposition was solved only recently. It was found that during prolonged dry milling in air or vacuum, gas pressure has a major influence on structure and morphology of the final powder particles [21]. Also it was found that chemical decomposition takes place through structural evolution of crystalline (complex oxide) - amorphous - crystalline (simple oxide) [22]. Final annealing at the temperature 1000 °C for 1-4 h can produce submicron size material [23], with an altered H_c value, ~ 5.6 kOe for Ba-ferrite and ~ 5 kOe for Sr-ferrite [24-25].

2.2.2. Wet milling - influence of surfactants

Wet grinding is often used for preparation of fine stress "free" powder particles. Low energy wet milling results in fast particle size decrease and the crystal structure of Ba-ferrite is preserved [20]. With increasing milling time , M_S decreases(~10%) and H_c increases from ~0.9 up to ~1.3 kOe. Only for powders milled above 60 h as a result of further annealing was α-Fe_2O_3 detected. A similar situation was reported for low energy milling of Ba-ferrite with organometallic surface active substances (surfactant). The results showed only a slight increase in squareness with mill time, but unchanged coercivity [26]. A systematic study of surfactant-assisted ball milling of Ba-ferrite dispersions was published only recently [27]. Different types of surfactants (cationic or anionic) and different pH values used during prolonged milling (300 h) cause surface induced reactions that are responsible for fast decomposition of the ferrite material, and chemical reduction due to interaction with active $-CH_x-$ groups. The nanostructural powders (<100 nm) produced after thermal treatment (1h at 550 °C) exhibit $4\pi M_S$ and H_c values in a range 4.5 - 5.6 kG and 1.7 - 2.5 kOe respectively [28].

3. CONCLUSIONS

Mechnochemical routes can be used to prepare new nanophase bulk, simple or composite type ferrites and metal-inserted ceramics. The method is promising at a production scale for the cost and quantities which can be processed.

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