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USE OF SPECIFIC PROPERTIES OF ZINC FERRITE IN INNOVATIVE TECHNOLOGIES

Zinc ferrite $ZnFe_2O_4$ both in the micro and nano scale is widely used in various fields. The article discusses the structure of this compound and its properties in the nanoscale, which is clearly different from those which the ferrite shows in the microscale. The properties of dust generated electric arc furnace, which can contain up to 40% zinc, substantially in the form of $ZnFe_2O_4$ are disscused here. Specific properties (electric, magnetic, thermal) of zinc ferrite nanoparticles determine the very wide possibilities of their use, *inter alia* as catalysts, absorbents, gas sensors, and a tool to combat cancer.

1. Introduction

Recently, transition metal ferrite nanoparticles have fund great concern because of their unique properties enable them to be used in fields as magnetic storage, biomedicine, ferrofluids, catalysis and magnetic refrigeration system [1 - 4]. Among them, zinc ferrite which has high electric resistivity and low eddy current lost. This ferrite posses unique magnetic, magneto-optical, magneto-resistive, electric, thermal and mechanical properties such as ferromagnetism, excellent creep and radiation damage resistance, high thermal conductivity, high electrical resistivity, controllable saturation magnetization, moderate thermal expansion coefficients, energy transfer efficiency and narrow line width in ferromagnetic resonance [5 - 8]. These properties make zinc ferrite suitable for numerous device applications, including magnetic materials, sensors, anode materials for batteries, catalysts, lasers, microwave and electrochemical devices.

2. Zinc ferrite in steelmaking dust

In the process of melting scrap steel in electric arc furnaces galvanized scrap in the form of packages galvanized sheet from the automotive industry, the household appliances or construction of galvanized steel are currently used as a feedstock in large part, which is mainly due to the greater availability and lower price. In the case of galvanized sheet metal car body (e.g. in the amount of 36% of the charge) is introduced into the furnace of about 10 kg Zn/Mg steel. When they are hot-dip galvanized sheet, the amount of zinc charged into the furnace ammounts up to 20 kg Zn/Mg of steel. The result is a significant increase in the amount of particulate matter emitted from the EAF (Electric Arc Furnace EAFD Dust) and the increase in the dust content of heavy metals such as Zn, Pb, Cd. The amount of dust emitted from this process is 10 to 25 kg per 1 Mg of molten steel. Because of high contents of valuable metals like Pb, Zn and As as well as due to environmental issues caused by the presence of Cd, As and other heavy metals in this materials its landfilling is not sustainable. Since dumping of zinc-containing steel mill dusts is no longer acceptable from the environmental and economical point, a lot of investigations have been done to find appropriate processes that make recycling of these dusts economically and technically possible. One of the troublesome elements is zinc. Zinc is present in the EAFD as zincite ZnO and franklinite $ZnFe_2O_4$ or sometimes in complex ferrite forms like $(ZnMnFe)_2O_4$ or Zn_2SiO_4. Zinc ferrites can be very difficult to chemically decompose so that zinc can be recovered [9 - 11].

Zinc conveing dust can be processed by pyrometallurgical of hydrometallurgical methods. Today's commercial operations reach almost complete winding of zinc from ferrite mostly are based on fuming operations that reduce ferrite and vaporizes zinc. Such pyrometallurgical applications use a reduction media such as carbon monoxide, hydrogen or coke [12]. The main technology of zinc recovery process from EAFD is the Waelz process, which converts about 80% of metallurgical dust [13]. Other pyrometallurgical processes used for processing metallurgical zinc coinveing dust are: technology Contop [13] or ENVIROPLAS process [14]. A number of hydrometallurgical processes have been develop in order to treat these dusts from steel plant for recovering zinc from ferrite – phases such as acidic or caustic leaching, microwave assisted extractions [15]. EAFD leaching process generally includes two steps: [13]

- leaching of zinc into solution, which most often uses sulfuric acid;
- recovery of zinc or zinc compounds from the resulting solution by: electrolysis, crystallization, extraction by means of ion exchange or precipitation of insoluble zinc compounds.

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TABLE 1

Summary of selected components of dust when rendered different kinds of steel

Component	Fetot	SiO_2	CaO	Al_2O_3	MgO	MnO	Cr_2O_3	Zn	Pb
mas.%	10-65	0.6-9	2-20	0.3-4	0.5-6	1.1-6,9	0.13-20	2-43	0,4-10

Direct recycling of dust back to steel production is usually not possible because they contain metals and compounds that can harm the primary processes if the materials are not pretreated [16]. The EAFD, outside beams zinc include (table 1): Fe_2O_3 hematite, magnetite Fe_3O_4, PbO, MgO, MnO, CaO, Cr_2O_3, Al_2O_3, SiO_2, NaCl, KCl, CaF_2 [17].

Table 1 shows concentration ranges of the respective components of dust when melting steel grade.

The particle size distribution is heterogeneous with 60% between 0.90 µm and 4.30 µm and mean diameter of 1.88 µm [18].

3. Zinc ferrite: properties and structure

Many materials reveal dramatically change of properties upon decrease of grain size to the scale of single nanometers. It is also the case of zinc ferrite. Reducing the particle size of magnetic substances, among others the ferrites, from micron to nanometer size, results in a significant change of their properties: e.g. physical, optical, physico-chemical, electrical, technical, and magnetic [19]. Many of these properties, e.g. magnetic coercivity (Hc), magnetic susceptibility (X) depends not only on the size of the nanoparticles, but also on their shape and morphology [19]. Another important feature of nano zinc ferrite, inter alia, is their high surface area, thus they are used as catalysts in many chemical processes [20].

Zinc ferrite $ZnFe_2O_4$ is the chemical composition of a mixture of oxides belonging to a large group of ferrites of the general formula $(Me_{1-x}^{2+}\ Fe_x^{3+})[Me_x^{2+}\ Fe_{2-x}^{3+}]O_4$. Ferrites usually consist of two Fe^{3+} cations and a single divalent cation. They are usually ions: Zn^{2+}, Ni^{2+}, Mn^{2+}, Ba^{2+}, etc. Zinc ferrite has a normal spinel structure, crystallizing regular system ($a = b = c$, $\alpha = \beta = \gamma = 90$). The oxygen atoms are building a network of close-packed face-centered cubic packing of atoms. In such compounds AB_2O_4 divalent cations (A) occupy tetrahedral gaps and trivalent cations (B) octahedral gaps. Spinel unit cell is composed of 8 units builders. In the full unit cell is 8 cations Me^{+2}, 16 Fe^{+3} cations, and 32 anions oxide O^{-2}. The figure below (Fig. 1) shows the view of a portion of the crystal network of spinel [21].

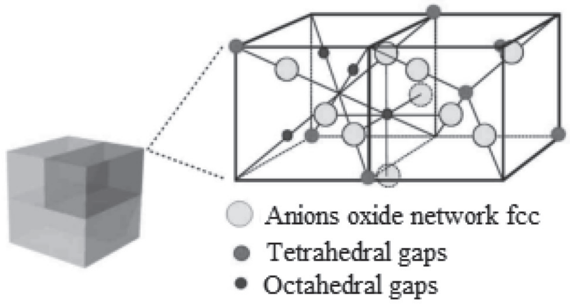

Fig. 1. Crystal structure of spinel [21]

Bulk $ZnFe_2O_4$ should have paramagnetic nature around room temperature, because it is the normal spinel with Zn incorporated mostly in the tetrahedral lattice sites, so the superexchange interaction between the two sublattices cannot be expected, and it should not come under ferrimagnetism [22]. However, upon increasing Fe/Zn molar ratio in nonstoichiometric zinc ferrite an increasing occupation of tetrahedral site by Fe ions is expected due to charge transfer from tetrahedral to octahedral Fe sites that are responsible for occurance of net magnetic moment.

In the case of the nanoparticles, the situation is more complicated and confused because of the inversion of the cations distribution, size effects, and nonstochiometry.

Superparamagnetisim or ferrimagnetism at room temperature is generally reported for nanosized zinc ferrite ($ZnFe_2O_4$) and this described to the unusually occupancy of the magnetic ferric ions in the tetrahedral sites and divalent zinc ions the octahedral sites. There have been several attempts to synthesize $ZnFe_2O_4$ with different degrees of distributions of Zn^{2+} and Fe^{3+} ions in the tetrahedral and octahedral sites [20].

Increase in the degree of inversion $ZnFe_2O_4$ with decreasing particle size was found with neutron powder diffraction analysis. Apart from the particle size, the preparation method and synthesis conditions or parameters can affect the x value [22]

Currently, magnetic oxide nanoparticles are attracting significant interest due to their extensive applications, ranging from fundamental research to industrial use. Spinel ferrite nanocrystals are regarded as two of the most important inorganic nanomaterials because of their electronic, optical, electrical, high density memory storage capacity, high resistivity, magnetic, and catalytic properties and low cost.

Among the spinel ferrite compounds, zinc ferrite ($ZnFe_2O_4$) has been studied extensively due to its high electromagnetic performance, excellent chemical stability, moderate thermal coefficients, energy-transfer efficiency, mechanical hardness, low coercivity, and moderate saturation magnetization, which make it a good contender for applications as soft magnets and low-loss materials at high frequencies [23].

4. Use of zinc ferrite innovative technologies

The magnetic as well as other properties zinc ferrite, especially in nano fraction, make that is has a range of applications. It is true that steel industry annually produces a significant amount of this compound as a constituent of particulate matter coming from electric arc furnace dust removal, but it is highly contaminated and particle size is in the micro range. Namely, first, we have large amounts of zinc ferrite, from which we recover zinc and iron at great cost, and on the other hand we bear the cost of zinc ferrite with the required properties production.

4.1. Zinc ferrite catalyst in the hydrogen production from the decomposition of water

Solar fuels, which are produced by solar chemical energy conversion system, can be stored until required and transported to any consuming site. Water can be directly split using solar process heat via direct thermal dissociation above 2500 K [24]. However, the gaseous products need to be separated at high temperature to avoid recombination or otherwise obtaining an explosive mixture [24]. To solve these problems, two-step water splitting reactions using metal oxides (oxidized and reduced states) have been suggested.

Decomposition reaction of zinc ferrite is also used in the context of hydrogen production from water (two-stage) with the use of solar energy by redox reactions [24] :

I step (O_2 generation): Zn-ferrite reacts releasing Zn and forming Fe_3O_4 above 1500 K in an air flow obtained by irradiating with concentrated solar beam:

(O_2 generation at 1500 K)

(thermal energy)

$6\ ZnFe_2O_4 = 6\ ZnO + 4\ Fe_3O_4 + O_2(g)$

II step (H_2 generation): the mixture of Fe_3O_4 and Zn reacts with water vapor to generate hydrogen and forms $ZnFe_2O_4$ at 873 K:

(H_2 generation at 873 K)

$2Fe_3O_4 + H_2O(g) = 3Fe_2O_3 + H_2(g)$

Schematic of water splitting system with Zn ferrite/Zn, Fe_3O_4 system is on the figure 2.

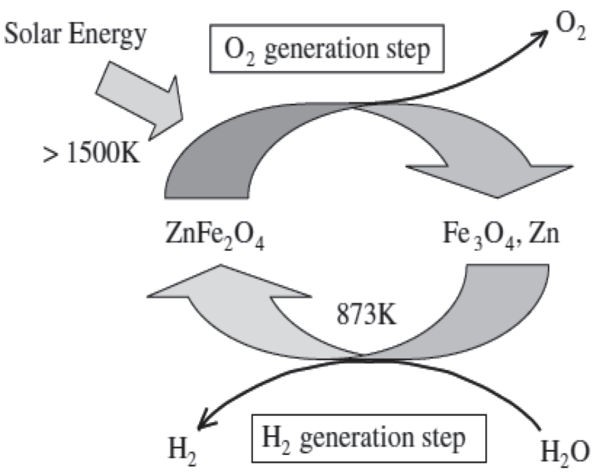

Fig. 2. The schematic outline of two-step water spliting system with Zn-ferrite /Zn, Fe_3O_4 system [25]

The solar decomposition of the Zn ferrite commenced above 1500 K and its decomposition ratio at 1750 K was evaluated to be 40% form the lattice constant measurement and chemical analysis. The solar decomposition of Zn ferrite can be readily with increasing temperature. These results encourage further investigation for solar operation to enhance the solar decomposition ratio of the Zn ferrite. The thermochemical cycles for H_2 production with Zn ferrite, Fe_2O_3 system will be realized by the enhancement of solar decomposition of the Zn ferrite [25].

4.2. Nanoparticles of zinc ferrite catalysts

Due to its properties zinc ferrite nanoparticles are used as catalysts in many reactions [26], e.g. as catalysts in methanol decomposition on CO and hydrogen [27] or as decomposition catalyst green house gases (CO_2) [28]. There are two reaction routes for decomposing CO_2 by oxygen deficient ferrites. One is the decomposition to carbon and oxygen, while the other one is decomposition into carbon monoxide and oxygen that can be expressed as following equations, where represents the degree of oxygen deficiency [28]:

$\delta/2CO_2 + ZnFe_2O_{4-\delta} \rightarrow \delta/2C(s) + ZnFe_2O_4$

$\delta\ CO_2 + ZnFe_2O_{4-\delta} \rightarrow \delta\ CO + ZnFe_2O_4$

The reactivity toward CO_2 decomposition is dependent on the redox processes of zinc ferrite nanoparticles [28]

4.3. The influence of zinc ferrite on the properties of rubber nanocomposite

One of the drawbacks of zinc ferrite is in the ceramic form is that it is not moldable and flexible to form complex shapes of product. Thus the incorporation of ferrite filter in rubber composites is important, because such material is referred to as rubber ferrite composites exhibits high flexibility and easily takes complex shapes. These composites are widely used in electrical and electronics industry. The addition of zinc ferrite rubber nanocomposite enhancing the thermal stability of the nanocomposite and reduces the thermal degradation. As it was shown by Yaghmour S J et al. [8] the mechanical parameters nanocomposites were increased by increase the zinc ferrite contents: tensile strength by 605%, tear strength – 519 % and hardness – 276 % compared with unfilled rubber nanocomposite [8]. The influence of zinc ferrite on the thermal stability showed that the zinc ferrite enhanced thermal stability and reduced the rate of thermal degradation of rubber nanocomposite.

4.4. Zinc ferrite as high – temperature desulfurizing sorbents

Gases from coal gasification can contain high levels of sulfur compounds. Increasingly stringent regulations on environmental protection as well as modern technology mean that the content of impurities in these gases, particularly sulfur, should be at the level of a few ppm. [29, 30] Commercial desulfurization processes are based on liquid scrubbing at or below ambient temperature, resulting in considerable thermal efficiency loss as well as costly wastewater treatment. For more efficient use of energy, at high temperature, the desulfurization process should take place at high temperature (500 – 800°C).

High hopes in this respect are connected with the zinc ferrite desulfurization sorbents. In this case, zinc ferrite is first decomposed into ferric and zinc oxides. The ferric oxide is further reduced to ferrous oxide and /or iron, and sulfidation then takes place on these phases of lower oxidation state. Furthermore, when the temperature exceeds 650 °C, the ZnO may also be reduced to metallic zinc, which then evaporates.

The desulfurization reaction in this case can be written as follows:

$$ZnFe_2O_4 + 4H_2S \rightarrow 2FeS + ZnS + 4H_2O + (1/n)S_n$$

Zinc ferrite sorbents represent an attractive alternative in high temperature desulfurization processes where the high hydrogen sulfide removal efficiency of zinc oxide is desirable but where zinc loss represents a serious problem. A zinc ferrite sorbent reduced the H_2S in coal gasifier gas to less than 20 ppm in a single stage fluidized – bed.

4.5. Zinc ferrite nanoparticle as a magnetic catalyst

The presence of dyes in wastewater is one of the main problems, because they have complex aromatic structure and are difficult to degrade. In addition they produce toxic or carcinogenic by-products by several reactions in aqueous media. Advanced oxidation processes (AOPs) are used to degrade pollutants in aqueous media by strong oxidants such as hydroxyl radicals (HO*). Homogeneous or heterogeneous catalysts (e.g. metal oxide) can be used to produce hydroxyl radicals from H_2O_2. Considering that the hydrogen peroxide alone is not effective to oxidize dyes in the wastewater, it needs to be activated by a catalyst. The novelty in this regard is the use of catalysts with magnetic properties [31 - 33].

The properties of magnetic catalysts will be used in separation technology of the substance since the ease of direction of magnetization would very depending on the ordering of atoms in the magnetic structure. They pay special attention to the iron-based nanoparticles that are highly effective in removing organic and inorganic contaminants. Applying a magnetic field of low intensity to induce magnetization of the material and thus it makes use of a magnetic force possible, but when the magnetic field is cut off the magnetization immediately decreases to zero. This makes it easy to remove decomposition products pollutants from the water environment. Effective photocatalysts are ferrites. As the research by N. M. Mahmoodi shows [31] zinc ferrite nanoparticles could be used as a magnetic photocatalyst to degrade dyes in wastewater. Hydrogen peroxide can be activated on the $ZnFe_2O_4$ surface to generate hydroxyl free radicals.

5. Summary

Over the past decades, magnetic spinel ferrites [M(II) $Fe(III)_2O_4$; M represents Co, Mn, Ni, Zn or Fe] nanoparticles have attracted considerable research interest for their wide range of technological application in magnetic recording, microwave technology, catalytic and biomedical fields. $ZnFe_2O_4$ is a typical representative of normal spinel structure. Furthermore, for the recent years, there have been many applications of $ZnFe_2O_4$ in various fields such as hyperthermia treatment of cancer, gas sensor, absorbent material for hot gas desulphurization, photochemical hydrogen production, semiconductor photo catalysts, component of composites, etc. The article discusses some examples of the use of zinc ferrite nanoparticles. Also, zinc ferrite in microscale is a valuable raw material for zinc production. This compound is a component of the dust extraction from electric arc furnaces used for steelmaking. The zinc content of the dust reaches 40%. These dusts are a hazardous waste due to contamination with heavy metals, and their storage is expensive. Therefore, a number of methods for recovery of the zinc dust with the use of pyro- or hydrometallurgical methods was developed.

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