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RF Thermal Plasma Synthesis of Ferrite Nanopowders from Metallurgical Wastes

J.Szépvölgyi[1], I.Mohai[1], J. Gubicza[2] and I. Sáray[2]

[1] Research Laboratory of Materials and Environmental Chemistry,
Chemical Research Center, Hungarian Academy of Sciences
H-1025 Budapest, Pusztaszeri út 59-67. Hungary

[2] Department of General Physics, Eötvös University
H-1518 Budapest, P.O.B. 32 Hungary

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Abstract. RF thermal plasma synthesis of zinc-ferrite nanopowders has been studied from metallurgical wastes of high iron oxide and zinc oxide and/or hydroxide content. XRD measurements of the products revealed that an extensive spinel formation took place on RF plasma treatment. However, instead of expectable $ZnFe_2O_4$, formation of zinc ferrous ferrites ($Zn_{0,7}Fe_{2,3}O_4$ and $Zn_{0,4}Fe_{2,6}O_4$) was concluded from the XRD investigations. Addition of some nickel salt to the waste mixture resulted in the formation of Ni-Zn ferrites of different composition.
Measurements of magnetic properties revealed that the saturation magnetization of ferrite powders produced by thermal plasma treatment was much higher than that of ferrites synthesized by the conventional ceramic route.

Introduction

Radiofrequency (RF) thermal plasmas offer unique advantages for the synthesis of special ceramic powders due to their high temperatures and energy densities. In addition, a high temperature gradient exists between the hot plasma flame and the surrounding gas phase. The resulting rapid quenching rate is favourable for producing fine particles with unstable structures (e.g. the inverse spinel structure) in thermodynamic terms. In our previous paper synthesis of zinc ferrites from pure oxides and from co-precipitated hydroxides was described [1]. It was concluded, that nanosized (30-60 nm) spinel phases of various composition can be produced in RF plasma reactor in spite of the very short residence time in the hot zone, although, conversion of precursors was not complete. In this paper, results on the thermal plasma synthesis of zinc ferrites from metallurgical wastes are presented.

Experimental

Two wastes of different origin and composition, a precipitated, dried sludge from the hot galvanizing process (HPS) and a converter flue dust from steelmaking (CFD) were mixed in a proper amount for setting the optimum Fe/Zn ratio in the final product. The starting mixtures were treated in a RF thermal plasma reactor (3-5 MHz, max. 35 kW plate power, TEKNA PL-35 torch). In each run products were collected from the reactor wall (R) and from the reactor bottom (RB).

For bulk chemical compositions the samples were digested in diluted HNO_3 solution using a CEM microwave digestion system. Dissolved samples were analysed by ICP-AES technique (Labtest PSX7521). Crystalline phases were identified by X-ray diffraction (XRD) using a Philips Xpert diffractometer and CuKα radiation (λ=0.15418 nm). The lattice parameters (a) of the crystalline phases were determined from the positions of the diffraction peaks. The spinel composition was estimated by assuming the change of lattice parameter due to Zn incorporation to be proportional the Zn concentration.

Results and Discussion

Chemical compositions of the industrial samples are shown in Table 1. Iron and zinc have the highest concentration in both samples. Chlorine content of HPS (6.99%) is also worth mentioning. In addition to data in Table 1 both CFD and HPS samples contained other components, such as Al, Cr, Ni, Mn, Cu, Cd, P and C in a total amount of less than 1%.

Table 1. Bulk chemical composition of CFD and HPS samples

Sample	Concentration [wt%][a]						
	Fe	Zn	Pb	Ca	Mg	Si	Cl
CFD	65.0	4.22	0.98	1.96	0.15	1.02	0
HPS	17.5	39.5	0.23	2.76	0.29	2.22	6.99

[a] concentrations refer to the dried (105°C) samples

The main crystalline phase of CFD sample was magnetite ($FeFe_2O_4$). Traces of hematite (Fe_2O_3) were also detected. Main diffraction peaks of the HPS sample could be assigned as simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$). Iron compounds was most probably present in the original HPS sample as amorphous hydroxides. During plasma treatment it was expected that these compositions release HCl and H_2O vapours. A considerable part of the plasma energy may be lost on the dissociation of particular gases. For this reason, prior to the plasma treatment sample HPS was preheated at 300°C to eliminate H_2O vapour.

For the synthesis of zinc ferrite of stoichiometric composition ($ZnFe_2O_4$) CFD and HPS samples were mixed in an appropriate ratio. From the chemical analysis the Fe/Zn molar ratio of the mixture was 2.18. Conditions of the plasma treatments can be seen in Table 2. In order to improve heat transport between the hot gases and the particles O_2 was mixed to the sheath gas. Although during conventional ferrite production the starting oxide mixture is heated for several hours above 1000°C, in the RF plasma a residence time of some milliseconds was high enough to produce fine ferrite powders from the waste mixture.

Table 2. Conditions of the ferrite synthesis

Waste powder	Flow rate of gases (l/min)				Power	Feed rate	E_{spec}
	Plasma	Sheath	Auxiliary	Carrier	kW	g/min	kWh/g
CFD+HPS	11 (Ar)	20 (Ar)	20 (O_2)	2	22.3	2.4	0.16
CFD+HPS+Ni salt	10 (Ar)	20 (Ar)	20 (O_2)	3	24.5	1.9	0.22

Both powders collected from the reactor wall (R) and from the reactor bottom (RB) showed similar diffraction patterns (Fig. 1.). It indicated presence of spinel as dominant phase. From the lattice parameter (a) for the compositions of sample R and sample RB $Zn_{0.7}Fe_{2.3}O_4$ and $Zn_{0.4}Fe_{2.6}O_4$ were calculated, respectively. Consequently, some of the Zn content of the starting mixture could not build into the spinel structure and left the system in the form of very fine ZnO powder through the exhaust. Chemical analysis of the products supported results of XRD (Fig. 2): Fe/Zn ratio from the ICP and XRD data were very close to each other.

NiZn ferrites could also be synthesized in RF plasma reactor from the CFD and HPS powders by admixing $Ni_3H_4CO_7 \cdot 4H_2O$ to the waste mixture. Molar ratio of the metals was set for Ni/Zn/Fe=0.4/0.6/2. For comparison, a $NiO/ZnO/Fe_2O_3$ mixture, containing Ni/Zn/Fe with the same ratio, and the waste/Ni-carbonate mixture were treated in a resistively heated furnace at 900°C for 6h as well.

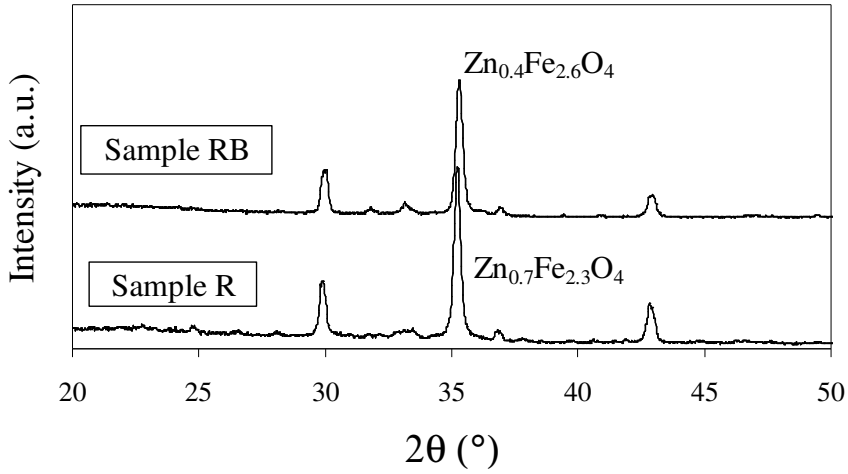

Figure 1. X-ray diffractograms of the zinc ferrites synthetised from the mixture of CFD and HPS samples.

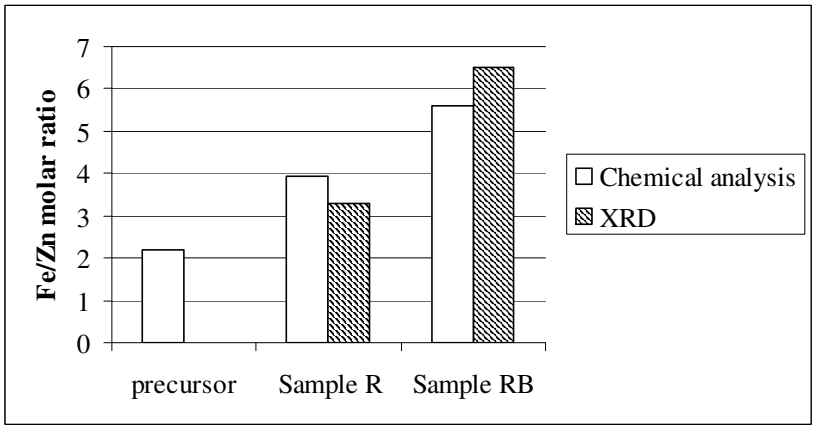

Figure 2. Comparison of results of chemical analysis and XRD

XRD diffractograms of the products (Fig. 3) showed that conventional synthesis of Ni/Zn ferrite from the correspondent oxides was not succesful in these conditions. Heat treated sample consists of zinc ferrite, Fe_2O_3 and NiO. Some of the Fe_2O_3 and all of the NiO did not build into the spinel structure. From the CFD/HPS/Ni-carbonate mixture, however, the desired spinel composition ($Ni_{0.4}Zn_{0.6}Fe_2O_4$) was formed in the same conditions. Plasma treatment in sample R resulted in a mixed spinel phase consisted of $Ni_{0.2}Zn_{0.5}Fe_{2.3}O_4$ and $Ni_{0.6}Zn_{0.3}Fe_{2.1}O_4$, while in sample RB for the composition of the spinel (in accordance with the chemical analysis) $Ni_{0.2}Zn_{0.5}Fe_{2.3}O_4$ could be estimated from the lattice parameter. For comparing magnetic characteristics of ferrite samples produced by the conventional and the plasma treatment, respectively, saturation magnetisation of the samples was determined at room temperature by the Faraday method. Results are summarised in Table 3. Although CFD sample consists of mainly magnetite phase its saturation magnetisation is less than that of the pure $FeFe_2O_4$ (92 emu·g^{-1}) [2]. The difference can be explained by the presence of non-magnetic phases (e.g. silicates, carbon, amorphous ZnO) in the industrial waste. $ZnFe_2O_4$ having the normal spinel structure is paramagnetic at room temperature. Plasma synthetised zinc ferrites with $Zn_{0.7}Fe_{2.3}O_4$ and $Zn_{0.4}Fe_{2.6}O_4$ composition, however, have ferrimagnetic characteristics with high saturation magnetisation due to the zinc substitution in the magnetite structure. Especially high saturation magnetisation was found in sample plasma RB (63 emu·g^{-1}) taking into account that the precursor contained CFD of only about 50%. Saturation magnetisation of the Ni/Zn ferrite

synthetised by the conventional route and having the optimal Ni/Zn/Fe ratio was 35 emu·g^{-1}. Although plasma produced samples (R and RB) did not have optimal composition, their saturation magnetisation was even higher (48 emu·g^{-1}). These results verify the advantageous effect of plasma treatment on the formation of fine ferrite powders with the inverse spinel structure.

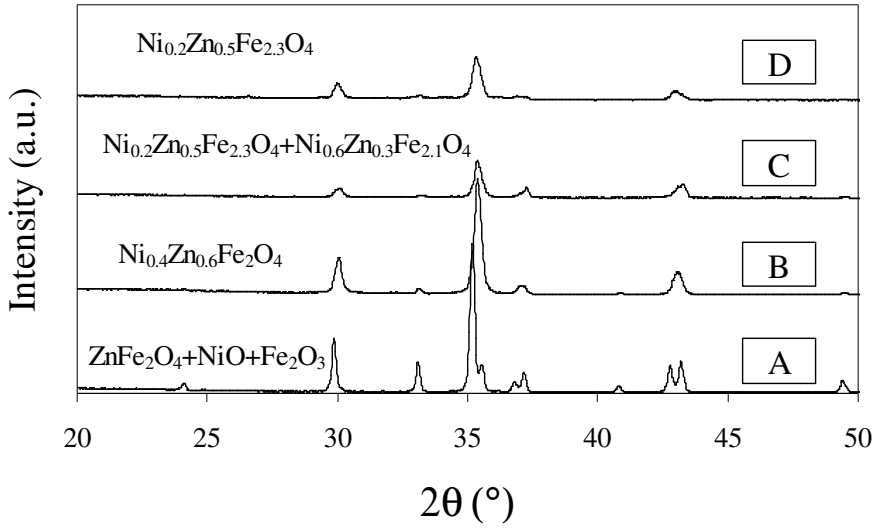

Figure 3. X-ray diffractograms of NiZn ferrites. **A**: from the corresponding oxide mixture at 900°C/6h. **B**: from the mixture of CFD/HPS/Ni-cabonate at 900°C/6h. **C**: from the mixture of CFD/HPS/Ni-cabonate, plasma, sample R. **D:** from the mixture of CFD/HPS/Ni-cabonate, plasma, sample RB

Table 3. Saturation magnetisation of samples produced by conventional and plasma treatment

Precursor	Method	Composition of the spinel (XRD)	Saturation magnetisation [emu·g^{-1}]
CFD	-	$FeFe_2O_4$	56
CFD+HPS	Plasma (R)	$Zn_{0.7}Fe_{2.3}O_4$	44
CFD+HPS	Plasma (RB)	$Zn_{0.4}Fe_{2.6}O_4$	63
CFD+HPS+Ni salt	Plasma (R)	$Ni_{0.2}Zn_{0.5}Fe_{2.3}O_4$+ $Ni_{0.6}Zn_{0.3}Fe_{2.1}O_4$	48
CFD+HPS+Ni salt	Plasma (RB)	$Ni_{0.2}Zn_{0.5}Fe_{2.3}O_4$	48
CFD+HPS+Ni salt	900°C, 6h	$Ni_{0.4}Zn_{0.6}Fe_2O_4$	35
Fe_2O_3+ZnO+NiO	900°C, 6h	$ZnFe_2O_4$+Fe_2O_3+NiO	4

Summary

Fine spinel zinc and nickel zinc ferrite powders of various compositions can be synthesized in an RF plasma reactor from metal containing wastes. In spite of the short residence time in the hot plasma region conversion of the precursors was complete. Zinc ferrous ferrites can be synthesized by the plasma method as well, because partial pressure of oxygen can easily be adjusted. Measurement of saturation magnetization of the products synthesized by the conventional and the plasma method indicated formation of inverse ferrite spinels in the plasma reactor.

References

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