

Effect of Calcination Conditions on the Magnetic Properties of MnZn Ferrites Powders Produced by Co Precipitation

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Abstract

MnZn ferrites are conventionally produced by the ceramic method that involves the solid state reaction of metallic oxides or carbonates at high temperatures. The particles obtained by this method are rather large and non-uniform in size. In order to overcome the difficulties arising out of the ceramic process, the coprecipitation method has been used as an alternative route to produce chemically homogeneous powders with fine particle size. In this work MnZn ferrites powders were produced by the coprecipitation method. The calcination conditions, such as temperature (900°C to 1100°C) and atmosphere (air and nitrogen), were investigated. X ray diffractometry, scanning electron microscopy, thermomagnetic analysis and vibration sample magnetometry were used to characterize the obtained samples. The results indicated that when the sample was calcined in nitrogen atmosphere, the ferrite formation occurred at low calcination temperatures and presented better magnetic properties than that one calcined in air.

Introduction

MnZn ferrites are commercially important materials due to their high permeability and low core losses[1]. These ferrites are usually produced by the ceramic method but the particles obtained by this method are rather large and non-uniform in size. Besides, non-reproducible products in terms of magnetic properties are obtained. In order to overcome the limitations of the ceramic process and to improve the magnetic properties of the MnZn ferrite, the co precipitation method [2] have been considered an interesting alternative to produce chemically homogeneous powders with fine particle size and good reproducibility. Hirota and co-workers [3] observed that the magnetic and electric properties of the MnZn ferrites obtained by co precipitation are better than that produce by the ceramic process, due to the small particle size of the co precipitated powders. According to Jeyadevan and co-workers [4], the differences observed in the magnetic properties of the samples prepared by co precipitation are due to the random distribution of the Zn, Mn and Fe ions in the octahedral and tetrahedral sites of the spinel structure, as observed by EXAFS results

Many aspects of the production steps of MnZn ferrites by co precipitation can interfere on the final microstructure and magnetic properties such as the stoichiometry (Mn, Zn and Fe contents), reagent addition order, precipitation pH and calcination conditions [2,5,6]. The aim of this work

was to investigate the effects of some synthesis variables on the magnetic properties of MnZn ferrites obtained by co precipitation.

Experimental Procedure

MnZn ferrites powders with the composition $\text{Mn}_{0.57}\text{Zn}_{0.39}\text{Fe}_{2.04}\text{O}_4$, were produced by the co precipitation method using pure Mn, Zn and Fe chlorides as raw materials and a solution of KOH/ K_2CO_3 as precipitant agent. In the preparations the alkaline solution was added to the salt solution until the desired pH (10 and 12) was attained. The obtained precipitated was washed, dried and calcined inside a DTA furnace under static air or dynamic nitrogen atmospheres at temperatures from 900 °C to 1100 °C during 2 h.

The samples were characterized by X ray diffractometry, thermomagnetic analysis and vibrating sample magnetometry.

Results and Discussion

Fig. 1 shows the XRD patterns of samples calcined at 1000 °C in different atmospheres. When the sample was calcined in static air, we observed the formation of MnZn ferrite and hematite, indicating that the reaction was not completed. In the presence of nitrogen, only ferrite was present. The calcination temperature (Fig. 2) also had effect on the phases formation, mainly when the samples were calcined without atmosphere control. Increasing the calcination temperature from 900 °C to 1100 °C, the MnZn ferrite content increased, while that of hematite decreased. This indicates that to obtain only MnZn ferrite, it is necessary to control the calcination atmosphere and/or to use high calcination temperatures. However, it is well known that high calcination temperatures increase particle size. This increase is not desired since the main advantage of the co precipitation method in relation to the ceramic one is to obtain fine particles with a narrow size distribution in low calcination temperatures. Thus, the best way to produce MnZn ferrite as single phase is to increase the calcination time.

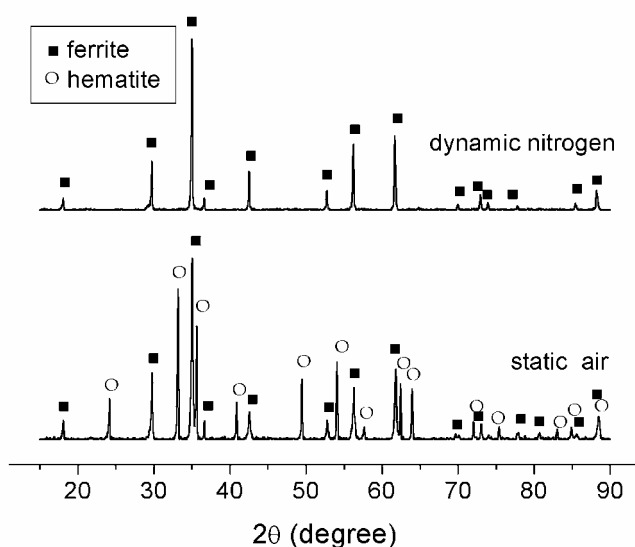


Fig. 1: XRD patterns of samples calcined at 1000 °C.

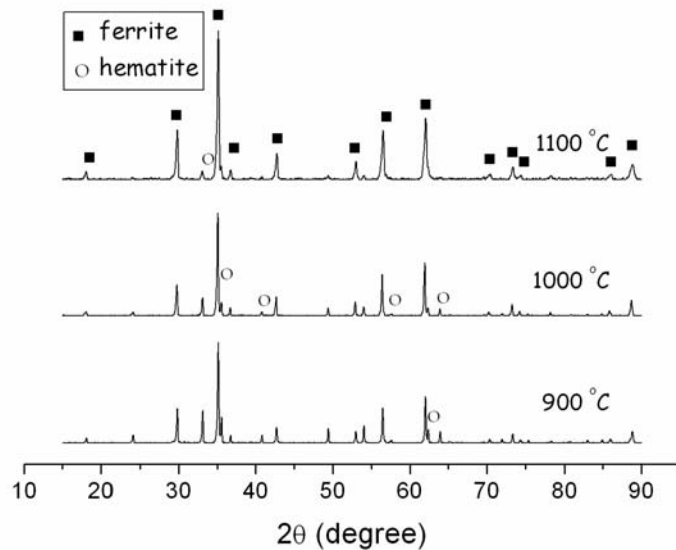


Fig. 2: XRD patterns of samples calcined at different temperatures without atmosphere control (air)

The VSM results showed in Figure 3 and resumed in Table 1 confirm the DRX results, since the saturation magnetization σ_s values were also affected by the calcination conditions. When calcination was conducted without atmosphere control (static air), the samples presented too low σ_s values, showing that only a small amount of ferrite was formed and a non magnetic phase (hematite) is present, as it was observed by the DRX results (Fig. 1). With the atmosphere control higher σ_s values were obtained.

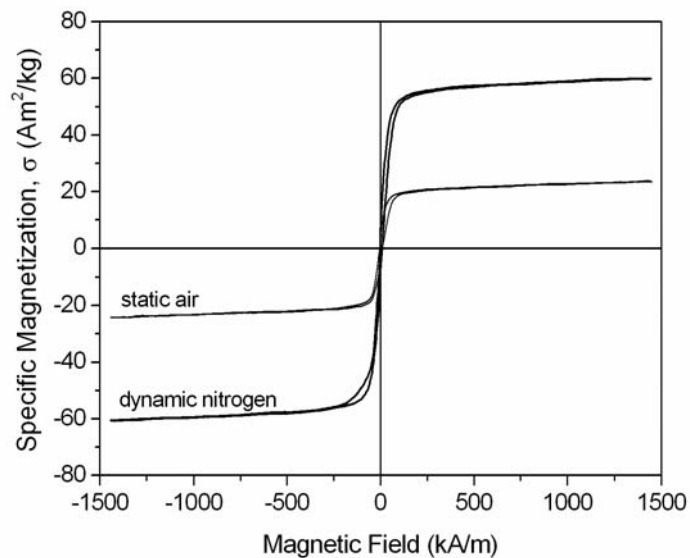


Fig. 3: Hysteresis curves of the samples calcined at 1100 °C at different atmospheres.

The hysteresis curves of Fig. 4 shows the effect of the calcination temperature on the magnetic properties of MnZn ferrite powder produced by co precipitation.

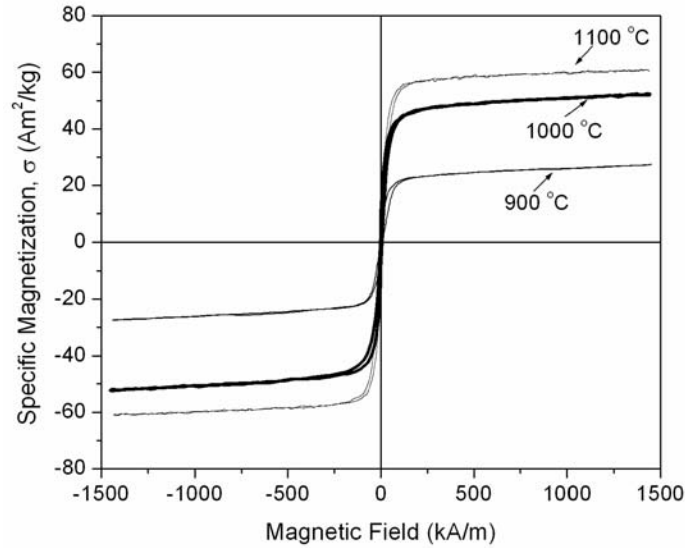


Fig. 4: Hysteresis curves of the samples calcined in the presence of nitrogen at different temperatures.

Table 1: Saturation magnetization σ_s values and Curie temperatures (T_c) of the calcined samples.

Sample	pH	Calcination conditions		T_c ($^{\circ}\text{C}$)	σ_s (Am^2/kg) [#]
		T ($^{\circ}\text{C}$)	Atmosphere		
A1	10	900	static air	-	4.1
A2			nitrogen	56	40.0
A3		1000	static air	-	6.9
A4			nitrogen	98	53.9
A5		1100	static air	417	24.2
A6			nitrogen	92	60.3
B1	12	900	static air	-	2.7
B2			nitrogen	41	27.5
B3		1000	static air	-	6.6
B4			nitrogen	85	52.3
B5		1100	static air	390	28.9
B6			nitrogen	110	61.0

[#] $1 \text{ Am}^2/\text{kg} = 1 \text{ emu/g}$

The thermomagnetic curves of the samples calcined at 1100 $^{\circ}\text{C}$ at different atmosphere conditions are showed in Fig. 5 and the Curie Temperatures values are resumed in Table 1. When the samples were calcined in the presence of nitrogen it was observed well defined transitions at low temperatures. According to Wang and co-workers [7], the Curie temperature of MnZn ferrites decreases with the increase of zinc content due to the substitution of magnetic ions by non magnetic ions (zinc) in the spinel structure. Thus, it is reasonable to conclude that in the presence of nitrogen, a phase with a high zinc content was obtained. When the calcination was conducted without atmosphere control (static air) higher T_c values were obtained. Probably, it is due to zinc losses during calcination, leading to the formation of a Mn rich phase.

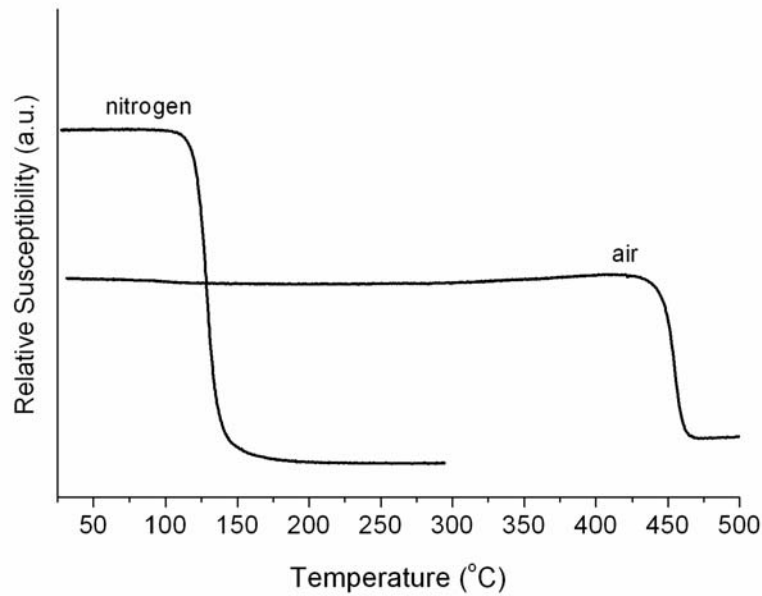


Fig. 5: Thermomagnetic curves of the samples calcined at 1100 °C showing the atmosphere effect.

The increase in the calcination temperature also had effect in the phases formation, as already observed by the XRD and VSM results and confirmed by the thermomagnetic curves of Fig. 6. We can observe that the Curie Temperature values increase with the increase of calcination temperature. Since the Curie temperature is a sensible indicator of chemical compositions in magnetic materials, these results indicate that MnZn ferrite with different compositions were obtained with the increase of calcination temperature. This effect can be due to: (1) the increase in the temperature (even with the atmosphere control) leads to a zinc loss or, (2) it is necessary to use high temperatures (> 900 °C) to attain the desired chemical composition.

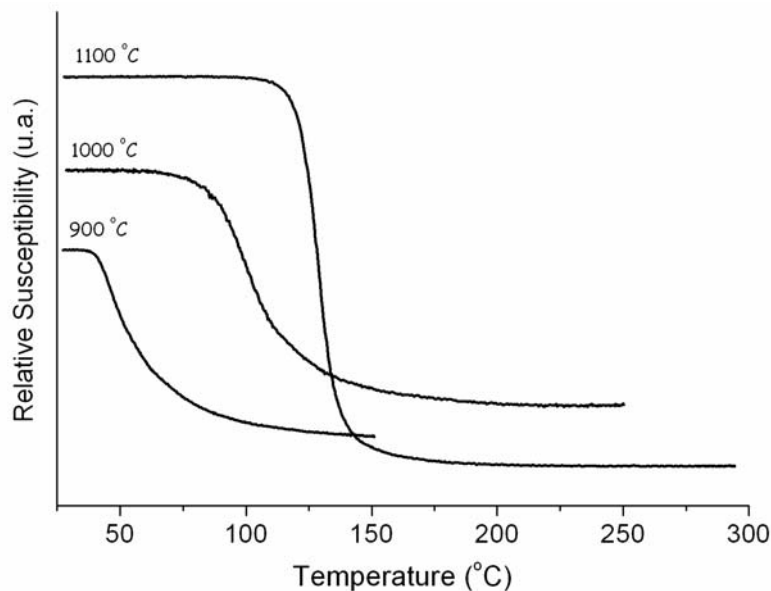


Fig. 6: Thermomagnetic curves of the samples calcined in dynamic nitrogen at different temperatures.

Conclusions

The magnetic properties of the MnZn ferrites were strongly affected by the calcination conditions.

The precipitation pH did not have a significant effect in the properties of the obtained samples, although it was observed a slight increase in the saturation magnetization σ_S values when the precipitation was conducted at higher pH value (12).

To obtain MnZn ferrite powders with the desired composition, avoiding zinc losses, it is necessary a rigorous control of all the calcination conditions.

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