Journal of Bangladesh Academy of Sciences, Vol. 34, No. 2, 189-195, 2010

EFFECTS OF SINTERING TEMPERATURE ON MICROSTRUCTURE AND MAGNETIC PROPERTIES OF $NiFe_2O_4$ PREPARED FROM NANO SIZE POWDER OF NiO AND Fe_2O_3.

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ABSTRACT

Polycrystalline $NiFe_2O_4$ was prepared by solid state reaction from nano size powder of NiO and Fe_2O_3 which were synthesized by wet chemical method. The inverse spinel single phase of the sample has been confirmed by the X-ray diffraction patterns. SEM micrographs of the samples revealed that the grain size increases and the porosity decreases with the increase in sintering temperature and has great influence on the magnetic properties of $NiFe_2O_4$. Enhancement of real part of initial permeability (μ') as a function of frequency has been observed with the increase in sintering temperature. Temperature dependence real part of initial permeability has been observed at various sintering temperature and gives the manifestation of Hopkinson effect. Variation of Curie temperature (T_c) has been found with the variation of sintering temperature.

Key words: Sintering temperature, Microstructure, Magnetic properties

INTRODUCTION

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. The interesting properties of nanoparticles are therefore largely due to the large fraction of atoms that occupies the grain boundary area (Gopal *et al.*1999, Nai-Sheng *et al.* 2000, Calderer *et al.* 2000) which dominates the contributions made by the small bulk of the material.

Spinel ferrites are commercially important materials because of their excellent magnetic and electric properties at high frequency (> 1 MHz) (Rahman and Ahmed 2004, Parvatheeswara *et al*. 2004). And as the most of the properties needed for ferrite application are not intrinsic but extrinsic, the preparation of ferrites with optimized properties has always demanded delicate handling and cautious approach. The ferrite is not completely defined by its chemistry and crystal structure. So, in order to reduce the losses many parameters such as density, grain size, porosity and their intra- and intergranular distribution must be controlled (Ishino and Narumiya 1987). As the

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sintering in practice is the control of both densification and grain growth and many magnetic and electrical properties benefit from both a high relative density and a small grain size, to obtain the optimum sintering temperature is of great importance. This opens the doors for tailoring given properties by careful synthesis of the building blocks (atoms and molecules) and their assembly to fabricate functional materials with improved properties.

This new class of materials is used in important applications high frequency transformers, Ferro fluids, pigments in paints and ceramics, biomedical applications like drug delivery system, hyperthermia, NMR, high density magnetic recording, varistors and dye-sensitized solar cells (Iftimie *et al.* 2005, Xu *et al.*1990, Rezlescu *et al.* 2005, Doroftei *et al.* 2006, Gleiter 1989). In this study, effects of sintering temperature on microstructure and magnetic properties of the $NiFe_2O_4$ are investigated.

EXPERIMENTAL

Polycrystalline $NiFe_2O_4$ was prepared through the solid state reaction using conventional double sintering ceramic technique from nano size powder of NiO and Fe_2O_3 which were synthesized by wet chemical method. After thorough mixing the powder was presintered at 800^0C for 3 hr. The presintered ferrite powder was crushed and mixed with 1 wt. % polyvinyl alcohol (PVA) as a binder and uniaxially pressed into toroid and pellets. The compacts were successively sintered in a muffle furnace in air from the temperature range from 1000 to 1400^0C for 4 hr to eliminate the PVA and finally furnace cooled to room temperature.

The spinel phase formation of the ferrite system was confirmed by X-ray diffraction patterns obtained by using PHILIPS X Pert PRO X-ray diffractometer. The SEM micrographs with magnification × 10000 have been studied by using a Scanning Electron Microscope (EDS). Frequency dependence of permeability was measured up to 13 MHz. Temperature dependence permeability were measured by placing the samples in a tubular furnace according to the experimental setup described elsewhere from which Curie temperatures have been determined (Cedillo *et al.* 1980).

RESULTS AND DISCUSSION

Fig.1 shows the XRD pattern of the synthesized $NiFe_2O_4$ for various sintering temperatures. The X-ray lines show considerable broadening, indicating the fine particle nature of the ferrite. The observed peaks at (200), (311), (400), (422), (511), (440) and (533) confirmed the spinel structure of the samples. No extra peak other than $NiFe_2O_4$ has been found up to the calcinations temperature 600^0C which indicate the single phase of the prepared sample. But further increase in calcinations temperatures multiphase component of $NiFe_2O_4$ has been observed.

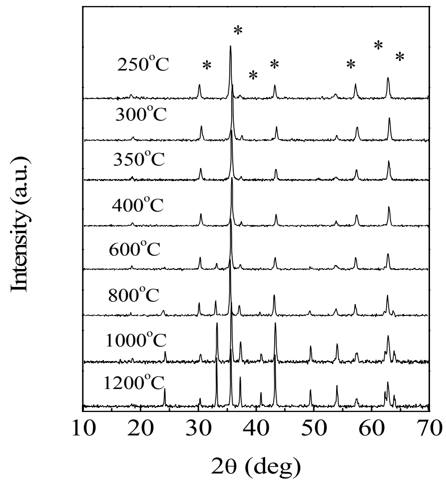

Fig 1. XRD patterns of $NiFe_2O_4$ for various calcinations temperatures.

SEM micrographs of polycrystalline $NiFe_2O_4$ with magnification × 10000 sintered at various temperatures have been presented in Fig. 2. It can be observed from the figure that the microstructure of the sample sintered at low temperature (1100^0C) is heterogeneous where as the microstructure of the sample become homogeneous at higher sintering temperatures (1200, 1300 and 1400^0C). It is also observed that the grain size increases with increasing sintering temperature. Further it may be noticed that the porosity of the samples sintered at 1100^0C is predominately intergranular, whereas the porosity of the samples sintered at 1200, 1300 and 1400^0C is located at grain boundaries and many of the very small pores disappear through diffusion kinetics. That's why the grain size increases and the number of grain boundary decreases and consequently the porosity decreases and results in the homogeneous grain size distribution.

Fig. 3 represents the initial permeability (μ) over the frequency range from 1 kHz to 13 MHz for the sample at different sintering temperatures. The real part of the initial permeability (μ') represents the real permeability with the magnetization in phase with the alternating magnetic field. From Fig. 3 it is observed that the real part of the initial permeability μ' is fairly constant with frequency up to certain high frequency and then it decreases. The decrease in permeability implies onset of ferromagnetic resonance (Verma and Chatterjee 2006). The flat μ' region up to the frequency where it starts declining rapidly gives the compositional stability and quality of prepared ferrite and is known as the zone of utility of the ferrite. And the higher stability of ferrites is a desirable characteristic for various applications such as broadband pulse transformation and wide band read-write heads for video recording etc

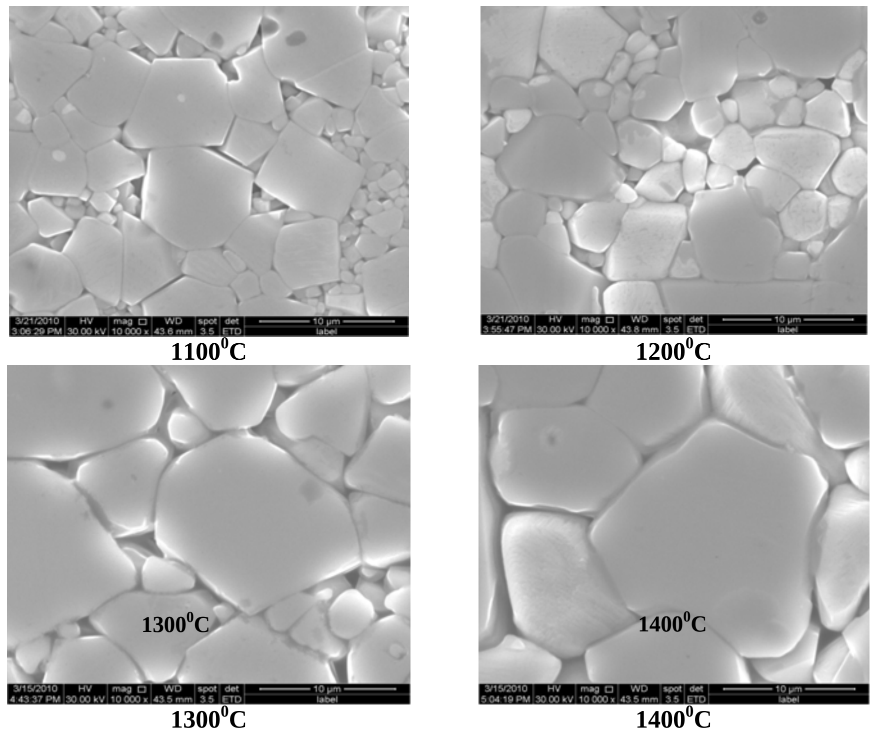

Fig. 2. SEM micrographs of polycrystalline $NiFe_2O_4$ with magnification(x10000) at various sintering temperatures.

It is also clear from Fig. 3 that the permeability is higher but the stability region is small for higher sintering temperature i.e. the permeability increases and stability decreases with increasing grain growth as expected.

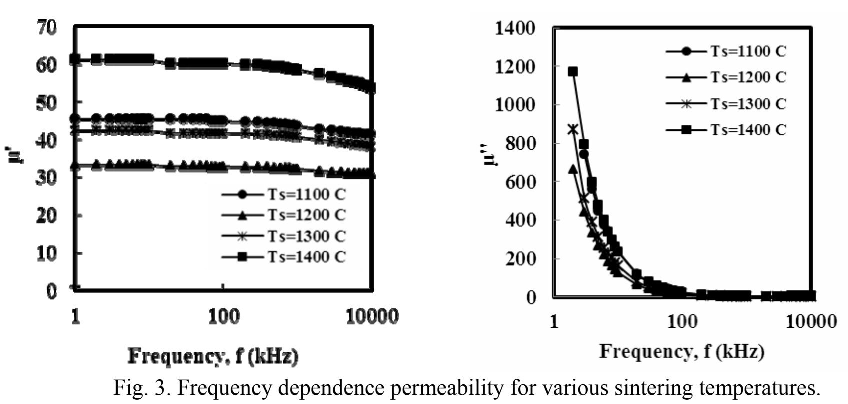

Fig. 3. Frequency dependence permeability for various sintering temperatures.

Higher the density and grain size, greater the grain to grain continuity in magnetic flux leading to higher permeability (Verma and Chatterjee 2006). That is, when the grain size is smaller, the permeability is lower but the stability is maximum because the presence of small grain size interferes with wall motion.

Again, the losses and their frequency dependence determine the ultimate operating frequency of magnetic devices. The imaginary part of the initial permeability (μ'') represents the loss component when the magnetization is 90^0 out of phase with the alternating magnetic field. The losses in ferrites are associated with domain wall relaxation and rotational resonance. Domain wall relaxation is usually observed at lower frequencies while the rotational resonance is observed in the megahertz range (Verma and Chatterjee 2006). From Fig. 3 it is observed that the loss component decreases with frequency up to the measured frequency of this study. This decrease in permeability is rapid at the low frequency region and then it becomes almost constant. At higher frequencies, losses are found to be lower because the domain wall motion is inhibited and the magnetization is forced to change by rotation. In addition to this, the increase of losses with increase in sintering temperature may be attributed to increase in grain size with sintering temperature and consequently increase in the number and size of magnetic domains which contribute to loss due to delay in domain wall motion.

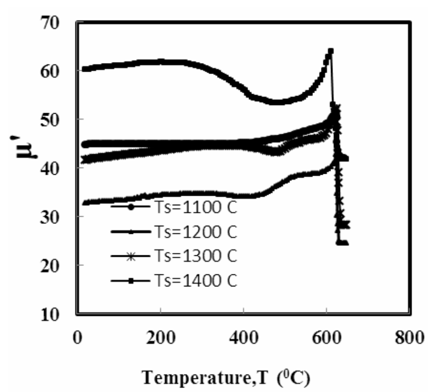

Fig. 4. Temperature dependence real part of initial permeability.

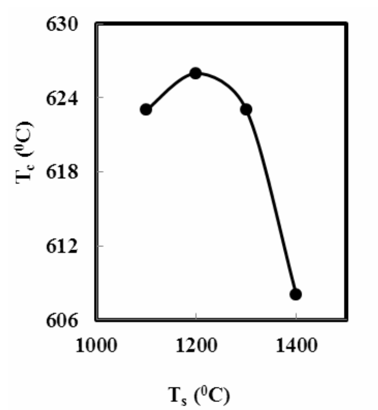

Fig. 5. Sintering temperature dependence Curie temperature.

To evaluate Curie temperature (T_c), the behavior of induction (or μ') as a function of temperature were obtained for various sintering temperatures as shown in Fig. 4. Permeability passes through a maximum just before a sharp fall which is a manifestation of Hopkinson effect. Permeability is proportional to saturation magnetization, M_s and inversely proportional to the magnetocrystalline anisotropy K_1 leading to $\mu' \alpha\ M_s/K_1$. When the measuring temperature increases the value of M_s decreases but K_1 decreases faster than M_s. Near the Curie temperature the value of K_1 becomes almost negligible as a result of which the peak is obtained. At Curie temperature T_c complete spin disorder take place and results a sharp drop of permeability. The sharpness of the induction drop has been associated to the compositional homogeneity of the sample (Globus and Valenzuela 1975, Yellup and Parker 1979).

The Curie temperature is primarily determined by the materials' main prescription and crystal structure and has little connection with the microstructure, e.g., lattice defect, porosity, grain size, etc. (Hua Su *et al*. 2004). But in Fig. 5 sintering temperature dependence Curie temperature has been observed for samples. Variation of Curie temperature has been explained by finite size scaling theory up to 1200^0C. At low sintering temperature the grain size are very small and these small particles have a significant fraction of atoms on the surface and their exchange interaction should be weaker because of the lower coordination. So, at this low sintering temperature they will have reduced average Curie temperature compared to that of the interior atoms, which accounts for the decrease in Curie temperature. Further increase in sintering temperature the Curie temperature decreases which have occurred due to the predominance of the effect due to change in cation distribution over the finite size effect on Curie temperature.

CONCLUSION

The influences of sintering temperature on the microstructure and magnetic properties of $NiFe_2O_4$ were investigated. With the increase in sintering temperature, the microstructure becomes more homogeneous and the grain size, density increases and consequently the porosity decreases. At lower sintering temperature, the permeability is lower but the stability is maximum because the presence of small grain size interferes with wall motion. Variation of Curie temperature with the variation of sintering temperature occurs because with the variation of sintering temperatures valence state of cations like $Fe^{3+} \leftrightarrow Fe^{2+}$ and $Ni^{2+} \leftrightarrow Ni^{3+}$ occurs. The variations in properties for this ferrite have many contributing factors, which include density, change in cation distribution and relative stability of Fe^{+3}/Fe^{2+} and/or Ni^{3+}/Ni^{2+} ions.

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(*Received revised manuscript on 3 November, 2010*)