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The effect of Cu substitution on the microstructure and magnetic properties of $MnFe_2O_4$ ferrite

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The effect of compositional variation on grain size and porosity of $Mn_{1-x}Cu_xFe_2O_4$ ferrite, where $x = 0.0$, 0.25, 0.50, 0.75, 1.00, prepared by standard ceramic method are reported. From microstructure analysis it follows that porosity increases with the Cu concentration where as coercivity increases up to $x = 0.50$. Above $x = 0.5$ the decrease in coercivity is explained on the basis of Neel's mathematical model treating the demagnetizing influence of non-magnetic material in cubic crystals. The coercivity, varies inversely with the grain size upto $x = 0.5$. The decrease in coercivity above $x = 0.5$ with grain size can be correlated with the inter-granular domain wall movement because of large porosity.

1. Introduction

Spinel ferrites are well known for their specialized applications and require low porosity and controlled microstructure [1, 2]. The influence of microstructure on magnetic properties of spinel ferrites has been investigated extensively [3]. Due to recent advances in ceramic processing of ferrites [4], it has become possible to prepare sintered MnZn ferrites with grain size smaller than 1 μm. MnZn ferrites with certain compositions display low crystalline anisotropy [5] and therefore have relatively broad domain walls. The domain size in MnZn ferrites has been measured using the neutron-depolarization technique [6]. Other techniques such as magnetic Kerr measurement and scanning electron microscope with polarization analyzer (SEMPA) are limited to the determination of domain structure at the surface of the sample. However, such domain patterns will not be representative of the domain structure throughout the bulk of material, due to presence of closure of domain structure which minimizes demagnetization energy at the sample surface. Another example of the importance of micro- or nanostructure is the size dependent Curie temperature T_c of nano scale $MnFe_2O_4$ ferrite particles which has been reported in Ref. [7–10]. T_c increases by as much as 97 K with decreasing particle size related to the preparation technique. A further example of the importance of the microstructure is the model for the permeability of ferrites proposed by Globus and co-workers [11]. They have considered domain-wall-size model (DWS) to account for the grain size dependence of both the initial permeability, μ, and the coercivity, H_c, of polycrystalline ferrites. Smit and Wijn [12] showed the variation of coercivity, H_c with porosity in Ni-Zn ferrites. It was assumed that H_c increases with increasing porosity. This may be caused by the fact that higher porosity samples contain smaller particles, which have high coercive force. The coercive force of mixed NiZn ferrites of varying porosity can be correlated fairly well with Neels' theoretical model treating the demagnetizing influence of non-magnetic materials in cubic crystals. In this model, the domain processes are considered as rotational. Economos [13], showed that coercive force decreases in Mg ferrites as the porosity decreases. Schwabe and Campbel [14] showed that for square loop materials, the threshold field (close to H_c) varies with the grain size for lithium ferrite i.e., H_c is inversely proportional to the grain size.

Igarashi [15], separated porosity and grain size effects in studying Ni-Zn ferrites. It was reported that remanent magnetization is independent of grain size but would vary with porosity as $(1 - p)4\pi M_o$, where M_o is the magnetization extrapolated to zero porosity. H_c is then proportional to $1/r$, r being the radius of grain that is independent of porosity. In the present study, the role of microstructural features such as grain size and porosity in $Mn_{1-x}Cu_xFe_2O_4$ ferrites for different concentration of copper and their effect on magnetic properties has been investigated.

2. Experimental

2.1. Sample preparation

Samples of $Mn_{1-x}Cu_xFe_2O_4$ system were prepared by standard solid state reaction technique using reagent grade constituents MnO, CuO and Fe_2O_3 supplied by Merk (Germany). The oxides were ground to the size of about 10 μm. The pellets were prepared using a hydraulic press at constant unidirectional pressure of 30 kN/mm^2. Initially, the samples were sintered in a tube furnace for 45 hrs at 1000°C. The final heat

TABLE I Magnetic properties and microstructure analysis of $Mn_{1-x}Cu_xFe_2O_4$ ferrite

Concent. (x)	T_c (K)	H_c (Oe)	Grain size (μm)	Porosity (%)	Chemical composition (EDS)
0.0	550	181.25	4.78 ± 3.37	22.48 ± 7.25	Fe = Balance, Mn ~40–45, Cu = 0
0.25	475	184.38	4.18 ± 1.30	24.38 ± 6.13	Fe = Balance, Mn ~22, Cu ~10
0.50	415	187.5	3.69 ± 1.20	28.25 ± 8.51	Fe = Balance, Mn ~18, Cu ~12–14
0.75	385	185.63	3.45 ± 1.05	36.33 ± 12.14	Fe = Balance, Mn ~14, Cu ~15–18
1.0	290	180.00	3.15 ± 1.03	39.86 ± 8.44	Fe = Balance, Mn ~0, Cu ~39–45

treatment was carried out at 1200°C for 5 hrs. The completion of the reaction and the production of single phase material was verified by X-ray diffraction studies carried out on a Shimadzu diffractometer.

2.2. SEM analysis

Mechanical behaviour and physical Properties of materials are strongly influenced by their microstructure. Thus microstructure studies are essential in order to understand the relationship between the processing parameters and behavior of the materials used in practical applications. In the present study,[a] JEOL 2000CX Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy, (EDS) and Wavelength Dispersive Spectroscopy, (WDS) was employed to examine the microstructural features. For the microstructures, samples were ground progressively and polished up to 0.5 μm using a diamond paste. Samples were then etched in 3% nital solution using a few drops of HF in order to reveal the microstructures. For the chemical analysis, EDS method was adopted and the results are presented in Table I.

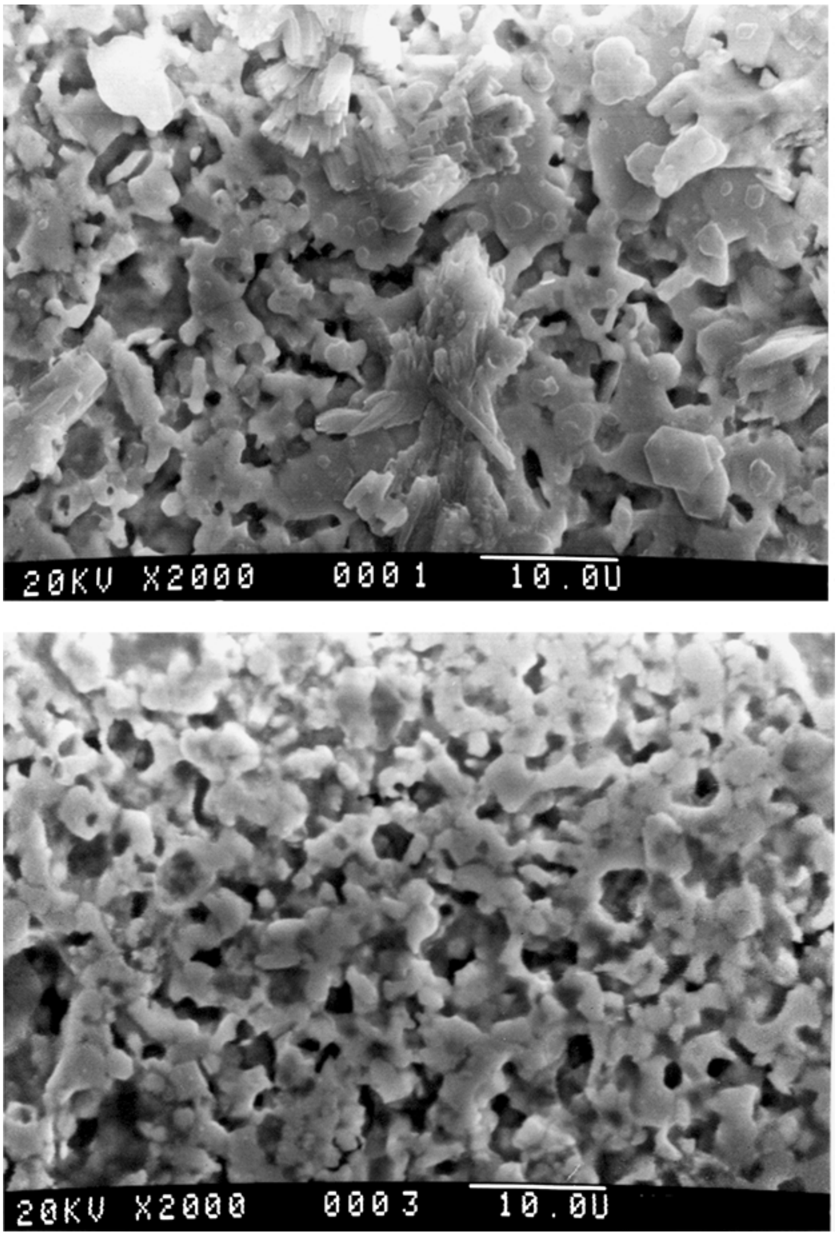

Figure 1 Representative micrographs of $Mn_{1-x}Cu_xFe_2O_4$ ferrites.

2.3. Methodology for grain size measurement

The line intercept method has been used to measure the grain size. Samples were examined in a Nikon optical microscope interfaced with micro-computer. For the accuracy at least 70 grains were measured in different sections of each sample. Porosity in the ferrite samples was also observed and the percentage porosity was calculated.

3. Results and discussion

Two representative micrographs for $Mn_{1-x}Cu_xFe_2O_4$ ferrite system taken at different magnification are shown in Fig. 1. In all the samples the morphology of grain structure as seen from the scanning electron microscope consist of equi-axed grains varying in size from 3 to 10 μm. No particles, inclusion or second phase could be identified in any of the samples. The chemical composition of various samples were calculated by EDS analysis. Oxygen is not included as it cannot be observed by EDS and the Fe is taken as balance. The observed composition is almost equal to that derived from stiochiometic calculations. The results of measurements of grain size, %porosity and chemical composition from EDS analysis are listed in Table I.

The variation in grain size and the percent porosity with the addition of Cu in $Mn_{1-x}Cu_xFe_2O_4$ (for $0 < x < 1$) ferrite system are shown in Figs 2 and 3 respectively. It is known that for mixed ferrites the coercivity increases linearly with porosity and decreases with the increase in the grain size ($H_c \propto 1/r$) [14, 16–18]. From microstructural analysis, our results show the decrease in the grain size and increase in the porosity with the substitution of Cu in MnCu-ferrites. Our results are thus are in good agreement with the results reported earlier for mixed ferrites [15, 19, 20]. The variation of coercive force with the addition of Cu as shown in Fig. 4. It can be observed that up to $x = 0.5$ the coercivity increases in a similar way as porosity increases. The coercivity follows $1/r$ rule up to $x = 0.5$ with the increase of Cu content. Above $x = 0.5$ the deviation of H_c from $1/r$ rule may be

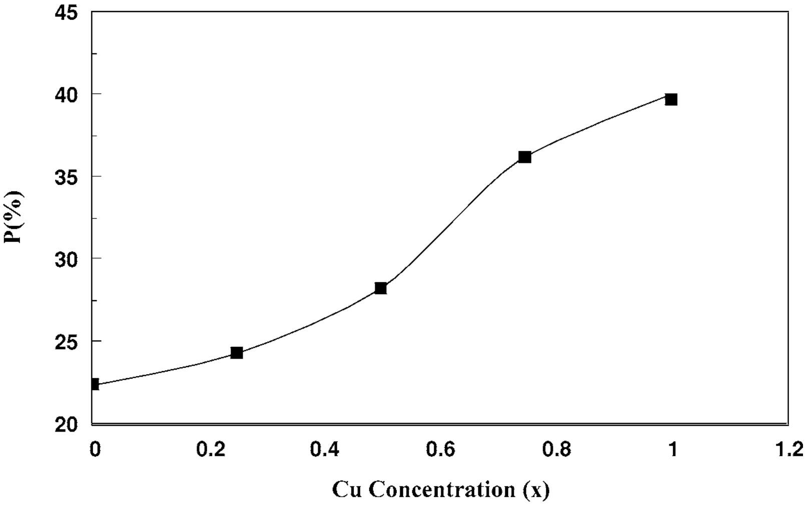

Figure 2 Porosity vs Cu-concentration of $Mn_{1-x}Cu_xFe_2O_4$ ferrites.

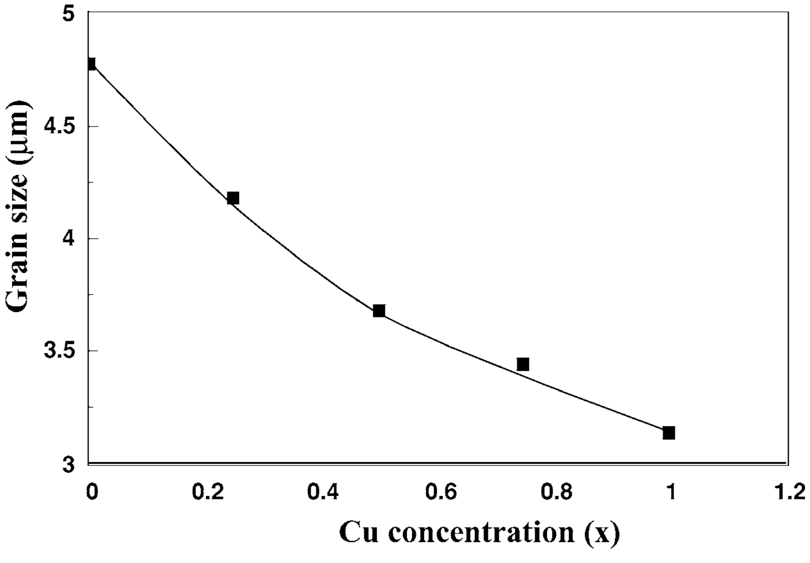

Figure 3 Grain size vs Cu-concentration of $Mn_{1-x}Cu_xFe_2O_4$ ferrites.

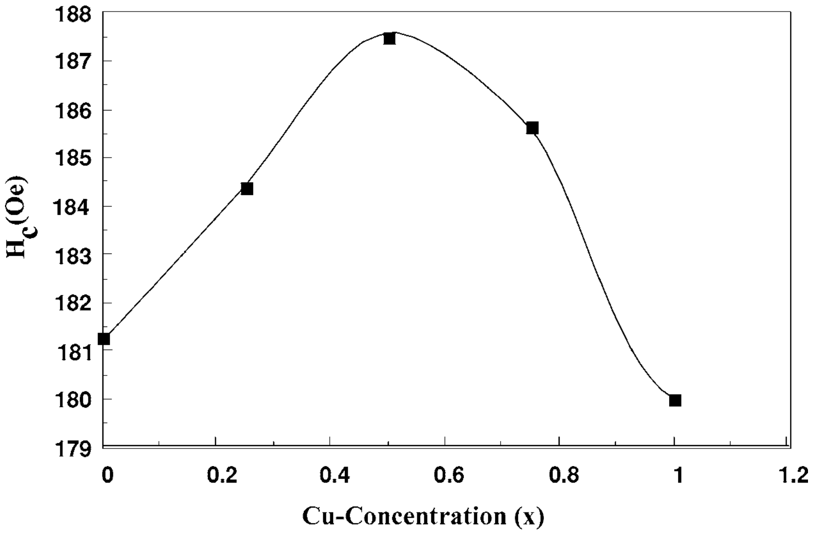

Figure 4 Coercivity vs Cu-concentration of $\mathrm{Mn}_{1-x}\mathrm{Cu}_x\mathrm{Fe}_2\mathrm{O}_4$ ferrites.

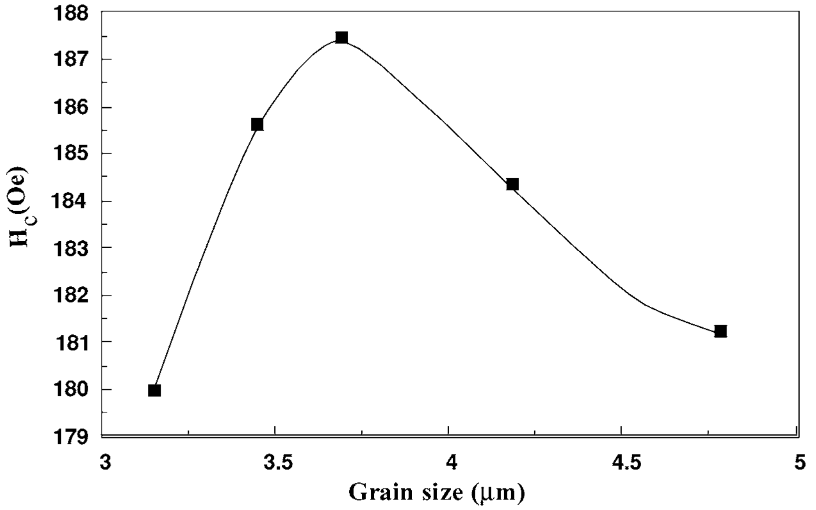

Figure 5 Coercivity vs Grain size of $\mathrm{Mn}_{1-x}\mathrm{Cu}_x\mathrm{Fe}_2\mathrm{O}_4$ ferrites.

explained by to the Neel's mathematical model treating the demagnetizing influence of non-magnetic material in cubic crystals [6–8, 19, 21, 22]. Also the dependence of coercivity, H_c on grain size as shown in Fig. 5, is related to the inter-granular domain wall movement [16–18, 20].

4. Conclusion

From microstructural analysis it has been revealed that with the substitution of Cu, the porosity increases while the grain size decreases in $\mathrm{Mn}_{1-x}\mathrm{Cu}_x\mathrm{Fe}_2\mathrm{O}_4$ ferrites. This results in decrease in Curie temperature, T_c. The increase in coercivity, H_c, was observed to be inversely proportional to grain size upto $x = 0.5$ which is in good agreement with the Neel's model treating the demagnetizing influence of nonmagnetic atoms in mixed ferrites.

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