Chapter 4

Effect of Sintering Conditions on the Magnetostriction of Cobalt Ferrite

4.1 Introduction

Magnetic materials with high permeability and low magnetic loss are used for many practical applications [1, 2]. In many of the applications, permeability is an important factor which mainly depends on the microstructure, density, porosity, grain size, etc, of the sintered products [2-4]. Therefore, sintering is the most crucial step in the processing of ceramic magnetic materials aimed at various applications. During sintering, the porosity decreases and a suitable microstructure of the material is developed, which is the deciding factor for its final performance. Sintering studies on different ferrites and the corresponding changes in the performance parameters are well documented in the literature [1-7]. It is known that the usual single stage sintering process of raising the temperature of a material, kept in a furnace, to a suitable temperature at a specific heating rate, hold the temperature for a specific period and cool the furnace back to room temperature at a particular rate, is always accompanied by rapid grain growth [8]. Chen and Wang have developed a new method called dual sintering or two-stage sintering for the effective sintering of Y₂O₃ [9]. By the dual sintering method, the grain boundary diffusion is maintained but grain boundary migration could be arrested. Therefore, using
the dual sintering technique, the grain growth at final stage sintering is suppressed to get ceramics with smaller sized grains. This method of sintering has been found to be effective in enhancing the performance parameters of various ceramic materials such as ZnO, Ni-Cu-Zn ferrite, BaTiO₃, etc [10-12].

Cobalt ferrite is an ideal material for future magnetostrictive applications because of its low cost, easy processability, etc. The main disadvantage of cobalt ferrite is that it is not much useful for high frequency applications because of its low permeability. Therefore, there are not much studies reported on the effect of sintering on the properties and especially on the magnetostriction of cobalt ferrite. Chen et al have studied the magnetostriction of sintered metal bonded cobalt ferrite composite which was proposed to be useful for magnetomechanical sensor applications [13]. It was observed that these composites show high magnetostrictive strain of 230 ppm at low applied magnetic fields. NiBedim et al have studied the effect of heat treatment and vacuum sintering on the magnetic and magnetostrictive properties of cobalt ferrite [14]. The studies showed that degradation of magnetostriction and strain derivative is due to the cation redistribution. Bhame and Joy have studied the effect of processing conditions and sintering temperature on the magnetostrictive properties of cobalt ferrite synthesized by the ceramic method [15]. It was found that the magnetostriction of sintered cobalt ferrite mainly depends on the microstructure of the sintered product.

It is widely known that sintered products derived from nanocrystalline powders exhibit improved magnetic permeability compared to the bulk counterparts [16, 17]. The advantage of the nanocrystalline powders is that they are more sinterable due to the fine particle nature as well as the high surface area [18-21]. Since very high magnetostriction coefficient is obtained for sintered cobalt ferrite derived from nanocrystalline powders of very small particle sizes synthesized by the auto combustion method using the corresponding metal nitrates and glycine as the fuel (Chapter 3), we have studied the effect of sintering conditions on the magnetostriction characteristics of the compacts made from small particles.
Figure 4.1: Schematic representations of the sintering schedules of (a) single-stage sintering and (b) two-stage sintering or dual sintering.
This chapter describes the effect of single and two-stage sintering on the microstructure and magnetostriction of sintered cobalt ferrite derived from nanocrystalline materials. The powder sample G2 with a particle size of 4 nm (Chapter 3, Table 3.3) which showed highest magnetostriction as well as high strain derivative after sintering at 1450 °C is used for the sintering studies. The schematics of the single and two-stage sintering processes are shown in Figure 4.1. In single stage sintering, the pressed compact is heated from room temperature to high temperature (T₁) and held at this temperature for a short time and then cooled back slowly (Figure 4.1a). This sintering process is known to be always accompanied by rapid grain growth. In the case of dual sintering, the sample is heated to a high temperature (T₁) and rapidly cooled down to a lower temperature (T₂), held at this temperature (T₂) for a long time, and finally cooled to room temperature slowly (Figure 4.1b). According to Chen and Wang [9], the success of the two-stage sintering strongly depends on the selection of high temperature (T₁), second low temperature (T₂), holding time as well as the heating and cooling rates. By the dual sintering method, the grain boundary diffusion is maintained but grain boundary migration could be arrested. Therefore, by the process of dual sintering, the grain growth at the final stage sintering can be suppressed to get ceramics with smaller sized grains. Objective of the present study is to investigate and compare the influence of these two sintering processes on the densification, microstructure, and magnetostriction of sintered cobalt ferrite derived from nanocrystalline materials.

4.2 The Sintering Process

In the single stage sintering process, the samples were heated from room temperature to high temperature and held at this temperature for a short time and then cooled back to room temperature slowly, as shown in Figure 4.1a. In this work, samples were sintered at 1500, 1450, 1400, 1300 and 1200 °C with a heating rate of 5 °C/min, cooling rate of 20 °C/min and holding time of 10 minutes, to determine the first heating temperature (T₁). From magnetostriction studies on the different sintered samples it was found that sample sintered at 1450 °C show the highest maximum value of magnetostriction. Therefore, in
the case of dual sintering, samples were initially heated to 1450 °C (T₁) and rapidly cooled down to a lower temperature (T₂), held at this temperature (T₂) for a long time, and finally cooled to room temperature slowly, as shown in Figure 4.1b. Samples were initially heated to 1450 °C with a heating rate of 5 °C/min and rapidly cooled to a lower temperature (T₂) fixed at 1300 °C and vary the holding time from 10 min to 60 h to determine the holding time. Next, keeping the higher temperature (T₁) constant, with a heating rate 5 °C/min, and holding time fixed, the lower temperature was varied as 1100, 1200, 1300 and 1400 °C with a cooling rate 30 °C/min to determine the best lower temperature (T₂). Finally, holding time was fixed; the higher (T₁) and lower temperatures (T₂) were varied.

**4.3 Studies on Sintered Samples**

**4.3.1 Microstructure and Density**

The changes in the microstructural features of the single-stage sintered samples with increase in the sintering temperature from 1200 °C to 1500 °C are shown in Figure 4.2. The grain size is increased drastically with increase in the sintering temperature. The sample sintered at a lower temperature of 1200 °C shows very small and non-uniform grain size whereas high sintering temperature of 1500 °C gives rise to larger sized pores in the grains. The larger sized pores are due to the release of oxygen from the spinel lattice as reported for other ferrites sintered at higher temperatures [22]. Similarly, density is also increased with increase in the sintering temperature, as shown in Figure 4.3. The sample sintered at 1200 °C shows the lowest density of 63% whereas sample sintered at 1500 °C shows highest density of 83% compared to the theoretical density of cobalt ferrite (5.275 g/cm³).
Figure 4.2: SEM images of the single stage sintered samples, sintered at (a) 1500 °C, (b) 1450 °C, (c) 1400 °C, (d) 1300 °C, and (e) 1200 °C.
The SEM images of the two-stage sintered samples, where $T_1 = 1450$ °C and $T_2 = 1300$ °C, with different holding times from 10 min to 60 hrs are shown in Figure 4.4. It can be seen that, there are large changes in the microstructure with increasing the holding time. The grain size is increased with increasing the holding time. There is a corresponding increase in the density of the sintered samples, when the holding time is increased. The density is found to be very low (79%) for a holding time of 10 minutes. However, the density increases almost linearly when the holding time is varied from 5 to 60 hours. The density varies from 82% to 90% with increasing holding time above 5 h, as shown in Figure 4.5. Figure 4.4 shows that the sintering temperature combination of the higher temperature at 1450 °C ($T_1$) and the lower temperature at 1300 °C ($T_2$) and holding time of 20 h give most clear microstructure with grain size of 10 µm with minimum amount of pores compared to the other sintered samples.
Figure 4.4: SEM images of two-stage sintered samples ($T_1 = 1450 \, ^\circ C$ and $T_2 = 1300 \, ^\circ C$) with different holding time at the lower temperature; (a) 10 min, (b) 1 h, (c) 5 h, (d) 10 h, (e) 20 h, (f) 40 h, and (g) 60 h.
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Figure 4.5: Variation of density as a function of holding time for $T_1 = 1450 \degree C$ and $T_2 = 1300 \degree C$.

The microstructures of the two-stage sintered samples with fixed higher temperature as 1450 $\degree$C, holding time as 20 hrs and different lower temperatures ($T_2$) are shown in Figure 4.6. The grain size increases with increasing the lower temperature. It is found that the best microstructure without many intra-grain pores is obtained for the sample sintered at 1450 $\degree$C ($T_1$)/1300 $\degree$C ($T_2$). The density, as indicated in the right hand side of the individual micrographs, increases with increase in the second sintering temperature ($T_2$).
Figure 4.6: SEM images of the two-stage sintered samples with $T_1 = 1450 \, ^\circ C$ and different lower temperatures, $T_2$ as (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C. The numbers on the right hand side corner indicate the density of the corresponding samples.

The SEM images of the two-stage sintered samples with different high temperatures ($T_1$) and lower temperatures ($T_2$) with the fixed holding time as 20 h are compared in Figure 4.7. The higher sintering temperature of 1450 °C ($T_1$) and lower sintering temperature of 1300 °C ($T_2$) with the holding time 20 h is ideal to get the best microstructure compared to other sintered samples.
Figure 4.7: SEM images of the two-stage sintered samples with fixed holding time at different $T_1$ and $T_2$ as (a) 1500/1300 °C, (b) 1450/1300 °C, (c) 1350/1200 °C, (d) 1300/1150 °C, (e) 1250/1100 °C and (f) 1100/1000 °C. The numbers on the right hand side corner in the individual micrographs indicate the density of the corresponding samples.
4.3.2 Magnetic Properties

Figure 4.8: Comparison of the room temperature initial magnetization curves of single stage sintered samples. Inset: Variation of coercivity as a function of sintering temperature.

Figure 4.8 shows the room temperature magnetization measurements of the single stage sintered samples. The saturation magnetization values of all the sintered samples are almost comparable with the literature reported value of 80 Am$^2$/kg for cobalt ferrite [23]. The minor variations are due to the sample shape and orientation (measurements were made on broken pieces of the sintered pellets with irregular shape). On the other hand, the coercivity, as shown in the inset of Figure 4.8 decreases steadily with increase in the sintering temperature. This is due to the increase in the grain size as evidenced from SEM micrographs shown in Figure 4. 2. Above the critical size at which coercivity is maximum when coercivity is plotted as a function of particle size, coercivity decreases with increasing particle size due to the increased number of domains [24].
Figure 4.9: Initial magnetization curves of two-stage sintered samples ($T_1 = 1450^\circ C$, $T_2 = 1300^\circ C$) for different holding times. Inset: coercivity as a function of holding time.

Figure 4.9 shows the room temperature initial magnetization curves of the two-stage sintered samples at $T_1 = 1450^\circ C$ and $T_2 = 1300^\circ C$ at different holding times. Inset in Figure 4.9 shows the coercivity as a function of holding time. The coercivity decreases drastically up to a holding time of 10 hrs and further slow decrease is observed as the holding time is increased. These changes are well correlated with the changes in the grain size with holding time, as shown in Figure 4.4. Figure 4.10 shows the room temperature initial magnetization curves of the two-stage sintered samples with different lower temperatures ($T_2$) and fixed high temperature as well as for those samples sintered with different high ($T_1$) and lower temperatures ($T_2$) for a holding time of 20 h. In all cases, coercivity decreases with increasing lower ($T_2$) temperature in the first case and the same trend is observed for samples sintered at different high ($T_1$) and lower temperatures ($T_2$). In all cases, the changes in the coercivity are well correlated with the microstructures. Saturation magnetizations of all the two-stage sintered samples are close to 80 Am$^2$/kg.
Figure 4.10: Room temperature initial magnetization curves of two-stage sintered samples, (a) for $T_1 = 1450 \, ^\circ\text{C}$ and at different $T_2$. Inset: variation of coercivity as a function of $T_2$; (b) both $T_1$ and $T_2$ varied as indicated, inset: variation of coercivity as a function of $T_1$. 

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4.3.3 Magnetostriction Studies

Magnetostriction curves of the single stage sintered samples are compared in Figure 4.11. A maximum magnetic field of 800 kA/m was applied in the parallel and perpendicular directions. Maximum value of magnetostrictive strain of 315 ppm is obtained in the parallel direction for the sample sintered at 1450 °C whereas lowest value of 201 ppm is obtained for the sample sintered at 1200 °C. Magnetostriction value increases with increasing sintering temperature from 1200 °C to 1450 °C and is then decreased for the sample sintered at 1500 °C. For all samples, the magnetostriction value is negative along the parallel direction. On the other hand, samples sintered at higher temperatures (≥ 1300 °C) show negative magnetostriction along the perpendicular direction (shown in Figure 4.11). The maximum value of magnetostriction as a function of sintering temperature and the corresponding strain derivative curves are shown in Figure 4.12. From Figure 4.12, it can be seen that the sample sintered at 1450 °C shows the maximum value of magnetostriction and largest strain derivative of 1.97 x 10^-9 A^-1m whereas higher magnetostriction is obtained at lower fields for samples sintered at lower temperatures. From these studies, it is concluded that magnetostriction strongly depends on the sintering temperature, which influences the microstructure.

The parallel and perpendicular magnetostriction curves of the two-stage sintered samples with T1 = 1450 °C and T2 = 1300 °C with different holding time are compared in Figure 4.13. Figure 4.14 shows the variation of maximum value of magnetostriction and strain derivative of the two-stage sintered samples as a function of holding time. Magnetostriction value initially increases with increasing holding time up to 20 h then decreases. Both the magnetostriction as well as the strain derivative shows the same trend as a function of the holding time. Maximum value of magnetostriction of 331 ppm is obtained for the sample sintered for 20 h and higher strain derivative is obtained for this sample.
Figure 4.11: Magnetostriction curves measured along the parallel ($\lambda_{\text{par}}$) and perpendicular ($\lambda_{\text{per}}$) directions to the applied magnetic field for the samples sintered (single stage) at different temperatures.
Figure 4.12: (a) Variation of the maximum value of magnetostriction as a function of sintering temperature and (b) strain derivative of samples sintered at different temperatures as a function of magnetic field, measured along the parallel direction.
Figure 4.13: Magnetostriction curves measured along the parallel ($\lambda_{\text{par}}$) and perpendicular ($\lambda_{\text{per}}$) directions to the applied magnetic field for the two-stage sintered samples ($T_1 = 1450 ^\circ \text{C}, T_2 = 1300 ^\circ \text{C}$) with different holding time, as indicated.
Figure 4.14: Variation of the (a) maximum value of magnetostriction and (b) strain derivative along the parallel direction as a function of holding time for the two-stage sintered samples for $T_1 = 1450 \, ^\circ C$ and $T_2 = 1300 \, ^\circ C$. 

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Figure 4.15: Magnetostriction curves measured in the parallel direction for the two-stage sintered samples for $T_1 = 1450 \, ^\circ C$ and for different $T_2$, as indicated.

Figure 4.16: Magnetostriction curves measured in the parallel direction to the applied magnetic field for the two-stage sintered samples for different values of $T_1$ and $T_2$, as indicated.
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Figure 4.15 shows the magnetostriction curves measured in the parallel direction for the two-stage sintered samples with $T_1 = 1450 \, ^\circ C$ and different lower temperature ($T_2$), sintered for 20 h. Similarly, Figure 4.16 shows the magnetostriction curves measured in the parallel direction for the two-stage sintered samples with different high temperatures ($T_1$) and lower temperatures ($T_2$), sintered for 20 h. Comparison of the magnetostriction characteristics of all the two-stage sintered samples, sintered under different combinations of higher sintering temperature, $T_1$, lower sintering temperature, $T_2$, and different holding times show that maximum value of magnetostriction of 331 ppm is obtained for the sample sintered at $T_1 = 1450 \, ^\circ C$ and $T_2 = 1300 \, ^\circ C$ for a holding time of 20 h.

4.3.4 Magnetic Field Annealing Studies

In the previous chapter (section 3.5), it was found that magnetic field annealing is effective in raising the magnetostriction as well as strain derivative, due to the induced uniaxial anisotropy. The sample sintered at 1450 $^\circ C$ (SG2) showed enhanced magnetostriction as well as strain derivative compared to the values for the same sample before annealing. In the present studies on the samples sintered under different conditions, magnetic annealing has been carried out on two samples, one is on the single stage sintered sample at a lower temperature ($1200 \, ^\circ C$) and the second one is on two-stage sintered sample ($T_1 = 1450 \, ^\circ C$ and $T_2 = 1300 \, ^\circ C$ for a holding time of 20 h) showing the highest magnetostriction among all the two-stage sintered samples. Magnetic field annealing of the sintered pellets was carried out at 300 $^\circ C$ in a magnetic field of 400 kA/m for 30 min. The annealing field was applied perpendicular to the cylindrical axis of the sintered pellet which is perpendicular to the measurement direction as well as the direction of the measuring field in the case of $\lambda_{par}$. 

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Figure 4.17: (a) Magnetostriction of single stage sintered sample (at 1200 °C) as a function of magnetic field, along the parallel (circles) and perpendicular (squares) directions. (b) Field derivative of magnetostriction along the parallel direction. The open and closed symbols represent before and after magnetic field annealing, respectively.
Figure 4.18: (a) Magnetostriction of two-stage sintered sample as a function of magnetic field, along the parallel (circles) and perpendicular (squares) directions. (b) Field derivative of magnetostriction along the parallel direction. The open and closed symbols represent before and after magnetic field annealing, respectively.
Figure 4.17 shows that the magnetostriction and strain derivative of the single stage sintered (at 1200 °C) sample measured as a function of magnetic field, parallel and perpendicular to the applied magnetic field direction before and after annealing in a field of 400 kA/m. It is found that the effect of magnetic field annealing is similar to that found in the case of SG2 (section 3.5) where improved magnetostriction and strain derivative are obtained after magnetic field annealing. Maximum value of magnetostriction for the single stage sintered sample (sintered at 1200 °C) is obtained as 201 ppm with a low strain derivative of $0.88 \times 10^{-9}$ A$^{-1}$m before annealing. However, after annealing the sample in a magnetic field, the maximum value of magnetostriction is increased to 295 ppm. Similarly, the strain derivative is doubled from $0.88 \times 10^{-9}$ A$^{-1}$m to $1.77 \times 10^{-9}$ A$^{-1}$m, after magnetic annealing.

Figure 4.18 shows the magnetostriction curves and the strain derivative for the two-stage sintered sample, before and after magnetic field annealing. In the case of the two-stage (1450/1300 °C for 20 h) sintered sample, the maximum value of magnetostriction is increased from 331 ppm to 356 ppm and the strain derivative is increased from $1.8 \times 10^{-9}$ A$^{-1}$m to $2.05 \times 10^{-9}$ A$^{-1}$m after magnetic annealing, with considerable increase in the value of magnetostriction at low magnetic fields. In chapter 3, it was found that the same sample sintered at 1450 °C for 10 minutes (single stage sintering) showed a maximum value of magnetostriction of 315 ppm before magnetic field annealing and the value increased to 345 ppm after annealing (Table 3.9). Comparable values are obtained (331 ppm before and 356 ppm after field annealing) when the same powder sample is processed under two-stage sintering at $T_1 = 1450$ °C and $T_2 = 1300$ °C when sintered for 20 h. The strain derivatives are also comparable for the single-stage and two-stage sintered samples. Thus, from the present study it is concluded that there is not much advantages on the two-stage sintering process over single stage sintering for getting higher magnetostriction and strain derivative for sintered cobalt ferrite.
4.4 Conclusions

Magnetostriction studies on sintered polycrystalline cobalt ferrite derived from nanocrystalline powders obtained by autocombustion method are made after sintering the material under different conditions to evaluate the effect of sintering and the related microstructure on the magnetostriction characteristics. Both single-stage as well as double-stage sintering studies have been performed. It is found that highest magnetostriction is obtained after sintering at 1450 °C under single-stage sintering conditions and the changes in the value of magnetostriction are somewhat correlated with the microstructure. In the two-stage sintering process, grain size remains constant while density continuously increases, unlike in normal sintering in which final stage densification is always accompanied by rapid grain growth. Out of all the experiments, maximum value of magnetostriction of 331 ppm and strain derivative of $1.8 \times 10^{-9}$ A$^{-1}$ m are achieved for the sample sintered at 1450 °C (T$_1$) and then at 1300 °C (T$_2$). It is observed that under suitable two-stage sintering conditions, high values of magnetostriction and strain derivative can be achieved. This is because the grain size and densification of the samples are better than those obtained from single-stage sintering. Magnetic field annealing has been shown to be very effective in enhancing the magnetostriction and strain derivative of single and two-stage sintered cobalt ferrite samples. Especially the sample sintered at a low temperature of 1200 °C shows huge increment of magnetostriction as well as strain derivative compared to the two-stage sintered samples after magnetic annealing. The values obtained are much larger than that reported for sintered polycrystalline cobalt ferrite derived from bulk powders, so far reported in the literature. Therefore, it is concluded that higher magnetostriction can be achieved after sintering at relatively low temperatures and with magnetic field annealing for sintered cobalt ferrite derived from nanocrystalline powders synthesized by the autocombustion method.
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References


