Manganese-substituted cobalt ferrite magnetostrictive materials for magnetic stress sensor applications

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Abstract

Metal bonded cobaltferrite composites have been shown to be promising candidate materials for use in magnetoelastic stress sensors, due to their large magnetostriction and high sensitivity of magnetization to stress. However previous results have shown that below 60°C" role="presentation" style="box-sizing: border-box; display: inline; word-wrap: normal; white-space: nowrap; float: none; direction: ltr; max-width: none; max-height: none; min-width: 0px; min-height: 0px; border: 0px; padding: 0px; margin: 0px; color: rgb(51, 51, 51); font-family: Arial, sans-serif; position: relative;">60°C60°C the cobaltferritematerial exhibits substantial magnetomechanical hysteresis. In the current study, measurements indicate that substituting Mn for some of the Fe in the cobaltferrite can lower the Curie temperature of the material while maintaining a suitable magnetostriction for stress sensing applications. These results demonstrate the possibility of optimizing the magnetomechanical hysteresis of cobalt ferrite-based composites for stress sensor applications, through control of the Curie temperature.

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Manganese-substituted cobalt ferrite magnetostrictive materials for magnetic stress sensor applications

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Metal bonded cobalt ferrite composites have been shown to be promising candidate materials for use in magnetoelastic stress sensors, due to their large magnetostriction and high sensitivity of magnetization to stress. However previous results have shown that below 60 °C the cobalt ferrite material exhibits substantial magnetomechanical hysteresis. In the current study, measurements indicate that substituting Mn for some of the Fe in the cobalt ferrite can lower the Curie temperature of the material while maintaining a suitable magnetostriction for stress sensing applications. These results demonstrate the possibility of optimizing the magnetomechanical hysteresis of cobalt ferrite-based composites for stress sensor applications, through control of the Curie temperature.
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I. INTRODUCTION

Magnetostrictive cobalt ferrite composites hold promise for use in advanced magnetomechanical stress and torque sensors because of their large strain derivative $(d\lambda/dH)_\sigma$ and their high sensitivity of magnetization to applied stress $(dB/d\sigma)_H$. Magnetoelastic stress sensors operate on the principle that magnetic properties of materials such as permeability and magnetization are altered by stress via the magnetoelastic coupling.[1] These magnetic property changes can be detected remotely, for example, by measuring magnetic field near the sensor surface using a Hall effect device.[2] Magnetoelastic materials therefore offer realistic prospects for development of contactless sensors for use in stress and torque applications.

Most stress sensor applications ideally require materials that exhibit large reversible changes in magnetization with applied stress together with minimal magnetomechanical hysteresis. In previous studies, metal bonded cobalt ferrite composites have been shown to be excellent candidates for stress sensors due to a large magnetomechanical effect and high sensitivity to stress.[2–4] They show almost linear magnetostrictive strains of magnitude up to 225×10^{-6} with a maximum rate of change of strain with applied field $(d\lambda/dH)_{max}$ of 1.3×10^{-9} A^{-1} m under no external load. They also exhibit good mechanical properties and excellent corrosion resistance.

A drawback to metal-bonded cobalt ferrite composite materials is that they also exhibit some magnetomechanical hysteresis at room temperature, and for these materials to be suitable for sensor applications it is desirable to reduce this hysteresis. It was observed that the magnetomechanical hysteresis became negligibly small at temperatures above 60 °C.[2] Since the temperature dependence of magnetic and magnetoelastic properties is strongly influenced by the Curie temperature (T_C), the objective of this study was to investigate whether T_C can be decreased through composition changes, while at the same time maintaining sufficient magnetostriction for stress sensor applications. This would thereby enhance the reversible magnetomechanical response within the temperature range of interest and allow control and reduction of magnetomechanical hysteresis.

Cobalt ferrite, which has the inverse spinel structure, can be used for investigation of the effects of microstructural changes and lattice strain on the magnetic properties. It has been shown for example that annealing of cobalt ferrite can be used to alter the cation distribution among the octahedral and tetrahedral lattice sites and thereby lead to differences in magnetic properties.[5,6] The substitution of Mn for Fe in cobalt ferrite can also cause migration of cobalt from the octahedral sites to the tetrahedral sites and structural changes have also been observed in films of this material as a result.[7] In these cases, it was found that saturation magnetization, coercivity and Curie temperature all decreased with increasing Mn content.

In this work, manganese-substituted cobalt ferrite was fabricated and its properties characterized to study the effects of composition on the Curie temperature and magnetostriction. Previous studies of Mn-substituted cobalt ferrite centered on thin films for magnetooptical applications and fine particles.[8] The effects of Mn on the magnetomechanical properties have not been reported. In the present study, we report results of the effect of manganese substitution for iron on Curie temperature, magnetization, and magnetostriction for a series of sintered bulk Mn-substituted cobalt ferrite of composition $CoMn_xFe_{2-x}O_4$ for $0\leqslant x\leqslant0.8$.

II. EXPERIMENTAL PROCEDURES

A series of manganese-doped cobalt ferrite samples with compositions of $CoFe_{2-x}Mn_xO_4$ (where x ranges from 0 to

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TABLE I. Target and final compositions for the series of manganese substituted cobalt ferrite samples with various amounts of manganese substituted for Fe.

Target composition	Composition by EDX analysis		
	Co	Fe	Mn
$CoFe_{1.8}Mn_{0.2}O_4$	0.95	1.83	0.22
$CoFe_{1.7}Mn_{0.3}O_4$	0.98	1.73	0.29
$CoFe_{1.6}Mn_{0.4}O_4$	0.95	1.62	0.44
$CoFe_{1.4}Mn_{0.6}O_4$	0.93	1.43	0.65
$CoFe_{1.2}Mn_{0.8}O_4$	0.96	1.2	0.84

0.8) were prepared by substituting manganese for iron. The samples were made using standard powder ceramic techniques. The process involved mixing Fe_2O_3, MnO_2, and Co_3O_4 powders in the targeted proportions. The powder was mixed, calcined, ball milled, mixed, and recalcined. The powder was then remilled, mixed, pressed into slugs, and sintered in air. The samples were cooled by removal from the furnace to room temperature. The microstructure of the samples was characterized using a scanning electron microscope. Energy-dispersive x-ray spectroscopy (EDX) was used to determine the final composition of the samples. This fabrication procedure was refined until it produced uniform microstructures and chemically homogeneous samples. The compositions of the samples are given in Table I.

To determine the Curie temperatures of the various manganese-substituted compounds, the magnetic moment was measured as a function of temperature using a vibrating sample magnetometer (VSM) with a high-temperature furnace and temperature controller. The magnetic moment measurements were performed over a temperature range of 100 °C to 650 °C. The samples were heated through the Curie temperature transition at a rate of 2 °C per minute, and then cooled back through the transition at the same rate. These measurements were performed under an applied field of 8 kA m^{-1} (100 Oe). Curie temperatures of the samples were determined from the cooling curves by linear extrapolation of the magnetic moment versus temperature curve from the region of maximum slope down to the temperature axis. Room-temperature saturation magnetization of the samples was measured using the VSM under an applied field of 560 kA m^{-1} (7 kOe).

III. RESULTS AND DISCUSSION

The temperature dependence of the normalized magnetic moment of the pure cobalt ferrite and the material with various amounts of manganese substituted for Fe is shown in Fig. 1. All of the samples exhibited a sharp increase in magnetic moment on cooling through the Curie temperature. It is evident that substituting Mn for Fe in cobalt ferrite reduced the Curie temperature, by as much as 300 °C in the case of $CoFe_{1.2}Mn_{0.8}O_4$.

Figure 2 shows the room-temperature saturation magnetization of pure cobalt ferrite along with the Mn-substituted ferrite samples. Although Mn substitution made a substantial decrease in Curie temperature, saturation magnetization showed only a modest decline (up to 20% over the range of $0 \leq x \leq 0.8$).

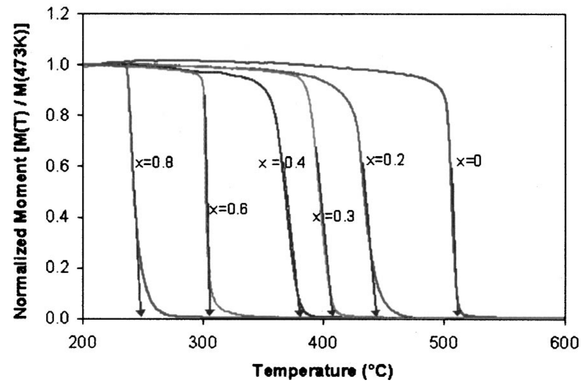

FIG. 1. Normalized magnetic moment vs temperature upon cooling for pure cobalt ferrite and manganese-substituted cobalt ferrite samples $CoFe_{2-x}Mn_xO_4$ with various manganese contents ($x=0$ to 0.8).

As shown in Fig. 3, samples with low Mn contents (e.g., $CoFe_{1.8}Mn_{0.2}O_4$ had maximum magnetostriction comparable with that of pure cobalt ferrite. Further increase in manganese content reduced the maximum magnetostriction. It should however be noted that even the lowest maximum magnetostriction (50 ppm for $x=0.8$) was higher than that of nickel which in the past has been considered for use in magnetomechanical sensors.[9] Furthermore, Mn substitution does not appear to adversely affect the slope of the magnetostriction curve ($d\lambda/dH$) at low field (in fact, for $x=0.2$ and 0.3, it increased with Mn content). This slope is related to the stress sensitivity of the magnetization,[10] and is an indication of potential performance of a magnetomechanical sensor based on this material.

The Curie temperature decreased approximately linearly with increasing manganese content as shown in Fig. 4. The magnitude of the maximum magnetostriction also decreased with increasing Mn content.

These results indicate that manganese-substituted cobalt ferrites offer improved scope for developing magnetomechanical sensors and actuators beyond that possible with the original cobalt ferrite material. Substitution of Mn for Fe has the effect of making a substantial decrease in Curie temperature, which thereby affects the temperature dependence of

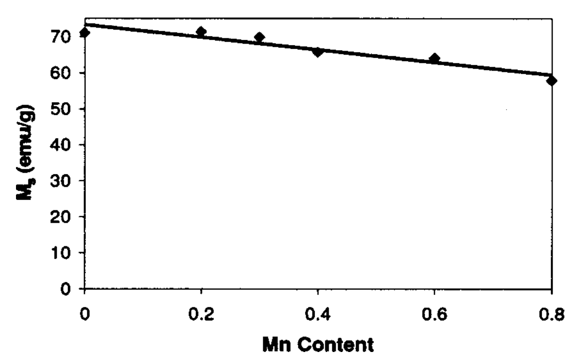

FIG. 2. Saturation magnetization M_s at room temperature of manganese-substituted cobalt ferrite $CoFe_{2-x}Mn_xO_4$ with various manganese contents. The applied field was 560 kA m^{-1} (7000 Oe).

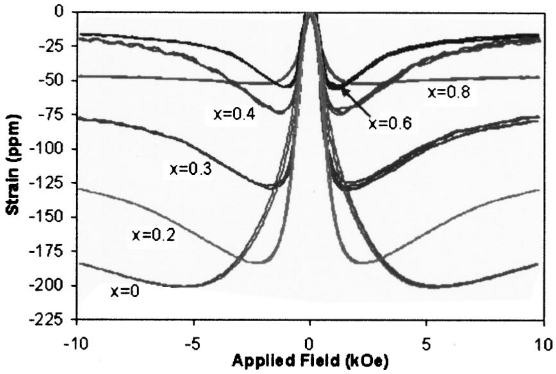

FIG. 3. Magnetostriction curves for $CoFe_{2-x}Mn_xO_4$ samples.

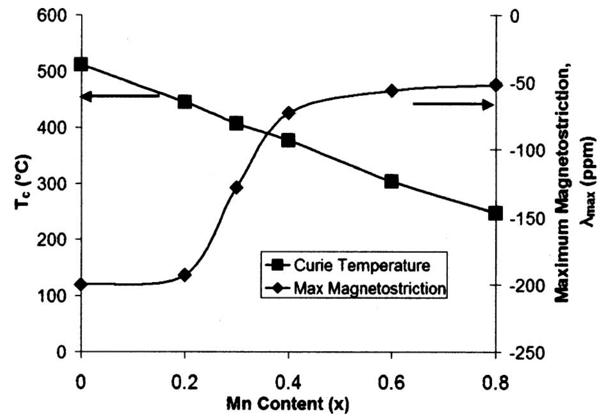

FIG. 4. Curie temperature T_C and maximum magnetostriction λ_{max} of the manganese substituted cobalt ferrite samples vs the manganese content.

magnetic and magnetomechanical properties contributing to magnetomechanical hysteresis. The maximum magnetostriction magnitude, although reduced, is still sizeable, and should be more than sufficient for use as a magnetomechanical stress sensing material for many applications. Saturation magnetization, upon which the magnitude of the external field used in noncontact sensing will depend, shows only a modest decrease throughout the compositional range. Similarly, the slope of the magnetostriction curve at low field, upon which the sensitivity for stress sensing applications depends, does not appear to be adversely affected. Thus, it should be possible to adjust the temperature dependence of magnetomechanical hysteresis while still maintaining sufficient magnetomechanical sensor material performance.

IV. CONCLUSIONS

The effects of composition on the magnetic and magnetomechanical properties of manganese-substituted cobalt ferrite have been studied. The results show that the Curie temperature of cobalt ferrite can be reduced over a substantial range by the substitution of Mn for Fe. The fact that the Curie temperature and magnetostriction of manganese substituted cobalt ferrite are selectable by adjusting manganese content allows the material properties to be optimized for use in magnetomechanical stress sensors over a range of operational temperatures.

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