Study of the Curie Temperature of Cobalt Ferrite Based Composites for Stress Sensor Applications

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***Abstract*—Cobalt ferrite has been shown to be an excellent candidate material for high sensitivity magnetic stress sensors due to its large magnetomechanical effect and high sensitivity to strain. However, near room temperature, the material exhibits some magnetomechanical hysteresis, which becomes negligible for temperatures of 60 °C and above. Measurements indicate that doping the cobalt ferrite with silicon lowers the Curie temperature of the material. It was also found that the Curie temperature of the material depends on the fabrication and processing procedure. These results offer the possibility of decreasing the room temperature magnetomechanical hysteresis through control of the Curie temperature, thereby altering the temperature dependence of magnetic and magnetomechanical properties.**

***Index Terms*—Cobalt ferrite, Curie temperature, magnetoelastic materials, stress sensors.**

I. Introduction

The development of new magnetoelastic materials for use in magnetic stress sensors is of scientific and technological interest due to the growing number of possible applications including automated control systems, noncontact torque sensing and embedded stress-sensing applications. Most sensor applications ideally require materials that exhibit large reversible changes in magnetization with applied stress or torque together with minimal magnetomechanical hysteresis at ambient temperatures. 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. They show linear magnetostrictive strains of up to 225 $\times$ 10^{-6} with a $(d\lambda/dH)_{\max}$ of 1.3 $\times$ 10^{-9} $A^{-1}m$ under no external load. They also show good mechanical properties, excellent corrosion resistance, and low cost [1]–[3].

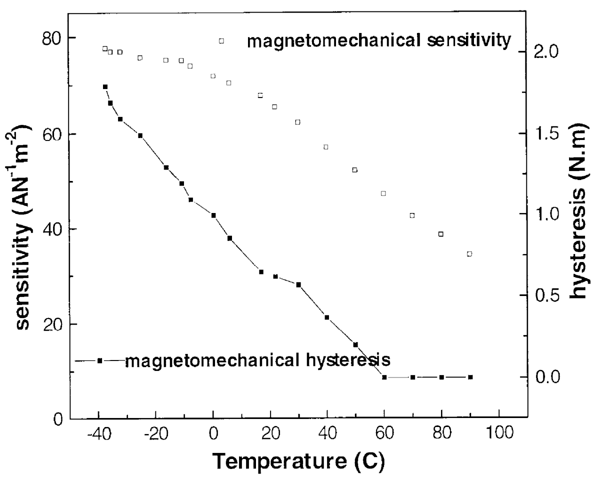

Fig. 1. Variations in sensitivity (rate of change in axial surface magnetic field with applied torque) and magnetomechanical hysteresis of a metal-bonded cobalt ferrite composite (98 vol % $CoO \cdot Fe_2O_3$ + 2 vol % $Ag_{0.97}Ni_{0.03}$) toroid with temperature [2].

Nevertheless, metal bonded cobalt ferrite composites exhibit magnetomechanical hysteresis, and for these materials to be suitable for sensor applications, it is desirable to reduce this hysteresis. It was observed that the magnetomechanical hysteresis of toroid samples of metal-bonded cobalt ferrite composite became negligibly small at temperatures above 60 °C as shown in Fig. 1 [2]. Therefore, the objective of this study is to investigate whether this temperature can be decreased by composition changes that decrease the Curie temperature of the ferrite, thus enabling operation within the temperature range of reversible magnetomechanical response.

II. Materials

A. Chemical Composition

Silicon has been identified as a material for use in doping cobalt ferrite material to lower the Curie point [4]. To investigate this possibility, a series of samples with compositions of $Co_{1+x}Si_xFe_{2-2x}O_4$ (where x is 0 to 0.3) were prepared. The doped cobalt ferrite samples were made by mixing Fe_2O_3, SiO_2, and Co_3O_4 powders in the targeted proportions and the materials were fabricated in the following way: The powder was pressed and calcined at 1000 °C for 24 h, ball milled, pressed and calcined again at 1000 °C for 24 h. The powder was then re-milled, mixed, pressed into slugs and sintered at 1250 °C for 15 minutes. The samples were cooled by removal from the furnace to room temperature air.

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Images of the microstructure of the samples were taken using a scanning electron microscope (SEM) to ensure that the samples were homogeneous. 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 structures and chemically homogeneous samples.

B. Sintering Temperatures

To investigate whether the Curie temperature could be further altered by means of the fabrication process another set of five samples was prepared. The initial composition of these samples was $Co_{1.6}Si_{0.6}Fe0_{0.8}O_4$ and the procedure for the sample preparation was the same as before except the powder was ground and mixed used a ball-milling method and the final sintering temperature was varied between 1050 °C and 1275 °C for the series of samples.

III. Experiments

The final sample compositions were examined by EDX in an SEM to determine the actual composition after processing. This compositional analysis method could accurately measure the Co, Fe, and Si content, but was unable to give accurate results for O content. To determine the Curie temperatures, the magnetic moment was measured as a function of temperature using a vibrating sample magnetometer (VSM) with a high temperature furnace and temperature controller, under computer control. The magnetic moment measurements were performed over a temperature range of 100 °C–650 °C. The samples were heated through the Curie temperature transition at a rate of 2 °C per min, then cooled back through the transition at the same rate. The cooling curves retraced the heating curves without hysteresis.

VSM measurement results for the sample series with varying Si content are shown in Fig. 2. Curie temperature was determined for each sample by linearly extrapolating the magnetization versus temperature curve from the region of maximum slope down to the temperature axis ($M = 0, T = T_c$).

IV. Results and Discussion

A. Effects of Composition

EDX measurement results of the actual finished compositions of these samples are shown in the second column of Table I. The oxygen content is shown as O_x, since this could not be determined accurately by EDX. After fabrication and processing, the third and fourth samples had more Co and Si, and less Fe than in the starting material.

The values determined for Curie temperature are shown in the third column of Table I. It can be seen that substituting Si and Co for Fe in the series caused a decrease in Curie temperature, in the case of the fourth sample, by as much as 44 °C.

The Curie temperature for the pure cobalt-ferrite was determined to be 552 °C, which is higher than that reported previously, 520 °C, by Smit and Wijn [5]. However the sample produced in the present study was richer in cobalt than the stoichiometric composition $CoFe_2O_4$, as shown in Table I. Furthermore differences in thermal preparation, including both temperatures and times, could affect compositional homogeneity

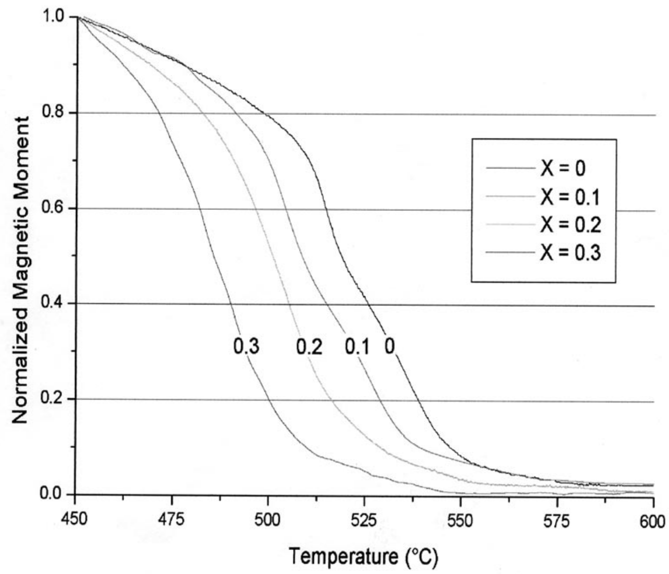

Fig. 2. Normalized magnetic moment of Si-doped cobalt ferrite as a function of temperature, for various Si contents.

TABLE I
COMPOSITIONS AND CURIE TEMPERATURES FOR THE SERIES OF Si-DOPED Co-FERRITE SAMPLES WITH VARYING AMOUNT OF Si AND Co SUBSTITUTION FOR Fe

Initial Composition	Final Composition	Curie Temperature (°C)
$CoFe_2O_4$	$Co_{1.1}Fe_{1.9}O_x$	552
$Co_{1.1}Si_{0.1}Fe_{1.8}O_4$	$Co_{1.11}Si_{0.08}Fe_{1.81}O_x$	535
$Co_{1.2}Si_{0.2}Fe_{1.6}O_4$	$Co_{1.42}Si_{0.31}Fe_{1.26}O_x$	521
$Co_{1.3}Si_{0.3}Fe_{1.4}O_4$	$Co_{1.67}Si_{0.47}Fe_{0.86}O_x$	508

and possible presence of secondary phases or could affect the site occupancy of Co and Fe among the A and B sites, thereby affecting the strength of the exchange interactions. For these reasons one might expect differences in Curie temperatures between nominally identical materials that were prepared in different ways.

The rate of decrease of Curie temperature with added Si content found in this study is considerably less than that found by Shinde and Jadhav [4]. However, thermal preparation conditions were different in the two investigations. They performed their final sintering at 1050 °C and the samples were slow-cooled at a rate of 2 °C/min. In the present study, the samples were sintered at 1250 °C and then rapidly cooled by removing from the furnace to room temperature air. Thermal treatment could affect the possible presence and percentages of secondary phases and compositional homogeneity in either the samples prepared in the present work or those prepared by Shinde and Jadhav. X-ray diffraction investigations are currently underway to identify the presence and amounts of any secondary phases. Furthermore, thermal treatment has also been reported to influence the site occupancies of the Co and Fe [6]. which could also affect the Curie temperature.

A possible explanation of the reduced Curie temperature observed in the silicon doped cobalt ferrites is that the pres-

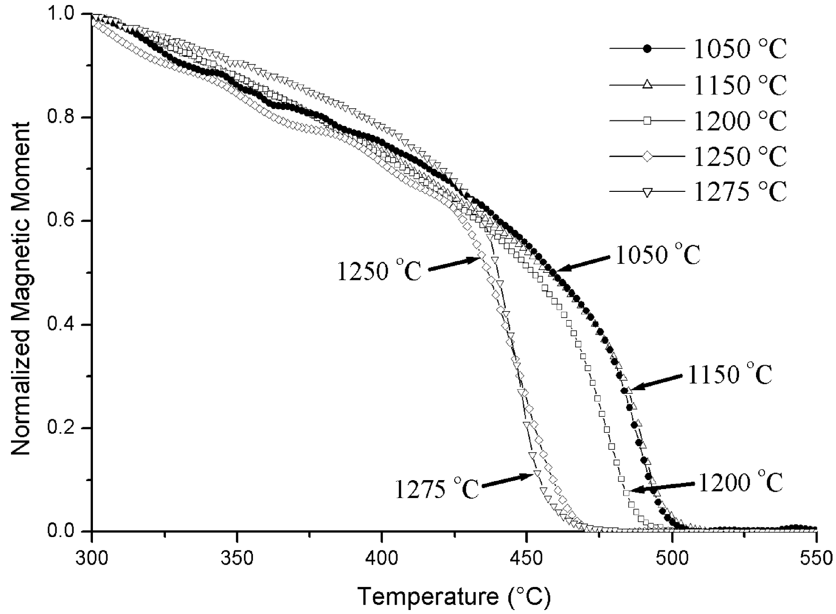

Fig. 3. Normalized magnetic moment of Si-doped cobalt ferrite versus temperature, for various final sintering temperatures.

TABLE II
EDX AND CURIE TEMPERATURES FOR THE SERIES OF Si-DOPED Co-FERRITE SAMPLES WITH THE SAME STARTING COMPOSITION ($Co_{1.6}Si_{0.6}Fe0_{0.8}O_4$), AND DIFFERENT FINAL SINTERING TEMPERATURES

Sintering Temperature (°C)	Final Composition	Curie Temperature (°C)
1050	$Co_{1.61}Si_{0.48}Fe_{0.91}O_x$	500
1150	$Co_{1.60}Si_{0.50}Fe_{0.90}O_x$	500
1200	$Co_{1.61}Si_{0.52}Fe_{0.88}O_x$	490
1250	$Co_{1.57}Si_{0.46}Fe_{0.97}O_x$	458
1275	$Co_{1.45}Si_{0.42}Fe_{1.13}O_x$	455

ence of silicon disrupts the exchange interaction in the material. This is expected to affect the temperature dependence of magnetocrystalline anisotropy and in turn change the magnetomechanical hysteresis at a given temperature. The fact that the magnetocrystalline anisotropy of cobalt ferrites becomes zero at temperatures below the Curie point [5] suggests that if the Curie temperature of cobalt ferrite can be reduced, the temperature of zero anisotropy may decrease accordingly. Therefore the magnetomechanical hysteresis, which depends on the anisotropy, is expected to decrease as the Curie temperature is reduced.

B. *Effects of Sintering Temperatures*

VSM results for the series of samples with different sintering temperatures are shown in Fig. 3. The final compositions and Curie temperatures are shown in Table II. The results for the samples sintered at 1050 °C and 1150 °C are essentially identical. However, for further increase in sintering temperature up to 1250 °C, the Curie temperature was found to decrease. Then for further increase of the sintering temperature to 1275 °C, the Curie temperature changed only slightly. The overall range of Curie temperatures was from 455 °C to 500 °C.

V. CONCLUSION

These results show that the Curie temperature of cobalt ferrite ($CoFe_2O_4$) can be adjusted over a substantial range by the substitution of Si and Co for Fe, and by varying the thermal treatment. This suggests that the temperature dependence of magnetic and magnetomechanical properties can be adjusted by such substitutions and thermal treatments, in order to control the temperature dependence of magnetomechanical hysteresis. This could enable ambient temperature operation of devices, such as magnetic stress sensors, based on effectively hysteresis-free material and thereby opens up a wide variety of new potential technological applications.

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